UNIVERSITY OF SOUTHAMPTON

THE GEOCHEMISTRY AND MINERALOGY OF SEDIMENTS OF THE OXFORD CLAY AND KELLAWAYS FORMATIONS FROM SOUTHERN ENGLAND

(WINTERBORNE KINGSTON AND WARLINGHAM BOREHOLES)

by

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B.Sc.(Hons), M.Sc.(Karachi)

Thesis submitted for the degree
of
Doctor of Philosophy

Department of Geology

June 1982

بسم الله الرحمن الرحيم

أفلا ينظرون الى الإبل كيف
خلقت ۝ والى السماء كيف
رفعت ۝ والى الجبال كيف
نصبت ۝ والى الارض كيف
سطحت

To the Geoscientists,

" See they not the camels how they are created,
And the heaven how it is raised high,
And the mountains how they are fixed,
And the earth how it is spread out."

(AL-QURʾĀN; 88:17-20)

بسم الله الرحمن الرحيم

خلق الانسٰن من
صلصٰل كالفخار

" He created man from dry clay like earthen vessels"

(AL-QURʾĀN; 55:14)

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

GEOLOGY

Doctor of Philosophy

THE GEOCHEMISTRY AND MINERALOGY OF SEDIMENTS OF THE OXFORD CLAY AND KELLAWAYS FORMATIONS FROM SOUTHERN ENGLAND

by Muhammad Atique Ahmed Baig

Seventy-eight samples of the Oxford Clay and Kellaways Formations from the Warlingham Borehole (W.B.) in Surrey and sixty-three from the Winterborne Kingston Borehole (W.K.B.) in Dorset were investigated for both their geochemical and mineralogical properties. Well crystallized smectite attributed to air-fall volcanic ash occurs in the sediments of the (W.K.B.), whereas the sediments of the (W.B.) contain non-expanding mixed-layer clays. Illite and kaolinite in the (W.K.B.) sediments show a better crystallinity than the same two minerals in the (W.B.) sediments. Enriched abundances of kaolinite and chlorite in the (W.K.B.) sediments are related to the significant contribution of the igneous and low-grade metamorphic rocks of the 'Cornubian Massif', whereas enhanced abundances of degraded illite associated with a comparatively less crystalline kaolinite and non-expanding mixed-layer clays in the (W.B.) sediments point to a major contribution of re-cycled material supplied by the sedimentary rocks of Palaeozoic age in the 'East Anglian Massif'.

Ten major and nineteen trace elements were analysed by X-ray spectrometry in the bulk rock and clay fraction samples of both boreholes. Sediments of the (W.K.B.), on the whole, contain enriched abundances of Fe_2O_3, CaO, Na_2O, P_2O_5, S, C_{org}, Sr, Fe^{+2}, Fe^{+3}, Cr, Mn, Zn, Pb, Ni and H_2O^+, whereas the (W.B.) showed enrichment in SiO_2, TiO_2, Al_2O_3, K_2O, MgO, Ba, La, Ce, Y, Zr and Nb. There were also considerable differences in chemistry within the stratigraphic horizons represented in each borehole, and between the horizons in each borehole. Characteristic element associations were found for different clay minerals, carbonates, sulphides, phosphates and organic carbon plus an adsorbed group possibly related to Fe-Mn oxides/hydroxides coatings.

An acid-reducing agent leaching study revealed that most elements in the (W.K.B.) sediments were strongly associated with the lithogenous fraction, whereas in the (W.B.) sediments the strongly lattice-held elements were only Mg, Fe, K, Al, Cu and Cr.

In general, sediments of the (W.K.B.) are less mature than those of the (W.B.), and experienced relatively stronger reducing conditions. The sediments of the (W.B.) were rich in detrital components and showed diagenetic formation of dolomite (ferroan). The 'Cornubian Massif' to the west and the 'East Anglian Massif' to the north were the provenances for the (W.K.B.) and (W.B.) sediments respectively.

DEDICATION

I dedicate this thesis firstly to my wife 'ZAKIA RANA', as a token of my deepest gratitude for the great patience shown by her and the continuous financial and moral support during the last two years - a most distressing period of financial crisis. Secondly, to my three sweet and most understanding children, SHAMOON, SAMIN and MUZNA, for all the fun and entertainments they kept alive in our life by their innocent activities throughout the entire period of my studies, preparation of the present thesis, and our stay in England.

ACKNOWLEDGEMENTS

I am indebted to the University of Sind at Jamshoro in Pakistan for financial support during the initial period of three years and to the Dr. Wali Muhammad Trust, London, for financial assistance received in the final phases of the research.

I also wish to express my deepest gratitude to my wife 'Zakia Rana' for the financial and moral support to me during the last two years by undertaking a job when the financial support from my sponsoring authority ceased.

I am grateful to the Director of the Institute of Geological Sciences, London, for his permission to collect samples of the Oxford Clay and Kellaways Formations from the Warlingham and Winterborne Kingston Boreholes.

I express my deepest gratitude to my research Supervisor, Dr. M.E. Cosgrove, for his keen interest and active supervision of my Project, and all possible help during the entire period of my studies. His valuable comments, suggestions and constructive criticisms during the period of the preparation of this thesis are also acknowledged here. I also express my most sincere thanks to Professor F. Hodson and Professor R.W. Nesbitt, for their interest in my research Project and their kind permission to use the Laboratory and other facilities of the Geology Department. Further, I gratefully acknowledge the benefits gained from the useful discussions with Dr. D. Moore, regarding the Palaeogeography and general geology of Southern England, Dr. I.M. West on the carbonates in the studied sediments and Mr. T. Clayton for the computer techniques. I also express my sincere thanks to Mr. P. Shelford for his interest and concern in my research, and continued moral support.

I also acknowledge the technical assistance of Messrs. R.A. Saunders, G. Jack, K. Gosden, D. Spanner, B. Marsh and Mrs. A. Dunkley. Further, I wish to thank Mrs. K. Sharpe for typing this thesis, particularly the lengthy and complex tables, and for her valuable help and suggestions during the processes of the preparation of the typescript.

Finally, I should thank my wife, Zakia Rana and my children, Shamoon, Samin and Muzna, for their patience and the co-operation throughout my research studies at Southampton University, and to all the members of my and my wife's families in Pakistan, particularly Drs.Zeenat Mahmood, and Mr. M.I. Karim in Liverpool, and our friends and well-wishers in Southampton for the successful completion of my research studies.

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LIST OF PLATES

LIST OF ABBREVIATIONS

In the present thesis the various abbreviations used are listed as follows:

(W.K.B.)	Winterborne Kingston Borehole
(W.B.)	Warlingham Borehole
(U.O.C.)	Upper Oxford Clay
(M.O.C.)	Middle Oxford Clay
(L.O.C.)	Lower Oxford Clay
(K.F.)	Kellaways Formation
KR	Kellaways Rocks
KC	Kellaways Clays
CB	Cornbrash
IL	Illite abundance in Bulk rock
ILL	Illite abundance in Clay fraction ($< 2\mu$)
KOL	Kaolinite abundance in Bulk rock
KOAL	Kaolinite abundance in Clay fraction ($< 2\mu$)
CH	Chlorite abundance in Bulk rock
CHLR/Chlr	Chlorite abundance in Clay fraction ($< 2\mu$)
SMEC	Smectite abundance in Bulk rock
SMECT	Smectite abundance in Clay fraction ($< 2\mu$)
MLYR	Mixed-layer mineral abundance in Bulk rock
MIXLYR/M.L	Mixed-layer mineral abundance in Clay fraction ($< 2\mu$)
TClay/T.C	Abundance of Total Clays
Carbonates(T)	Total Carbonates
CAL/Cal	Calcite
DOL/Dol	Dolomite(ferroan)
Pyt	Pyrite
C_{org}	Organic carbon
QTZ/Qtz	Quartz
L.G.F.B.M.	Lithogenous fraction obtained by adding the percentages of Qtz + C_{org} + T.C
L.G.F.	Lithogenous fraction (residue)
Fe_2O_3(T)	Total iron
L.H.	Lattice-held
R	Residue
CC	Corrected for carbonates
L.C.G.G.	Lower Calcareous Grit Group

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

The present study is concerned with the chemical and mineral compositions of the Oxford Clay and Kellaways Formations, as represented by samples from two boreholes, namely the Winterborne Kingston in Dorset and Warlingham in Surrey, both located in southern England (Fig.1.1). These boreholes provided complete cored sections of the Oxford Clay and Kellaways Formations. 78 samples were selected from the Warlingham Borehole cores and 63 from the Winterborne Kingston Borehole cores, access to which was kindly provided by The Director, Institute of Geological Sciences, London.

All these samples, and their separated clay fractions ($<2\mu$) were analysed and studied for ten major elements (e.g. Si, Ti, Al, Fe, Mg, Ca, Na, K, S and P) and eighteen minor elements (e.g. V, Cr, Mn, Ba, La, Ce, Th, Pb, As, Zn, Cu, Ni, Rb, Sr, Y, Zr, Nb and Mo). Major elements were analysed as oxides in percentages by Telsec Beta-probe and the minor elements as parts per million by X.R.F. The details pertaining to sample preparation, etc. are given in Chapter Two (see 2.III.1 & 2.III.2). In addition to these elements, three major components, i.e. H_2O^+, CO_2 and C_{org}, were also determined for all the samples. Iron abundances, as Fe^{+2} and Fe^{+3} were also determined for all samples. Twelve representative samples from each borehole collection were subjected to a leaching study by acetic acid and hydroxylamine hydrochloride (CHESTER and HUGHES, 1967), to observe the partitioning trends of the major and minor elements in the various phases present in the studied sediments.

Abundances of minerals such as quartz, calcite, dolomite(ferroan), pyrite and feldspar were determined in the bulk rock samples, and illite, kaolinite, chlorite, smectite and mixed-layer minerals in the clay fraction ($<2\mu$) of the sediments of both boreholes through X-ray diffractometry. The vertical distribution of mineral phases for the (W.K.B.) is shown in Figure (3.3) and that for the (W.B.) in Figure (3.4) respectively. All numerical analytical data obtained was processed on the University Computer (ICL-2970) in bi-variant correlations and multi-variant analysis programmes, the results of which are described in the present thesis.

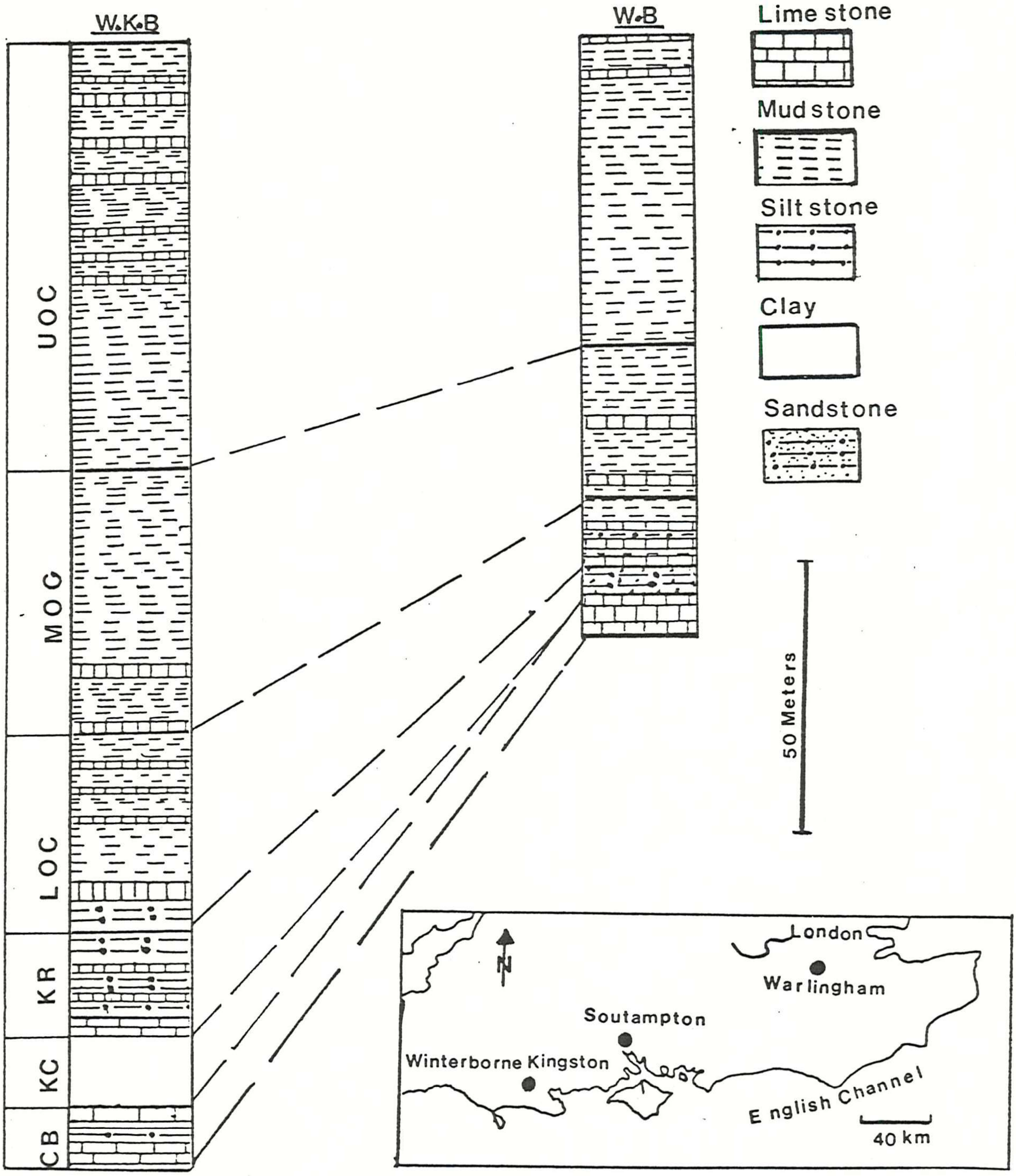
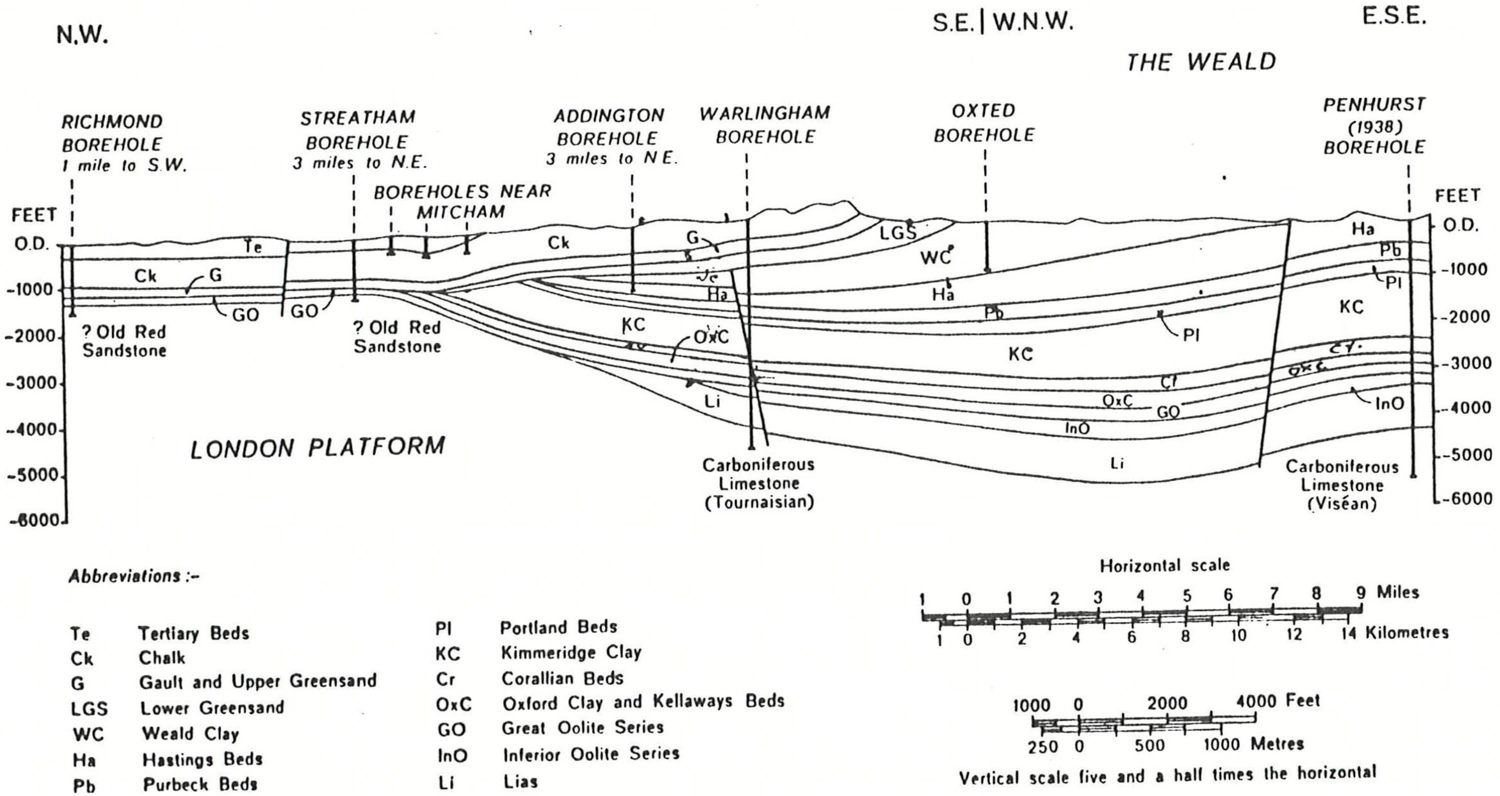


FIG.(1.1): Showing the lithological logs and locations of the Winterborne Kingston and Warlingham Boreholes in Southern England.

Stages		Zones[1]	Subzones	Divisions	Peterborough (Brinkmann, cms.)
OXFORDIAN	Lower	*Cardioceras cordatum*	C.*cordatum* C.*costicardia* C.*bukowskii*	Upper Oxford Clay (100 ft.+)	
		Quenstedioceras mariae	C.*praecordatum* C.*scarburgense*		
CALLOVIAN	Upper	*Quenstedioceras lamberti*		Middle Oxford Clay (c.50 ft.)	2800-c.3100
		Peltoceras athleta	Upper Middle Lower		1600-c.2800
				Lower Oxford Clay (50-75ft.)	1095-1600
	Middle	*Erymnoceras coronatum*	K.(*Zugokosmokeras*) *grossouvrei*		560-1094
			K.(*Zugokosmokeras*) *obductum*		136-559
		Kosmoceras jason	K.(*Gulielmites*) *jason*		56-135
			K.(*Gulielmites*) *medea*		21-55
	Lower	*Sigaloceras calloviense*	S.(*Catasigaloceras*) *enodatum* [2]		0-20
			Sigaloceras calloviense *Proplanulites koenigi*	Kellaways Rock (2-12 ft.)	
		Macrocephalites macrocephalus	M.(*Kamptokephalites*) *kamptus* M.(*Macrocephalites*) *macrocephalus*	Kellaways Clay (3-12 ft.) & Upper Cornbrash	

1. The standard zones of the Callovian and Oxfordian, their authors, synonyms and type-localities were recently reviewed by Callomon (1964).
2. Formerly S.*planicerclus* Subzone. Comparison of the type of S.*planicerclus* (Buckman 1923) with a plaster-cast of the holotype of S.*enodatum* (Nikitin 1881) kindly supplied by the Geological Institute of Leningrad shows them to be conspecific. The holotype is refigured by Tintant (1963).

TABLE (1.1) has been reproduced from CALLOMON (1968).



Abbreviations :-

Te	Tertiary Beds	Pl	Portland Beds
Ck	Chalk	KC	Kimmeridge Clay
G	Gault and Upper Greensand	Cr	Corallian Beds
LGS	Lower Greensand	OxC	Oxford Clay and Kellaways Beds
WC	Weald Clay	GO	Great Oolite Series
Ha	Hastings Beds	InO	Inferior Oolite Series
Pb	Purbeck Beds	Li	Lias

FIG. 3. ***Diagrammatic section through the Warlingham Borehole site along the line A B C shown in Fig. 2***

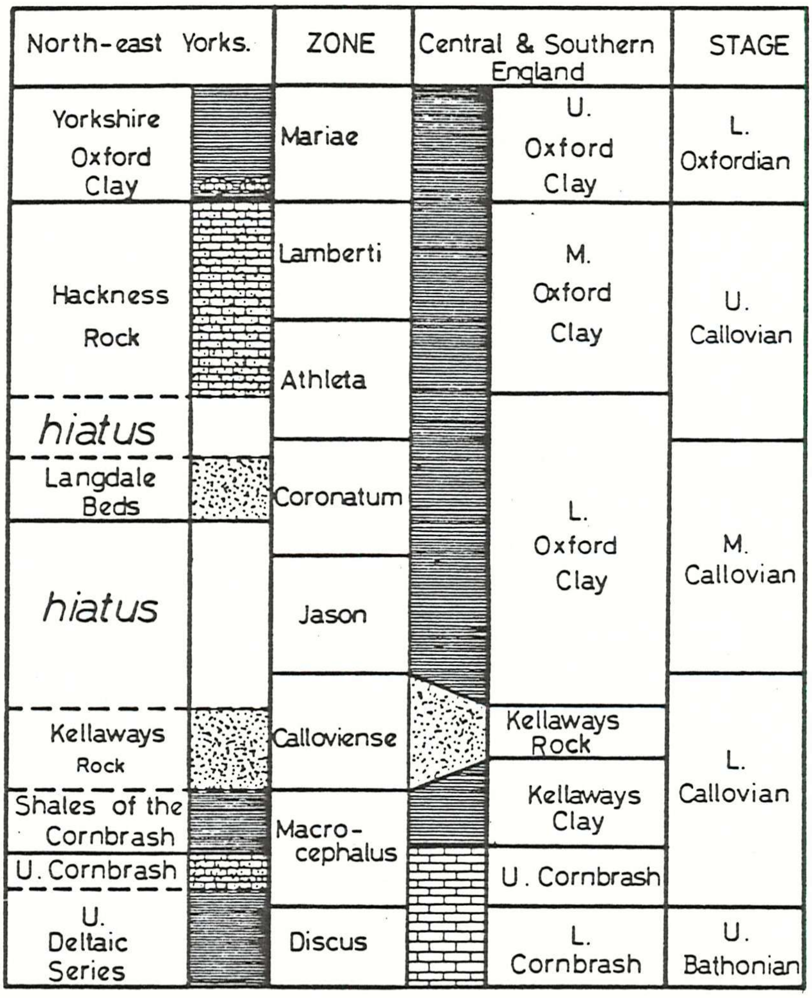
FIG.(1.2) has been reproduced from WORSSAM et al., 1971.

1.2 General Geology and Stratigraphy

The general geology and stratigraphy of the Oxford Clay and Kellaways Formations is well established (CALLOMON, 1971). It is well documented since the early days, and there exists a voluminous bibliography on these Formations. It is beyond the scope of the present thesis to summarize here the entire bibliography. However, some of the workers are mentioned here, and these include NEAVERSON (1925), ARKELL (1933, 1939, 1941 and 1948), SPATH (1939), CALLOMON (1955, 1962, 1964 and 1968), RUTTEN (1956), HUDSON and PALFRAMAN (1969), CALLOMON and COPE (1971), JACKSON (1972), JACKSON and FOOKES (1974), DUFF (1975) and RUSSELL (1977). Recently COPE et al. (1980) have correlated the Middle and Upper Jurassic rocks in the British Isles. CHOWDHURY (1980), during his studies of the Corallian sediments of southern England, has analysed the tectonic and depositional events of the Mesozoic era in England, and has contributed valuable information regarding the Mesozoic sediments, particularly of the Oxfordian stage. The latest stratigraphic and facies analysis work is that published by BRADSHAW and PENNEY (1982). These authors studied a cored sequence of Jurassic sediments from north Lincolnshire, England, and mentioned that Kellaways Clay separating the argillaceous Cornbrash from the Kellaways Sand and the organic-rich Lower Oxford Clay is thin, owing to a basal non-sequence, whilst the Upper Oxford Clay is condensed and less organic-rich than in the East Midlands. They have mentioned thicknesses for the Oxford Clay (35·36 metres) and for Kellaways Beds (8·38 metres) from the studied Borehole.

Taking into consideration the above-mentioned work, the present writer does not find himself in a position to add any further towards the general stratigraphy of the Oxford Clay and Kellaways sediments. However, a brief and generalised stratigraphic setting of the Oxford clay and Kellaways Formations is given here.

The Oxford Clay and Kellaways Formations in the studied boreholes are underlain conformably by the Cornbrash - the lowest succession of the Upper Jurassics - and overlain by Corallian Beds of variable composition (WILSON, 1968; CALLOMON, 1969), as shown in Figure (1.1). The Oxford Clay, on the basis of lithological and faunal variations, may be divided into an Upper, Middle and Lower division (CALLOMON, 1968, WORSSAM, 1971), as shown in Table (1.1). The boundaries between



TEXT-FIG. 1. Comparison of the lower part of the Upper Jurassic of Yorkshire and southern England, showing the development of a marginal facies in Yorkshire during Callovian times. After Wright (1968). All zones drawn to equal thickness, therefore the lithological sections are not to scale.

<u>TABLE (1.2)</u> (After DUFF, 1975)

the three divisions are shown in Table (1.2), as observed by DUFF (1975) in the Oxford Clay sediments from central and southern England. The boundary between the Kellaways rock and the Lower Oxford Clay is marked by the 'Jason Zone' and between the Lower and Middle Oxford Clay by a transition from brown and shaly Lower Athleta Zone to the greenish and plastic Middle Athleta Zone. The Middle and Upper Oxford clay divisions are distinguished by the Lambarti Zone, as shown in Table (1.1).

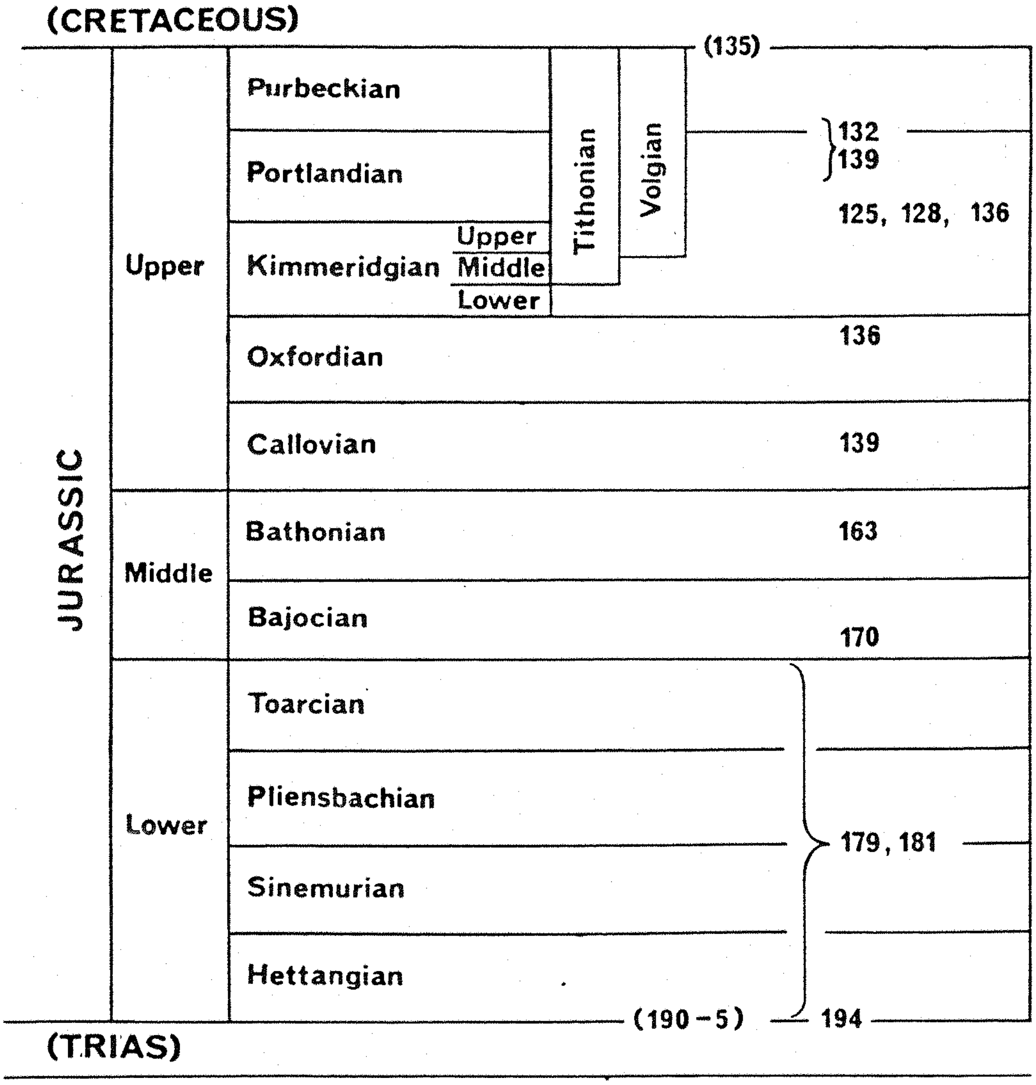
Generally speaking, the Lower Oxford Clay is shaly and bituminous, and the Middle and Upper Oxford Clay is calcareous, more plastic and poorer in fauna. The Lower Oxford Clay of the (W.B.) sediments contains the highest abundances of organic carbon and total clays, and that of the (W.K.B.) also contains appreciably higher concentrations of C_{org} and total clays; and therefore shows agreement with the published characteristics of these clays. Similarly, the sediments of the Upper Oxford Clay of both the boreholes contain the highest abundances of carbonates and mixed-layer minerals, as shown in Figures (3.3 & 3.4), and thus agree with the published properties of these sediments.

The Kellaways Formation consists of sandy clay in its upper parts, and clays in the lower sediment. Table (1.3) indicates the standard divisions of the Jurassic into stages, with radiometric ages as reported by HOWARTH (1964).

The Oxford Clay and Kellaways Beds have been divided into various groups and sub-groups, on the basis of faunal variation. ARKELL (1933) has summarized the various schemes given by different authors, which is reproduced in Table (1.4). CALLOMON (1968) has revised these zones and sub-zones, which are shown in Table (1.1). These zonal divisions are now widely accepted.

The Warlingham and Winterborne Kingston Boreholes provided a complete succession of the Oxford Clay and Kellaways Formations. Figure (1.2) shows the diagrammatic section at Warlingham, as reported by WORSSAM et al. (1971), and indicates the underlying structure and the presence of the London Platform. SMALLEY and WESTBROOK (1982) presented geophysical evidence concerning the southern boundary of the London Platform beneath the Hog's Back, Surrey. According to these authors "the pre-Mesozoic basement beneath the thin Mesozoic succession

Standard subdivisions of the Jurassic into stages, with radiometric ages (in m.y.) inserted



(CRETACEOUS)						(135)
JURASSIC	Upper	Purbeckian		Tithonian	Volgian	
		Portlandian				132 139 125, 128, 136
		Kimmeridgian	Upper			
			Middle			
			Lower			
		Oxfordian				136
		Callovian				139
	Middle	Bathonian				163
		Bajocian				170
	Lower	Toarcian				
		Pliensbachian				179, 181
		Sinemurian				
		Hettangian				(190 - 5) 194
(TRIAS)						

<u>TABLE (1.3)</u> (After HOWARTH, 1964)

north of the Hog's Back is of a lower density than that underlying the thick Mesozoic succession to the south. This lower density basement was probably the principal cause of the relative stability of the London Platform during the Mesozoic era. The southern boundary of the London Platform may have been initiated by Variscan thrusting with subsequent reversal of displacement, or may be inherited from older crustal lineament." It suggests that the London Platform might have influenced greatly the history of deposition of the studied sediments from the Warlingham Borehole.

Table (1.5) shows a comparison of the successions of Oxford Clay and Kellaways Formations at Warlingham and at Warboys in the English Midlands. It shows that, at Warlingham, the Upper and Middle Oxford Clay divisions are relatively thicker than those of Warboys, which shows a relatively thicker sequence of the Lower Oxford Clay division and the Kellaways Formation. Figure (1.1) shows the stratigraphic logs of the (W.K.B.) and (W.B.), and indicates that, in the (W.K.B.), all divisions of the Oxford Clay and Kellaways Formations are much thicker than their counterparts in the (W.B.), indicating, comparatively, much deeper basin conditions in the western part of southern England. This Figure also shows the presence of the lowest unit of the (K.F.), i.e. Kellaways Clay, in the (W.K.B.), which is absent in the (W.B.) sequence, further indicating a deeper environment of deposition for the (W.K.B.) than for (W.B.) sediments.

The depositional environments of the Oxford Clay sediments have been described by ARKELL (1933), as a deep-sea environment. RUTTEN (1956) proposed a periodic 'water-bloom' theory for the deposition of the Oxford Clay sediments at Woodham brick-pit. According to HUDSON and PALFRAMAN (1969), the sea-bottom of the Oxford Clay at Woodham was not stagnant and anaerobic. DUFF (1975) recognised the Lower Oxford Clay as a deepening water sequence in which two distinct environmental cycles are present. According to DUFF (op.cit.), the many small-scale alternations of lithology within the Lower Oxford Clay indicate relatively shallow-water deposition. HUDSON (1978) described 'non-stagnant' and 'non-anaerobic' conditions for the deposition of Oxford Clay at Woodham. JACKSON (1972) mentioned that, in general, the Lower Oxford Clay is shaly and bituminous, whereas the Middle and Upper Oxford Clays are more plastic, calcareous and poorer in the contents of fauna.

TABLE SHOWING THE ZONES INTO WHICH THE OXFORD CLAY AND KELLAWAYS BEDS HAVE BEEN DIVIDED BY DIFFERENT AUTHORS

Ages	Buckman 1913 and 1915	Morley Davies 1916	Neaverson 1925	Spath 1926	Morley Davies 1929	Brinkmann 1929	Pringle 1930	Adopted Here
base of CARDIOCERATAN (*cordatum* zone s.l.)	*scarburgense* *vernoni*	*praecordatum*		*precordatus* (with *vernoni* and *renggeri*)	*praecordatum*		*scarburgense*	*praecordatum*(=*scarburgense* auct.)
	gregarium					*tenuicostatum*		
QUENSTEDTOCERATAN (=Vertumniceratan (*lamberti* zone s.l.)	*vertumnus*			*mariae*(with *vertumnus* and *renggeri*)	*vertumnus*		*mariae*	
	renggeri *lamberti*	*renggeri*	*lamberti*	*lamberti* (with *lalandei* and *bicostata*)	*renggeri*	*lamberti*	*renggeri* *lamberti*	*renggeri* *lamberti*
	athleta	*athleta*	*athleta*		*athleta*	*spinosum* (=*ornatum* auct.)	*proniae* *athleta*	*athleta* (with *proniae* and *spinosum*)
		duncani	*duncani*	*duncani* (with *athleta* and *proniae*)	*duncani*		*duncani*	*duncani*

/contd.over

TABLE (1.4), reproduced from ARKELL (1933).

TABLE (1.4) contd.

Ages	Buckman 1913 and 1915	Morley Davies 1916	Neaverson 1925	Spath 1926	Morley Davies 1929	Brinkmann 1929	Pringle 1930	Adopted Here
KOSMOCERATAN (*ornatum* or *athleta* zone s.1)	*ornatum*	*reginaldi* (with *castor* and *pollux*)	*castor*		*reginaldi*		*castor*	*reginaldi* (with *coronatum*, *castor* and *pollux*)
	coronatum	*coronatum*	*coronatum*	*fraasi* (with *castor* and *pollux* and *coronatum*)		*castor* and *pollux* (with *coronatum*)	*coronatum*	
		elizabethae or *jason*	*elizabethae*		*stutchburii*		*elizabethae*	
	anceps							
			conlaxatum (with *jason*)			*jason* (=*conlaxatum*)	*conlaxatum*	*jason*(= *conlaxatum* with *elizabethae*, &c.)
REINECKEIAN (anceps zone s.1)	*calloviense*			*anceps*(with *calloviense* and *gulielmi*)	*calloviense*		*calloviense*	*calloviense*
	koenigi			*rehmanni* (with *konigi*)	*koenigi*		*koenigi*	*koenigi*

(Reproduced from ARKELL, 1933)

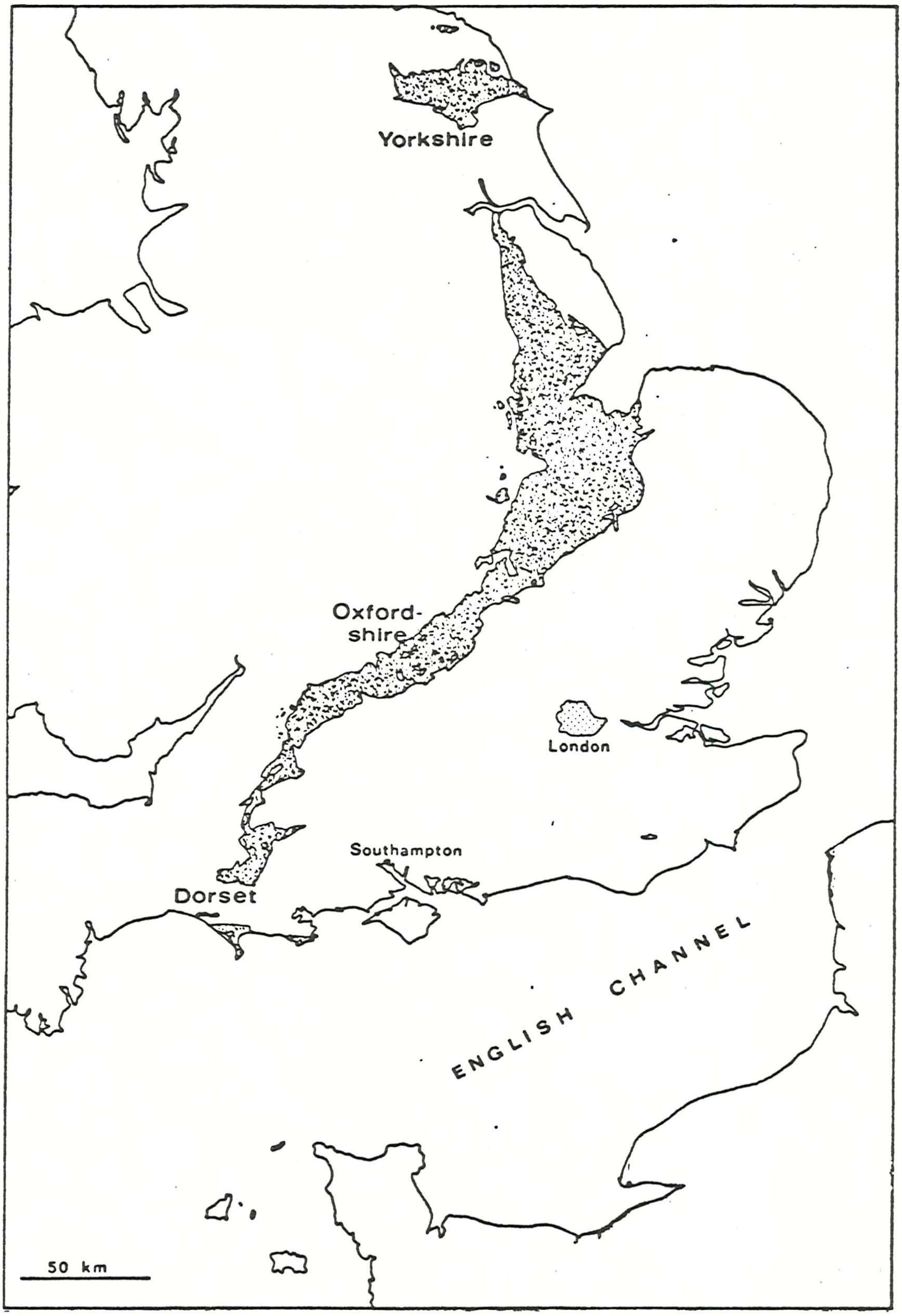


FIG.(1.3): Showing the outcrop of the Upper Jurassic rocks, including the Oxford Clay and Kellaways Formations (after FURSICH, F.T., 1977).

On the basis of field evidence, JACKSON (op.cit.) postulated that the Lower Oxford Clay was laid down in deep-sea water with a stagnant bottom, which facilitated the creation of reducing conditions and formed the bitumen present in these sediments. According to the same author, the Middle and Upper Oxford Clays were deposited in well aerated sea-water. HUDSON and PALFRAMAN (1969) found abundant benthonic fauna in the Middle and Upper Oxford Clay sediments at Woodham, and thus confirm the later views of JACKSON (op.cit.). CALLOMON (1968) found complete but immature shells of ammonites only in the Middle-Upper Oxford Clay. This observation creates some doubt about the theory of anaerobic and aerated water conditions of the Lower and Upper Oxford Clay divisions respectively, of the Oxfordian seas. The 'water-bloom' hypothesis postulated by RUTTEN (1956) may explain the situation observed by CALLOMON (op.cit.). HUDSON (1978) described 'non-stagnant' and 'non-anaerobic' conditions for the deposition of the Lower Oxford Clay at Woodham brick-pit.

The presence of pyrite and organic carbon in the entire sequences of the (W.K.B.) and (W.B.) sediments in the present study does, however, suggest the existence of reducing conditions, most probably either within the sediments or at the mud-sea-water interface. HUDSON and PALFRAMAN (1969), DUFF (1975) and HUDSON (1978) also suggested a similar mechanism regarding the occurrence of reducing conditions. The higher contents of organic carbon, pyrite and certain elements such as P, S, Cu, Mo, Fe^{+2}, etc. in the sediments of the Lower Oxford Clay, and their depleted abundances in the Middle-Upper Oxford Clay of both the boreholes, suggest that stronger reducing conditions occurred at the time of deposition of the Lower Oxford Clay sediments. The highest average value of quartz in the sediments of the (K.F.) from the (W.B.) suggests a near-shore deposition of these sediments.

The outcrops of the Jurassic rocks, including the Oxford Clay and Kellaways Formations, are exposed from the Dorset coast in the south to the Yorkshire coast in the north, as shown in Figure (1.3). JACKSON (1972) and JACKSON and FOOKES (1974) have described the thickness variation of the Oxford Clay Formations from different localities in central and southern England. The thickness of the Oxford Clay generally reduces from south to the north, as is shown in Figures (1.4 - 1.6). EVANS and THOMPSON (1979) have reported the thickest sequence of the

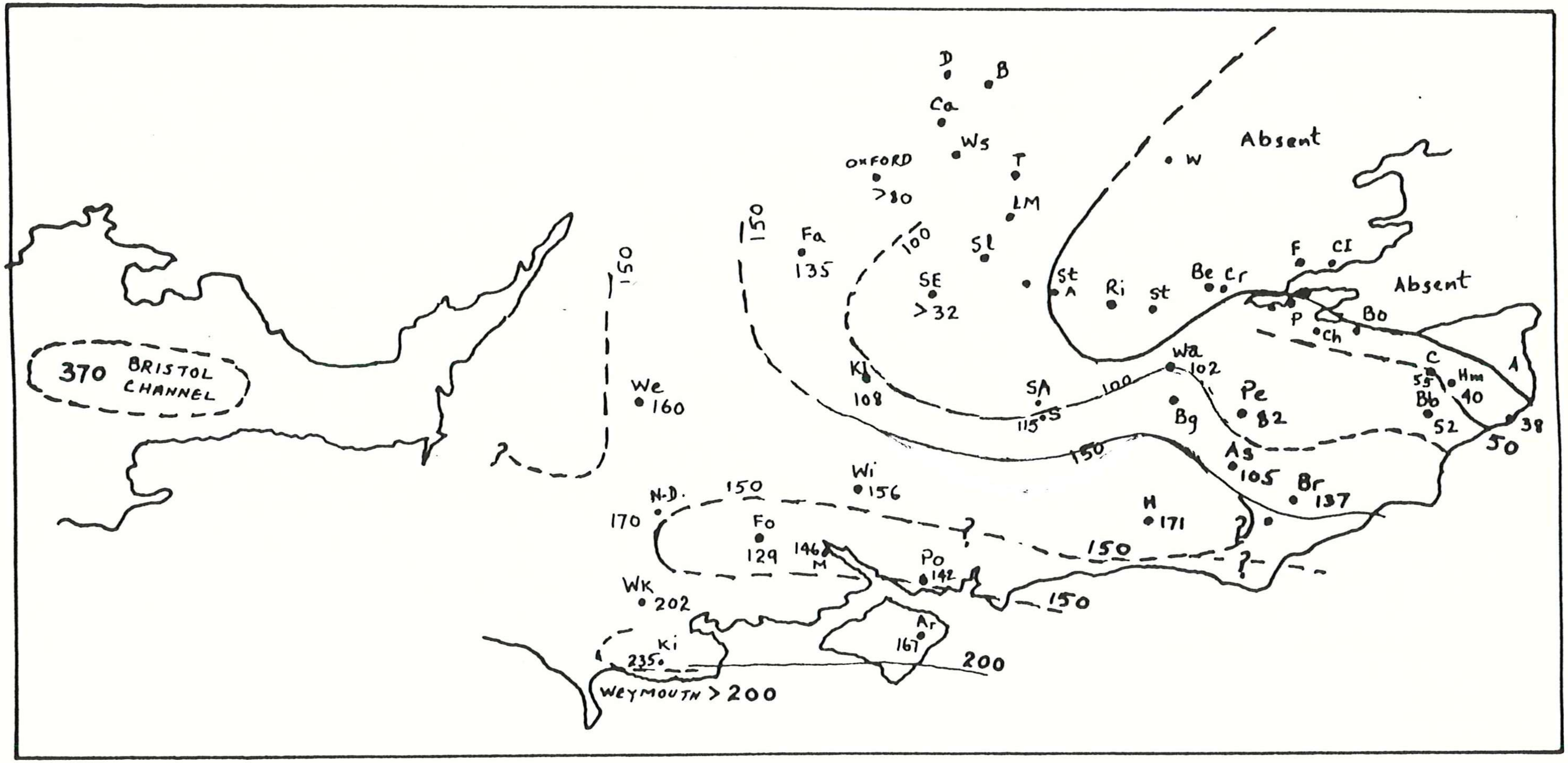


FIG.(1.4): Isopachyte map of the Oxford Clay. Thickness in metres. N.D. North Dorset, Boreholes: Ar = Arreton; As = Ashdown; B = Bletchley; Bb = Brabourne; Br = Brightling; Bo = Bobbing; C = Chilham; Ca = Calvert; Ch = Chatham; D = Deanshanger; Fa = Faringdon; Fo = Fordingbridge; H = Henfield; Hm = Harmansole; Ki = Kimmeridge; Kl = Kingsclere; LM = Little Missenden; M = Marchwood; N = Noke; Pe = Penshurst; Po = Portsdown; S = Shalford; St = Streatham; T = Tring; W = Ware; Wk = Winterborne Kingston; We = Westbury; Ws = Westcott; Wa = Warlingham; SE = Sonning Eye; Be = Beckton; Cr = Crossness; F = Fobbing; CI = Canvey Island; Sl = Slough; St = Staines; SA = Strat Al; Bg = Bletchingley.

(Modified from CHOWDHURY, 1980)

Oxford Clay from the central Bristol Channel where it measures 370 metres. The Oxford Clay and Kellaways Formations sequence at Winterborne Kingston in Dorset is thicker (202 metres) than that of Warlingham (102 metres).

1.3 History of Previous Work

The Oxford Clay and Kellaways Formations are well-known in the geological literature for the rich faunal assemblage and also as a source of raw material for the manufacture of bricks in England. Previous work on the Oxford Clay may be summarized as follows:

(a) Palaeontological, stratigraphical and sedimentalogical studies.

(b) Geo-technical and Isotopic studies.

(c) Mineralogical and geochemical studies.

(a) Palaeontological, stratigraphical and sedimentalogical studies

There is a voluminous bibliography on these aspects of the Oxford Clay and Kellaways Formations. It is not possible to summarize the entire bibliography in the present thesis. WILLIAM SMITH (1815-16) called it 'clunch clay and shale', purely on the lithological character of this Formation. BUCKLAND (1818) used the term 'Oxford Clay', 'Forest or Fan Clay' for this Formation. BUCKLAND and DE LA BECHE (1835) and DAMON (1884) described the geology of the Weymouth and adjacent areas of the Dorset coast, and studied the Oxford Clay. ANDREWS (1895) studied the skeleton of a young Plesiosaur from the Oxford Clay of Peterborough. ANDREWS (1909, 1910-13, 1915) studied New Steneosaurs from Peterborough; he described the catalogue of Marine reptiles of the Oxford Clay and wrote a note on a mounted skeleton of Opthalmosaurus icenicus seeley. NEAVERSON (1925) described the zones of the Oxford Clay near Peterborough. ARKELL (1932) described an unknown Kellaways locality in Dorset. ARKELL (1933, 1939, 1941 and 1948) described the Jurassic system in Great Britain and studied the ammonite succession at the Woodham brick-pit - situated at Woodham. He studied the Upper Oxford Clay at Purton, Wiltshire, and the zones of the Lower Oxfordian. ARKELL (op.cit.) also studied the Oxford Clay and Kellaways Beds of the Dorset coast in the south of England.

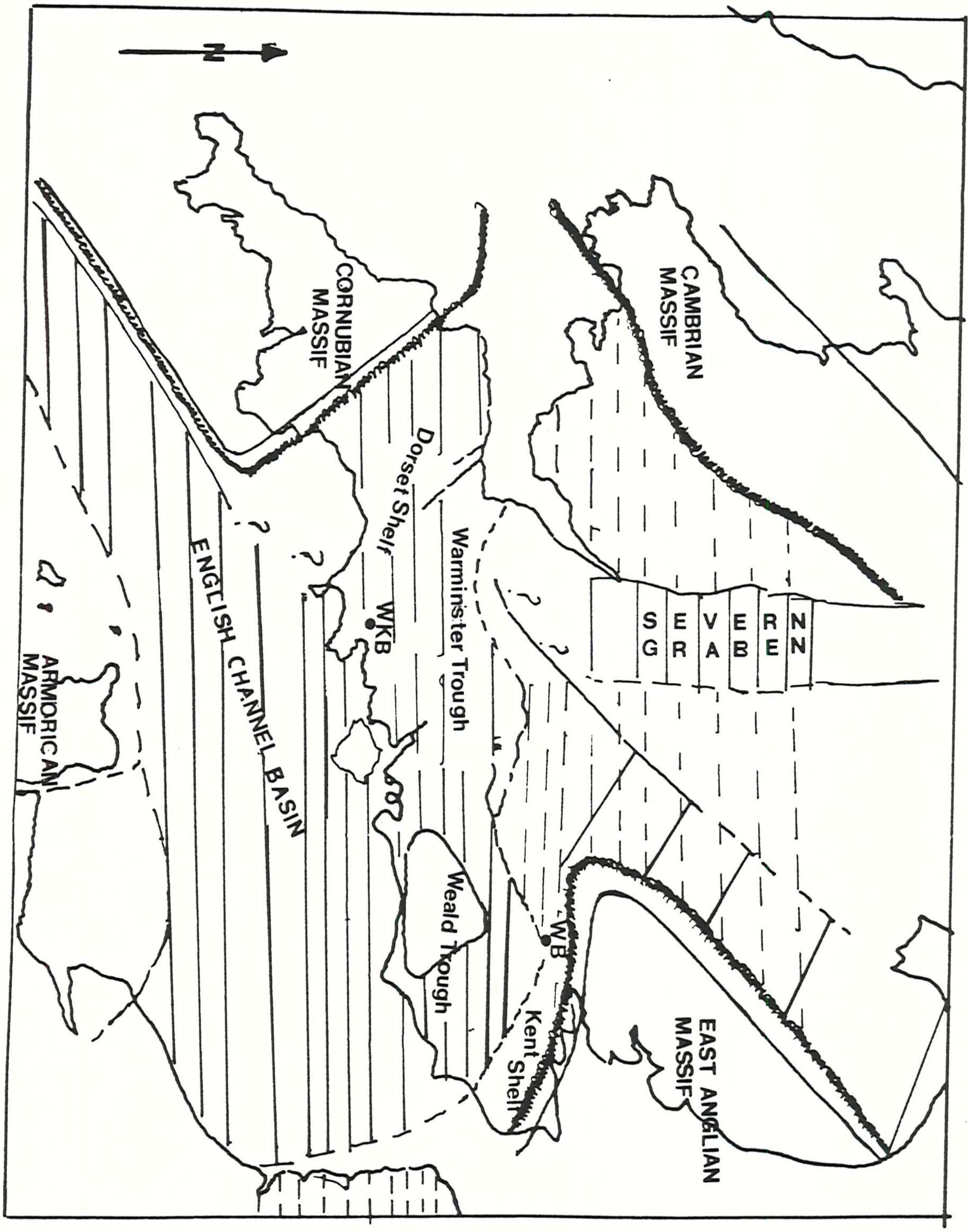


Fig.(1.5) Showing the positions of the Massifs and the Palaeo-topographic features in England and adjoining regions, during the Oxfordian time. Dr. D. Moore, Geology Department University of Southampton has compiled this map. (Personal communication)

Zonal and formational sequence in the Oxford Clay and Kellaways Beds

Stages	Zones	Subzones	Peterborough-Warboys Area[1] Ft in			Thickness Ft in	Warlingham Borehole		Depth Ft in
Middle Oxford-ian	*plicatilis*	*antecedens*	(absent through pre-Ampthill Clay erosion)				— — — FAULT — — — Corallian Beds[2] 159 ft 9 in+		2987 0 3146 9
		vertebrale				5 0+	Upper Oxford Clay 183 ft 9 in	Oxford Clay 319 ft 7 in	
Lower Oxfordian	*cordatum*	*cordatum* *costicardia* *bukowskii*	23 +	Upper 97 ft 7 in	Oxford Clay 236 ft 1 in	7 3 13 0 7 0			
	mariae	*praecordatum*	26 6			27 8			
		scarburgense	48 1			122 10			3330 6
Callovian	*lamberti*		12 5	Middle 83 ft 10 in'		94 10	Middle Oxford Clay 94 ft 10 in		
	athleta	(upper) (middle) (lower)	25 11 33 7 30 7						3425 4
	coronatum	*grossouvrei*	17 10	Lower 54 ft 8 in		27 8	Lower Oxford Clay 41 ft		
		obductum	13 10			7 0			
	jason	*jason*	2 7			4 1			
		medea	1 1			2 6			3466 4
	calloviense	*enodatum*	0 8	Rock 11 ft 6 in	Kellaways Beds 18 ft 6 in	1 8	Kellaways Beds 17 ft 4 in		
		calloviense *koenigi*	11 6			15 5			
	macrocephalus	*kamptus*	7 0+	Clay 7 ft					
		macrocephalus	5 0	Upper 5 ft	Cornbrash	?	?	?	3483 8
Bathon-ian	*discus*			Lower 5 ft			Cornbrash		

[1] Sources: *praecordatum* and *bukowskii* subzones from Warboys brickpit (Spath 1939; Arkell 1941); *scarburgense* Subzone to *athleta* Zone from Geological Survey boreholes at Warboys (unpublished); *coronatum* Zone to Kellaways Clay from Peterborough brickpits (Brinkmann 1929); Cornbrash from a borehole at Peterborough (Callomon 1968). Lowest 18 ft 8 in of *athleta* Zone still included in Lower Oxford Clay (Callomon 1968).

[2] Made up of 8 ft 10 in of clays (of same age and facies as Ringstead Waxy Clays of Dorset, *pseudocordata* Zone) on 150 ft 11 in of limestones in coralline facies without ammonites.

TABLE (1.5)

(After CALLOMON and COPE, 1971)

ARKELL (1933) described in great detail the structure of the troughs or basins in which the deposition of Jurassic sediments in England took place. He also interpreted the tectonic influence and the post-depositional tectonic effects on the Jurassic sediments. According to him, there were continued subsidence and uplifts of varying intensity during Jurassic times. ARKELL (op.cit.) concluded that the rate of subsidence varied from locality to locality, as shown in Table (1.6). He further postulated that the axes of uplifts sub-dived troughs into basins of deposition. Three of these axes are important from the point of view of the Oxford Clay outcrop; these are as follows:

(i) the Market Weighton axis;

(ii) the Weymouth anticline;

(iii) the Islip anticline.

Details of these axes are described by ARKELL (1933) and JACKSON (1972).

SPATH (1939) described the ammonite zones of the Upper Oxford Clay of Woodham. The Geological Survey of Great Britain published (in 1947) a memoire entitled 'The Geology of the Country around Weymouth, Swanage, Corfe and Lulworth', which describes all geological aspects of the Oxford Clay and Kellaways Formations in these areas. BARNARD (1952 & 1953) studied the foraminifera from the Upper Oxford Clay of Red Cliff Point and from Warboys. RUTTEN (1956) described the depositional environment of the Oxford Clay at Woodham brick-pit. CALLOMON (1955, 1964 and 1968) described the ammonite succession in the Lower Oxford Clay and Kellaways Beds at Kidlington brick-pit in Oxfordshire. CALLOMON (1962) published notes on the Callovian and Oxfordian stages. PALFRAMAN (1966) studied the variations and the ontogeny of some Oxfordian ammonites: Taramelliceras richei (de Loriol) and Creniceras renggere (oppel) from the Woodham brick-pit, Buckinghamshire. CALLOMON (1968) described the Oxford Clay and Kellaways Beds of the East Midlands, and revised the zonal scheme. (A summary of the revised stages is given in Table (1.1).) HUDSON and PALFRAMAN (1969) studied the ecology and preservation of the Oxford Clay fauna at Woodham brick-pit, Buckinghamshire. TORRENS (1969) edited an account of the International Field Symposium on the British Jurassic Guide for Dorset and south Somerset, which describes the

TABLE (1.6): Some Axes and their Period of Activity

PERIODS	Purbeck	N.Devon	Mendip	Market Weighton	Charnwood	Vale of Moreton	Malvern Range	Islip
	Weymouth	Wardour	Pewsey					
Tertiary	+	+	+	?	?	?	+ ?	+
Pre-Albian	+	+	+	+	+	-	?	+
Pre-Aptian	+	+	+	+	+	-	?	+
Kimmeridgian Portlandian	+ ?	-	-	+	+ ?	-	?	+
Corallian	-	-	-	+	?	-	?	-
Oxfordian	-	-	-	+	?	-	?	-
Bathonian	-	-	-	+	-	-	?	-

(After ARKELL, 1933)

+ Proved uplift
- Proved subsidence
? Activity unknown.

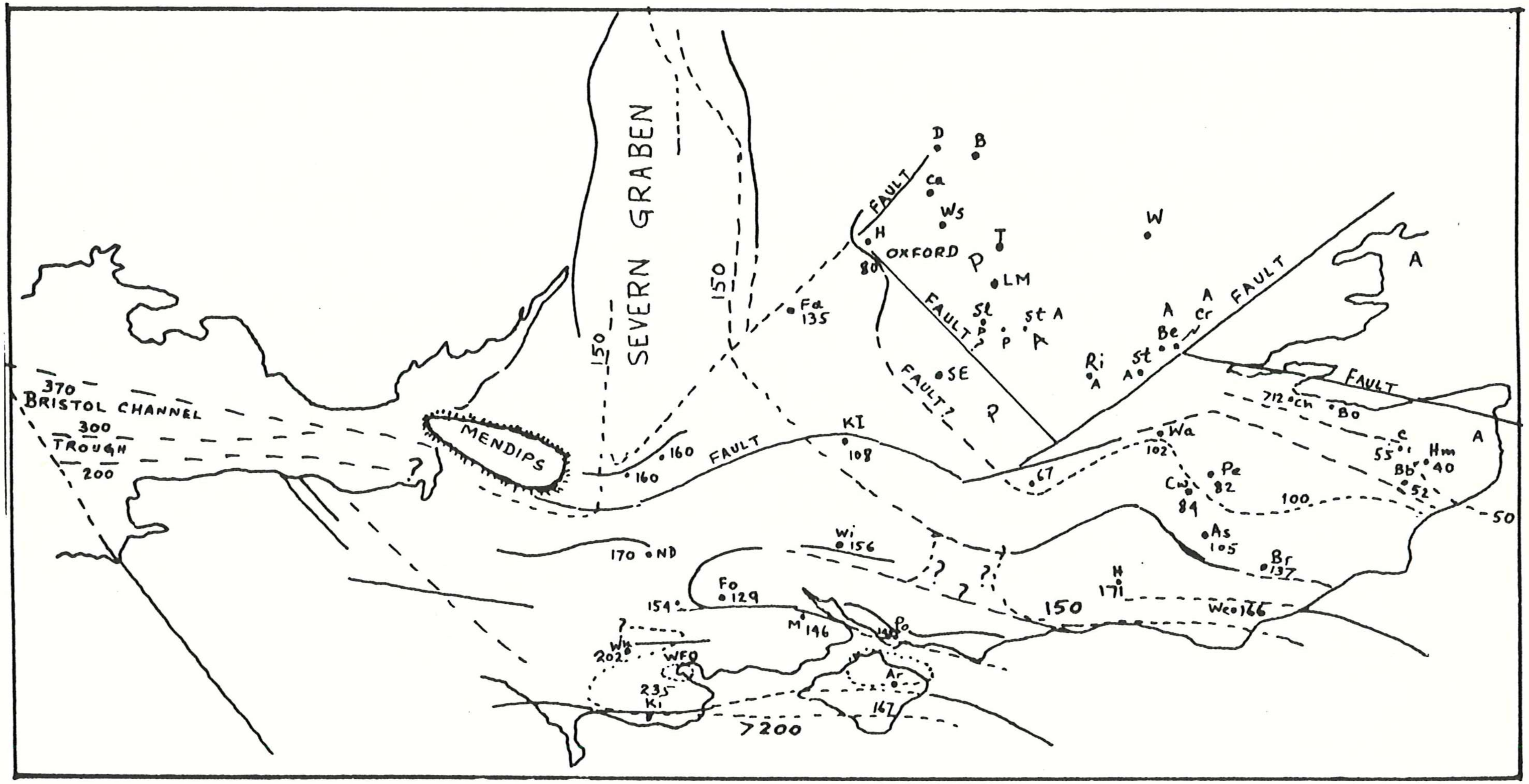


FIG.(1.6): Isopachyte map of the Oxford Clay showing the effects of tectonic control on thickness variations.
Ar = Arreton; As = Ashdown; B = Bletchley; Bb = Brabourne; Br = Brightling; C = Chilham; Ca = Calvert;
D = Deanshanger; Fa=Faringdon; Fo = Fordingbridge; H = Henfield; Hm=Harmansole; Ki = Kimmeridge;
Kl = Kingsclere; LM = Little Missenden; M = Marchwood; N = Noke; Pe = Penshurst; Po = Portsdown;
S = Shalford; SE = Sonning Eye; Cw = Cowden; We = Westham; St = Streatham; T = Tring; W = Ware;
Wa = Warlingham; Wk = Winterborne Kingston; Ws = Westcoll; WFO = Wytch Farm Oilfield.
A = Absent; P = Present.

(Modified from CHOWDHURY, 1980)

stratigraphy, fossils, lithological characters, palaeontological zones and thicknesses of the Oxford Clay and Kellaways Beds in Dorset. CALLOMON and COPE (1971) described the stratigraphy and ammonite succession of the Oxford Clay and Kellaways rocks and clays in the Warlingham Borehole, drilled in Surrey. Rood et al. (1971) described electron microscope studies of Oxford Clay coccoliths. DUFF (1975) studied the palaeoecology of the bituminous shale from the Lower Oxford Clay of central England. He noticed the presence of many benthonic burrows preserved in the Lower Oxford Clay, indicating that the bottom conditions during the Middle Callovian times were less anaerobic in comparison to those conditions under which the deposition of the bituminous shales of the Lias took place. PERKINS (1977) described the succession of the Oxford Clay and Kellaways Formations at Crook Hill brick-pit, Chickerell, East Fleet; Tidmore Point and Furzedown Cliff.

COPE et al. (1980) have recently correlated the Middle and Upper Jurassic rocks in the British Isles. BRADSHAW and PENNEY (1982) have described the stratigraphy and facies analysis of a cored sequence of Jurassic sediments from the north of Lincolnshire.

(b) Geotechnical and Isotopic studies

JACKSON (1972), JACKSON and FOOKES (1974) studied the geotechnical properties of the Lower Oxford Clay from different localities in central and southern England. These authors concluded "that the geological conditions of deposition for identical palaeontological zones of the clay were approximately similar and that the influence on engineering index, strength and low stress consolidation properties due to different depths of burial were small". RUSSELL et al. (1978) studied the shear strength anisotropy variations in weathered Oxford Clay in England. RUSSELL and PARKER (1979) described the geotechnical, mineralogical and chemical inter-relationships in the weathering profiles of Oxford Clay from localities including Sandy, Minety, Hillfield and Fleet in England.

HUDSON (1978) studied concretions, isotopes and the diagenetic history of the Oxford Clay from central England. He identified three types of concretions and the shales in which they occur. According to HUDSON (op.cit.), the calcite of the concretion bodies is non-ferroan. He further mentioned that "presumably Fe^{+2} activity in the pore waters was kept low by the continuous precipitation of highly insoluble iron sulphides, the precursor of eventual pyrite (BERNER, 1970)". Recently BLOOMER (1981) described the thermal conductivities of mud-rocks, including the Oxford Clay and Kellaways Formations, in the United Kingdom. SMALLEY and WESTBROOK (1982) presented the geophysical evidence concerning the southern boundary of the London Platform beneath the Hog's Back, Surrey.

(c) Mineralogical and Geochemical Studies

The majority of the workers concentrated on the stratigraphy and fauna, its preservation and conditions of deposition of the Oxford Clay. Their conclusions are drawn mainly on the basis of the outstanding marine fauna of the Oxford Clay. As far as geochemical and mineralogical work is concerned, some had been attempted, but on a very limited scale. FREEMAN (1956, 1958 and 1964) mentioned that illite is the dominant and kaolinite is the subsidiary clay mineral in the Oxford Clay. PERRIN (1971) stated that Lower Oxford Clay from the south-east Midlands contains only two clay minerals, i.e. illite (65 to 80%) and kaolinite (20 to 35%). He further mentioned that Upper Oxford Clay from the Dorset area contains illite (40 to 70%), smectite (5 to 40%), kaolinite (11 to 31%) and chlorite (4 to 10%). JACKSON (1972), JACKSON and FOOKES (1974) studied the clay mineral suites and other minerals such as quartz, gypsum, calcite(pure), calcite(Mg-rich), dolomite, pyrite, plagioclase and K-feldspars, in the Lower Oxford Clay from different sections exposed on the surface from central and southern England, and reported the presence of illite (54 to 75%), kaolinite (21 to 45%) and chlorite (from zero to 4%). ATTEWELL and TAYLOR (1973) reported the presence of mixed-layer clay mineral in the Oxford Clay, but they quantified this mineral with illite. WEIR and RAYNER (1974) studied a sample of the weathered Oxford Clay from the Denchworth Series soil and reported the presence of an interstratified illite and smectite mixed-layer mineral containing approximately 45% expandable layers. RUSSELL (1977) carried out studies on samples of weathered Oxford Clay from seven profiles from the Midlands to southern England, to observe the effects of weathering on the physical and chemical properties. He reported the presence of illite, kaolinite, chlorite, montmorillonite and mixed-layer minerals in the sediments studied by him. Recently SHAW (1981) described the mineralogy and petrology of all the argillaceous sedimentary rocks of the United Kingdom, and gave an average clay minerals composition (i.e. illite = 50%, kaolinite = 20%, swelling clay minerals = 30%) in the Upper Jurassic sediments.

As far as geochemical studies are concerned, as mentioned earlier, very limited work has been done, and this mainly on surface exposed sediments which are badly weathered. JACKSON (1972) reported a partial chemistry of Lower Oxford Clay samples collected from the brick-pit sites in the Midlands and Dorset. He carried out these investigations in connection with studies of the geotechnical properties of the Lower Oxford Clay. His samples, although suitable for geotechnical investigation, were not ideal for geochemical and mineralogical studies, being highly weathered. The weathering processes might have leached the carbonate minerals and also some elements, particularly Ca, Mg, Sr, Fe and P, as is proved by the present study. It is obvious that geochemical studies of such samples provided biased information and failed to represent the genuine distribution and actual concentration of the elements and their role in the history of the sedimentation. RUSSELL (1977) also studied the partial chemistry of the Oxford Clay sediments; again this study was done on weathered material.

1.4 Aims of Present Study

The thick sequences of fine-grained sediments containing clays and other minor lithological units, deposited during the Jurassic times, are ideal for geochemical and mineralogical investigations. GAD (1969), for example, studied the geochemistry of the Withbean (Upper Lias) sediments of the Yorkshire coast, and on the basis of geochemical findings, explained the conditions of deposition of the studied sediments. DUNN (1974) identified sedimentary cycles in the bituminous Kimmeridgian sediments from the Dorset coast, based on a detailed geochemical study.

The work of GAD (1969) on the Whitbean sediments, DUNN (1974) on the Kimmeridgian sediments, and that of JACKSON (1972) and HUDSON (1978) on the Lower Oxford Clay, directed the writer's attention to the need for detailed geochemical and mineralogical investigations of the un-weathered sediments of the Oxford Clay and Kellaways Formations from southern England. Keeping this background in mind, investigations were initiated with the aims listed below:

(1) to study in detail the clay mineral species;

(2) to study in detail non-clay mineral species, particularly those of non-detrital origin;

(3) to study the distribution and concentration of major and minor elements in the bulk rock and clay fraction ($< 2\mu$) samples;

(4) to study the partitioning characters of major and minor elements in the lithogenous part of the sediments;

(5) to observe the relationship between organic carbon and some minor elements;

(6) to investigate the geochemical and mineralogical parameters as evidence for the history of deposition of these sediments;

(7) to trace the provenance of the studied sediments.

1.5 Sample Collection

Having the described aims and objectives in mind, samples of the Oxford Clay and Kellaways Formations were first collected from the surface exposed sections at the Chickerell brick-pit, Jordan Cliff and Red Cliff sections in Dorset. Preliminary mineralogical and chemical findings on these samples were found to be unrealistic and unsatisfactory, owing to their highly weathered state. It was therefore decided to obtain samples of unweathered sediments from suitable borehole sites drilled in southern England. In this regard, the Institute of Geological Sciences, London, was approached, and only two boreholes, i.e. one at Warlingham and the other at Winterborne Kingston, were found to have complete cored successions of Oxford Clay and Kellaways Formations. Thus permission was obtained to select samples from the cores of the two boreholes. The Winterborne Kingston borehole is located near Blandford Forum (Grid No.SY-807979) in Dorset, and Warlingham is in Surrey (Grid No.TQ-34765719); both locations are shown in Figure (1.1).

CHAPTER TWO

ANALYTICAL TECHNIQUES AND APPARATUS

2.I Mineral Analysis of Bulk Rock

2.I.1 X-ray Diffractometry

KLUG and ALEXANDER (1954) described the technique of mineral analysis by X-ray Diffraction as the quickest and most accurate method. Many other workers, including STRAHI (1958), VAN ANDAL(1964), CALVERT (1966), COSGROVE (1972) and PAPAVASILIOU (1979), have used this technique for the identification and satisfactory semi-quantitative estimation of minerals in whole-rock, clay fraction and silt fraction of sediments, during various research studies.

In the present investigations all mineralogical studies of the whole-rock, and clay fractions of the sediments of the two boreholes were carried out using a Philip's PW1010, X-ray Diffractometer operating at 36kV. and 24 mA; using Ni-filtered Cu $K\alpha$-radiation throughout, in the Laboratories of the Geology Department, University of Southampton. Philip's PW1010 X-ray Diffractometer is shown in Plate (2.1).

2.I.2 Random Powder Sample Analysis (Qualitative Analysis

a) Sample Preparation

For random powder analysis, an aluminium powder holder, specially prepared for this purpose, and the ground powder of the rock were required. About 0·5 gm. of the sample powder was heaped into the central hole (2 cm. by 1 cm. in area, and about 1·5 m.m.deep) of the aluminium powder holder. The back of the central hole was covered with a glass slide to support the powder; the powder being spread for equal distribution in the sample hole. The powder is pressed into a smooth-surface using a second glass slide to present a uniform flat surface to the X-ray beam. All samples, including the bulk-rock and silt fractions, were prepared in this way. More details have been given by COSGROVE (1972) and SULAIMAN (1972).

b) Settings of X.R.D.

Different settings of slit widths, scan and paper speed and time constant are required depending on the nature of the sample.

PLATE 2.1

PHILIP'S PW1010 X-RAY DIFFRACTOMETER

For random powder sample analysis the X.R.D. settings used were as under:

Divergence slit and scatter slits = ½ degree
Receiving slit = 0·2 m.m.
Scanning speed of goniometer = 1 degree, 2 θ/minute
Recorder chart speed = 600 cms/hour
Time constant = 4 & 8.

c) X-ray Diffraction and Identification of Minerals

All random powder samples were scanned on the X.R.D. from 2°, 2θ to 65°, 2θ, using the X.R.D. setting described above. Between 2°,2θ to 65°, 2θ, all important peaks of minerals are recorded on the X.R.D diffractograms. The identification of specific minerals was done using the characteristics peak positions of common minerals used by SCHULTZ (1964), KLUG & ALEXANDER (1954). The common minerals identified in the sediments of the Warlingham Borehole include quartz, calcite, dolomite (ferroan), pyrite and feldspar (very small amounts) present only in a few samples. The sediments from the Winterborne Kingston borehole contain the same minerals with the exception of dolomite. The peak positions of these minerals on the X.R.D. trace are shown in Table (2.1).

TABLE (2.1)

Minerals	Peak Positions (Cu Kα-radiation)
Quartz	i) 26·66°, 2θ (3.34 Å)
	ii) 20·85°, 2θ (4·26 Å)
Calcite	i) 29·43°, 2θ (3·03 Å)
	ii) 39·43°, 2θ (2·28 Å
Dolomite (ferroan)	i) 30·84°, 2θ (2·72 Å)
	ii) 41·04°, 2θ (2·19 Å)
Pyrite	i) 33·07°, 2θ (2·70 Å)
	ii) 37·10°, 2θ (2·42 Å)
Feldspars	i) 27·41°, 2θ (3·22 Å)
	ii) 27·93°, 2θ (3·16 Å)
Total clays	19·91°, 2θ (4·45 Å)

2.I.3 Whole Rock Minerals Analysis (Semi-quantitative Analysis)

SCHULTZ (1964) used a method for semi-quantitative analysis of minerals present in the 'Pierre shales', in which 'intensity factors' for every mineral were used. The minerals of the Pierre shales include quartz, calcite, dolomite, pyrite, feldspar and total clays. SCHULTZ (op.cit.) determined intensity factors for these minerals using pure minerals. PAPAVASILIOU (1979) also used the same method for the semi-quantitative analysis of minerals present in Deep-sea sediments from the Indian Ocean. Both workers experienced some problems over the estimation of 'intensity factors', particularly for 'total clays'. They also faced the problem of the unknown mass absorption of the rocks. They concluded that the method only gives an idea of the relative proportions of the minerals. PAPAVASILIOU (op.cit.) experienced that the total mineral analysis achieved by this method sometimes is over 100%, and sometimes much less (i.e. 70%).

The sediments of the two boreholes, at present under study, contain 'total clays' as a dominant component, which plays a vital role in the mineralogical and chemical history of these sediments. It is very important that the component of total clays of these sediments should be estimated as accurately as possible. The amount of each sample was very limited, so it was not possible to separate the 'clay fraction' in sufficient quantity to be used in the determination of individual minerals' intensity factors. The method of semi-quantitative analysis applied here gives the quantities of minerals, determined independently, in parts per hundred

The mineral quartz was determined by the X.R.D. method of COSGROVE & SULAIMAN (1973). The amount of total carbonates was determined by the acid digestion method proposed by MOLINA (1974), using 10% acetic acid for sediments of the Winterborne Kingston Borehole and 0·1N HCl for the Warlingham Borehole sediments. The amount of calcite in the Winterborne Kingston Borehole sediments was calculated from the amounts of carbonate CO_2 obtained by the Infra-red gas analyser, which are shown in Appendix (2.1). The abundances of calcite and dolomite for the Warlingham Borehole sediments were estimated from the known values of calcite/dolomite ratios obtained by the X-ray Diffractometer, and the equivalent amount of CO_2 obtained by converting the abundances of total carbonates, determined by the acid digestion method, using 0·1N(HCl). The values of carbonate CO_2, C/D ratios, calcite and dolomite are shown in Appendix (2.2). The abundances of pyrite were calculated from the amounts of sulphur (S) as obtained from the analysis of major elements done by the Betaprobe. The amounts of organic carbon were estimated from the amounts of CO_2, representing organic carbon, and obtained by subtracting the carbonate CO_2 values from the total CO_2 values. The total CO_2 for both boreholes' sediments and carbonate CO_2 for the Winterborne Kingston Borehole were determined by the Infra-red gas analyser. The values of carbonate CO_2 for the Warlingham Borehole sediments were those obtained by converting the contents of total carbonates determined by 0·1N (HCl) acid digestion method. The amounts of total clays for each sample of the two boreholes' sediments were calculated by the difference method, i.e. %total clays = 100 - (quartz + calcite + dolomite + pyrite + organic carbon). COSGROVE (1972) and EL-SHAHAT (1977) used this method and satisfactorily estimated the abundances of total clays in the sediments studied by them.

2.I.4 Determination of Quartz

a) Rock Standards

For the determinations of quartz abundances in the samples, first of all the X-ray Diffractometer was calibrated, by running the samples of the rock standards in which the percentages of quartz had already been determined by the gravimetric method proposed by TROSTELL and WYNNE (1940). Eleven representative samples, which are shown in Table (2.2), were used as rock standards. These standards include 9 samples from the Warlingham Borehole collection and 2 samples from the exposure of the Oxford Clay at Chickrell brick-pit, near Weymouth in Dorset. The peak intensity of a mineral present in a rock sample, to be scanned on X.R.D., very much depends on the grain size of the sample. It is therefore necessary that the grain size of the standards and other samples should be of the same dimensions. It is believed that grain sizes

TABLE (2.2): Calibration of X-ray Diffractometer for Quartz Determination

Sample No.	(Calibration curve - 1978)				(Calibration curve - 1980)			
	c.p.s. Quartz Peak	µm	c.p.s. x µm	% Quartz	c.p.s. Quartz Peak	µm	c.p.s. x µm	% Quartz
BR-129	67	12.83	860	10	70	25.3607	1775	10
BR-236	198	11.08	2195	22	200	23.1323	4626	22
BR-278	255	11.19	2853	28	245	22.9801	5630	28
BR-606	252	10.61	2674	26	220	22.2091	4886	26
BR-958	157	12.82	2010	20	155	25.4590	3946	20
BR-1755	437	9.45	4130	40	390	21.0513	8210	40
BR-1795	765	9.27	7091	66	675	20.5684	13884	66
BR-1811	648	9.40	6091	57	570	21.0930	12023	57
BR-1852	1127	7.47	8416	78	1050	18.1079	19013	78
CH-1	288	8.11	2336	23	247	18.9460	4689	23
CH-15	254	8.26	2100	21	212	18.9858	4030	21

/contd.over

TABLE (2.2) contd.

Regression Results of the Quartz Calibrations

	1978	1980
Correlation Coefficient (r)	1·000	0·9992
(r^2)		0.998
Intercept of Calibration (A)	+2.114	+2.0621
Slope of Calibration (B)	0·009	0.0046
STD. Error Intercept	0·147	0.4481
STD. Error Slope	0·000	0.001
Number of Pellets	11	10

of standards and other samples, to be studied in the present investigation, are similar since both received the same treatments of grinding and pellet making.

b) Determination of Absolute amount of Quartz

The absolute amount of quartz in the 'rock standards' was determined by the gravimetric method of TROSTELL & WYNNE (op.cit.). Determinations, in some of the rock standards, were done in duplicate to ensure the precision of the method. The reproducibility of the method was found to be very good and satisfactory. A variation of ± 1% was noticed in the duplicate determinations, which is shown in Table (2.3).

c) Settings of X.R.D.

The rock standard pellets were scanned on the X.R.D., on the settings mentioned below:

Divergence and scatter slits	=	1° degree
Receiving slit	=	0·2 m.m.
Goniometer scanning speed	=	½ degree, 2θ/minute
Recorder chart speed	=	1200 cms
Time constant	=	4 seconds.

d) Calibration of the X.R.D.

For the calibration of the X.R.D., pellets of eleven (11) standards were scanned on the Philip's PW1010 X-ray Diffractometer from 19°, 2θ, to 22, 2θ; all the pellets were prepared according to the method already described. Each pellet was scanned four times; each time the position was rotated through 90° angle in order to cover the whole surface area of the pellet. The average of the four readings of the quartz peak height at 4·26Å (20 85°, 2θ) was taken as the final reading for that sample.

The two quartz peaks of highest intensity are at 3·34Å (26·66°, 2θ) and 4·26Å (20·85°, 2θ). The main peak at 3·34Å (26·66°, 2θ) is overlapped by the (003) illite peak; this peak was not used as illite is a dominant mineral in these sediments. The second peak at 4·26Å (20·85°, 2θ) is also overlapped by the gypsum peak at 4·27Å. However, since gypsum has not been recorded in any

TABLE (2.3): Reproducibility of Quartz Determination by the X.R.D. Method

Master Standard - WBK-01					Master Standard - BR-129				
No.of runs	^{1}I(counts/sec.)	μ m^2	I x μm	% Quartz	No.of runs	^{1}I(counts/sec)	μ m^2	I x μ m	% Quartz
1	195	22·9937	4483·8	22·7	1	67·5	12·750	860·6	09·9
2	232	"	5334·5	26·6	2	86·5	"	1102·9	12·0
3	195	"	4483·8	22·7	3	77·5	"	988·1	11·0
4	235	"	5403·5	26·9	4	77·5	"	988·1	11·0
5	195	"	4483·8	22·7	5	67·5	"	860·6	09·9
6	195	"	4483·8	22·7	6	72·5	"	924·4	10·4
7	232	"	5334·5	26·6	7	80·0	"	1020·0	11·3
8	230	"	5288·5	26·4	8	75·0	"	956·3	10·7
9	195	"	4483·8	22·7	9	70·0	"	892·5	10·1
10	232	"	5334·5	26·6	10	75·0	"	956·3	10·7

Note: 1. Peak intensity in counts per second on the X.R.D.
2. Mass absorption values obtained from the X.R.F. in the Molybdenum tube programme.

/contd.over

TABLE (2.3) contd.

Basic Statistics of the Quartz Determination for Two Master Standards

	Master Standard - WBK-01	Master Standard BR-129
Mean	24·7	10·7
Standard deviation	1·945	0·64
Standard error (mean)	0·615	0·202
Coefficient of variation	7·85%	5·98%
Number of runs	10	10

of the samples of the Oxford clay, the peak of quartz at 4·26Å (20·85°, 2θ) was therefore selected to record the amount of quartz present in the samples.

The intensity of the peak of a mineral depends on many factors; the mass absorption being perhaps the most important. COSGROVE and SULAIMAN (op.cit.) and EL-SHAHAT (1977) have observed the effects of mass absorption on the determination of quartz in sedimentary rocks, and showed that an improvement in the 'correlation coefficient', for the calibration curve, could be achieved by incorporating the mass absorption coefficient values. This mass absorption correction was done in the present investigations by incorporating the mass absorption values for the standards already obtained from the X-ray spectrometer, when the standards and other samples were being run on the Molybdenum tube programme for the analysis of the trace elements. These mass absorption values are suitable for Cu Kα-radiation (1·54Å), being on the short wave length side of the 'Fe' absorption edge, COSGROVE (1972).

Two calibrations, as shown in Figure (2.1a and b), one for the Warlingham and the other for the Winterborne Kingston Borehole samples, were constructed in 1978 and 1980 respectively for each borehole. The lines of the 'best fit' for (c.p.s. x μm) versus the already known percentages of quartz, which are shown in Table (2.2), were computed using the method of least squares. The reason for the two separate calibration lines was due to the changes made in the parameters of the Molybdenum tube programme in 1980. Due to changes in the programme, higher values of the mass-absorption coefficient were obtained for the same pellets of the 'standards', when they were run on the X.R.F. The variation in the mass absorption coefficient values is shown in Table (2.2).

The working equations for the estimation of quartz percentages for each regression are given below:

a) Regression Equation for the Warlingham Borehole sediments:

$$Y = 2{\cdot}114 + 0{\cdot}009X$$

OR

$$\%\ \text{Quartz} = 2{\cdot}114 + 0{\cdot}009 \times \text{c.p.s.} \times \mu\text{m}.$$

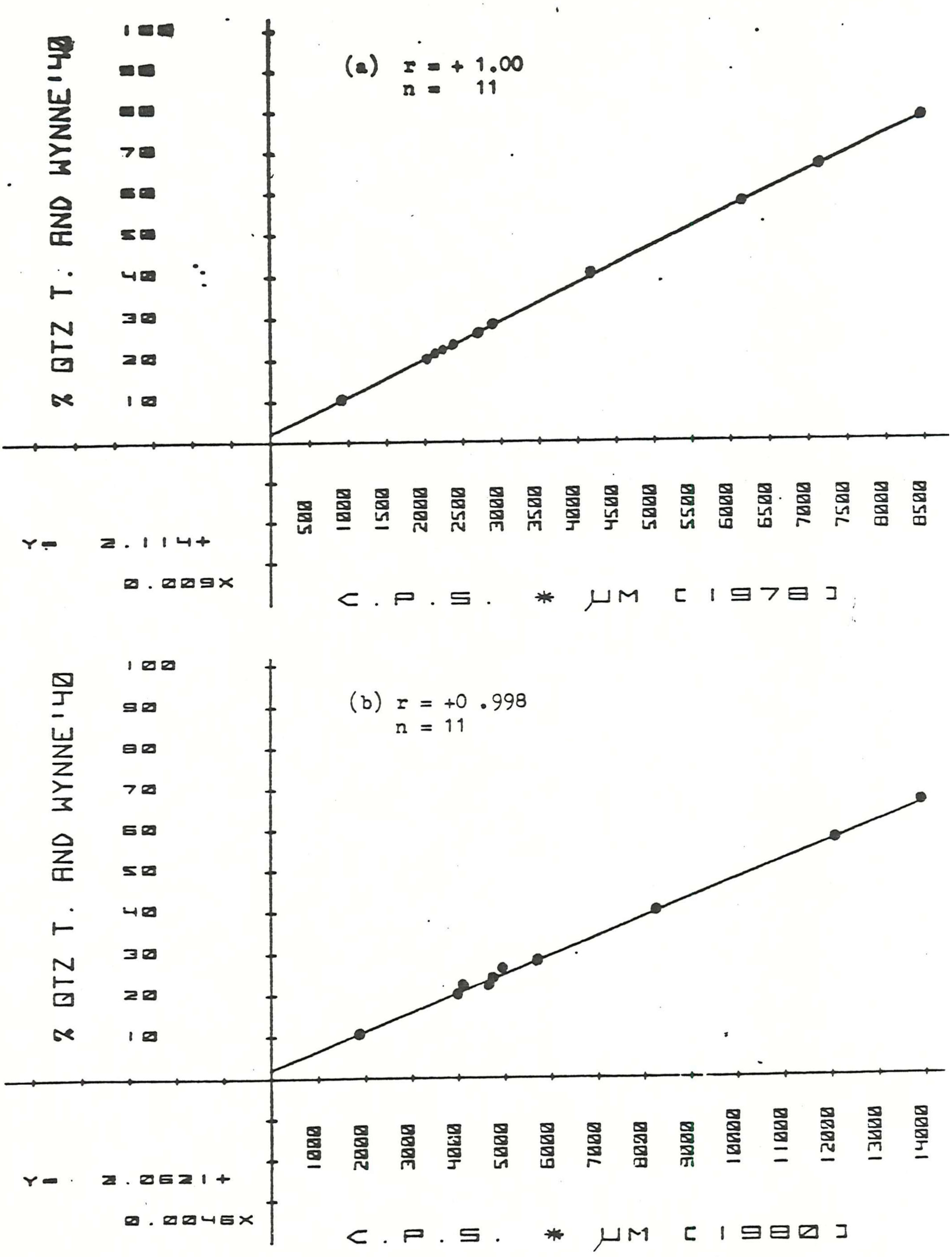
% QTZ T. AND WYNNE'40
10
20
30
40
50
60
70
80
90
100
(a) r = + 1.00
n = 11
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000
8500
Y= 2.114+
0.009X
C.P.S. * µM [1978]
% QTZ T. AND WYNNE'40
10
20
30
40
50
60
70
80
90
100
(b) r = +0 .998
n = 11
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
Y= 2.0621+
0.0046X
C.P.S. * µM [1980]

FIG.(2.1)

b) Regression Equation for the Winterborne Kingston Borehole sediments:

$$Y = 2{\cdot}0621 + 0{\cdot}0046X$$

OR

$$\% \text{ Quartz} = 2{\cdot}0621 + 0{\cdot}0046 \times \text{c.p.s.} \times \mu m.$$

where:

Y = Quartz percentage, determined in the unknown sample.

X = Peak intensity of quartz in counts per second (c.p.s.) x μm.

μm = Value of the mass absorption coefficient, obtained from the X.R.F. Molybdenum tube programme.

$+2{\cdot}114$ = Value of intercept for the calibration of the Warlingham Borehole sediments.

0.009 = Value of slope for the calibration of the Warlingham Borehole sediments.

$+2{\cdot}0621$ = Value of intercept for the calibration of the Winterborne Kingston sediments.

$0{\cdot}0046$ = Value of slope for the calibration of the Winterborne Kingston sediments.

The abundances of quartz in the sediments of the two boreholes were determined by using the values of peak intensity (c.p.s.) of quartz and mass absorption coefficient for each sample, and the respective regression equations.

The day to day drift of the X.R.D. which affects the peak intensity of quartz, as is shown in Table (2.3), was controlled by running two 'Master standard' samples, BR-129 for the Warlingham Borehole and WBK-1 for the Winterborne Kingston Borehole sediments. The Master standards were run every time with every batch of the samples.

The reproducibility of the method has been found very good, as is clear from the statistical data for the two Master standards shown in Table (2.3). Each Master standard was run on the X.R.D. ten times in both cases. The peak intensity of quartz showed some fluctuations every time, as is shown in Table (2.3). This fluctuation is due to drifts of the X.R.D. The variations of the peak intensity directly affects the amounts of quartz determined. A variance of ±1 to 2% of quartz values can be seen in Table (2.3).

2.I.5 Determination of Calcite/Dolomite Ratios

The sediments of the Warlingham Borehole contain two carbonate minerals, namely calcite and dolomite (ferroan). The abundances of calcite and dolomite were estimated by using the ratios of calcite/dolomite obtained by the peak heights of the respective minerals from the X-ray Diffractograms, and the amount of carbonate CO_2 calculated by the abundances of total carbonates, determined by the acid digestion method, using 0·1N (HCl). The values of CO_2, calcite/dolomite ratios are tabulated in Appendix (2.2).

a) Rock Standards

Rock standards of calcite and dolomite were selected from the Kimmeridge Clay of the Dorset coast, being the most similar rock types. For calcite, a coccolithic limestone (the white band), and for dolomite, a ferroan dolomite, were obtained from BELLAMY (1980). First of all these rocks were scanned by X.R.D. as a random powder for checking their composition, which was found satisfactory. The coccolithic limestone contained only pure calcite, and the dolomite also proved to be pure dolomite (ferroan).

b) Grinding and Pelleting the Standards

The Coccolithic limestone and dolomite (ferroan) samples obtained from BELLAMY (1980) were first crushed into pea-size fragments in the 'Jaw crusher'. The pea-sized fragments were ground in a Tema-mill for about 4 minutes. MILLIMAN (1974) noticed that increased grinding time affects the peak intensity of calcite + aragonite. GOODELL and KUNZLER (1965) noticed that, by the effect of heat produced due to over-grinding, aragonite is converted to calcite.

Weighted fractions of calcite and dolomite, as shown in Table (2.4), were again ground in plastic containers, having two plastic balls, in the grinder for about 10 minutes, in order to get the homogeneous mixture of calcite and dolomite. Pellets were prepared by using the homogenised mixture in the usual way, as explained elsewhere. These pellets were also run on the X-ray spectrometer to obtain the mass absorption values, in the Molybdenum tube programme.

c) Calibration of X.R.D. and Determination of Calcite/Dolomite Ratios

Pellets of calcite and dolomite, prepared from the homogenised mixtures, were run on the X.R.D., on the same settings used for the calibration of quartz. Each pellet was scanned four times from 28°, 2θ to 32°, 2θ, by rotating its position at 90°. The average of the four readings for calcite at $29\cdot45^{\circ}$, 2θ and for dolomite(ferroan) at $30\cdot85^{\circ}$, 2θ was taken as the final reading respectively.

The calibration line shown in Figure (2.2) was constructed using the values of the ratios of calcite/dolomite peak heights multiplied by the mass absorption values and the ratios of the weight percentages of calcite/dolomite, as shown in Table (2.4). The working equation obtained is mentioned below:

$$Y = A + BX + CX\uparrow 2$$

OR

$$Y = -0\cdot0098 + 0\cdot8313\,X + (-0\cdot0124X^{2})$$

where:

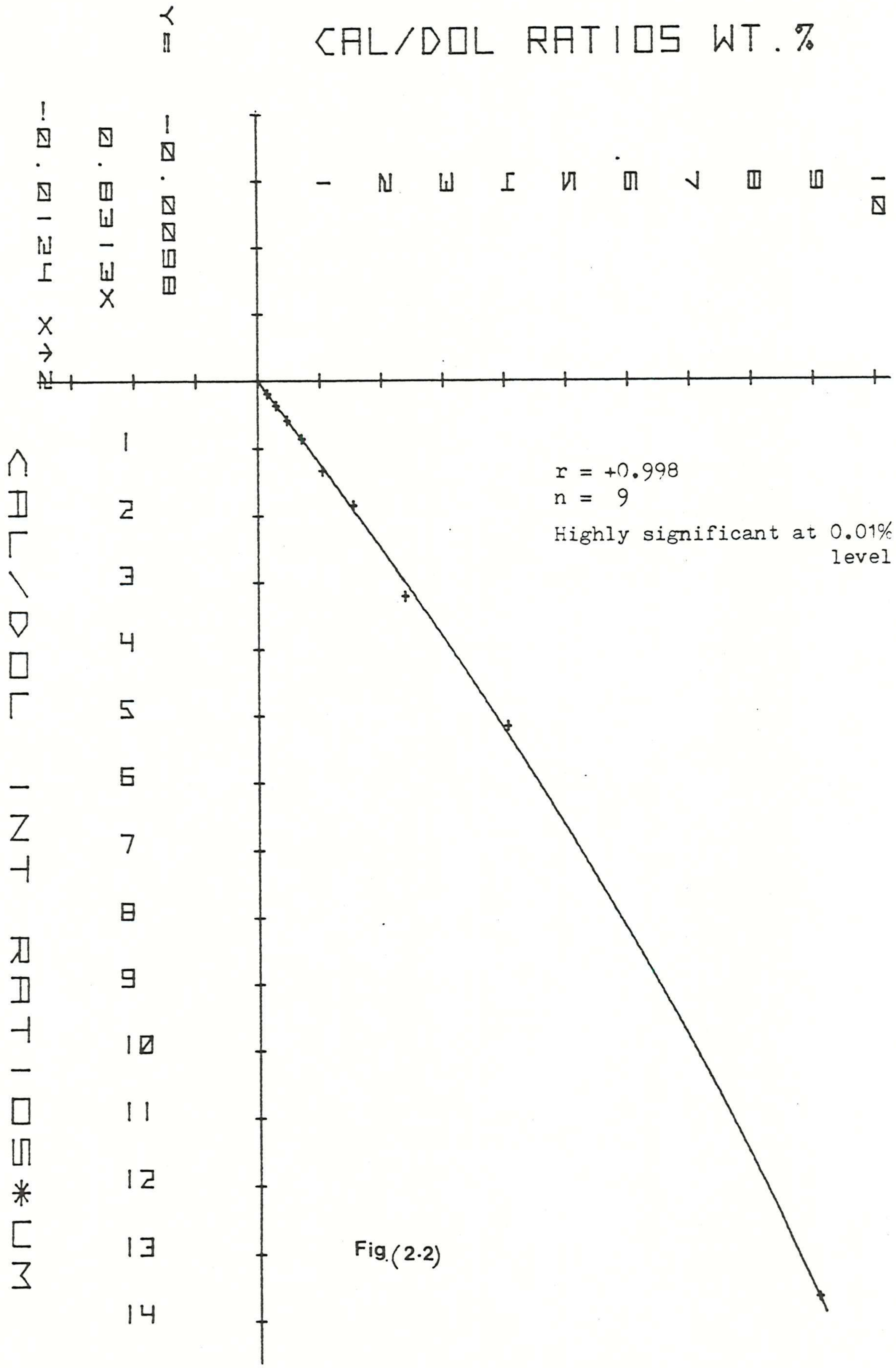
Y = Calcite/dolomite ratios weight %

X = Calcite/dolomite ratios of peak height x μm.

μm = Mass absorption values, obtained from Molybdenum tube programme X.R.F.

2.I.6 Determination of Carbonate Contents

The abundances of carbonates in the sediments of the two boreholes were determined as (i) total carbonates, and (ii) individual carbonate minerals. The two borehole sediments do not contain the same carbonate minerals. The Winterborne Kingston Borehole sediments contain only one carbonate mineral, i.e. calcite. The sediments of the Warlingham Borehole contain two carbonate minerals, i.e. calcite and dolomite (ferroan). Due to the variation of carbonate minerals, one single method for their determination was not possible to follow.



r = +0.998
n = 9
Highly significant at 0.01% level

Fig.(2·2)

TABLE (2.4): Calibration of X.R.D. for Calcite/Dolomite Ratios

Sample No.	Composition	Calcite/Dolomite wt.% ratios	Calcite/Dolomite peak height ratios, corrected for mass absorption
(1)	*L only	Infinity	
(2)	9L + 1D	9.000	13.601
(3)	8L + 2D	4.000	5.097
(4)	7L + 3D	2.333	3.155
(5)	6L + 4D	1.500	1.788
(6)	5L + 5D	1.000	1.280
(7)	4L + 6D	0.666	0.800
(8)	3L + 7D	0.428	0.531
(9)	2L + 8D	0.250	0.306
(10)	1L + 9D	0.111	0.131
(11)	+D only	0.000	0.000

* Limestone
\+ Dolomite

Regression Results of Calibration

Correlation coefficient (r) = 0.9976
(r^2) = 0.995
S.T.D. Error (A) = 0.0446
" " (B) = 0.0271
" " (C) = 0.0019
Number of Pellets (n) = 11

Therefore different methods were tried, to select the methods which are quick and give satisfactory results. It was noticed that the acid digestion method proposed by MOLINA (1974), and satisfactorily used by PAPAVASILIOU (1979) was only suitable for the Winterborne Kingston Borehole sediments, which contain calcite as the only carbonate mineral. In this method, acetic acid of 10% strength was used to dissociate the carbonate minerals. The other methods, in which the amounts of carbonate CO_2 obtained by various methods are used for the computation of carbonates, were found suitable for sediments containing more than one carbonate mineral, i.e. calcite and dolomite, etc. The estimation of carbonates for such sediments was done by using the amounts of carbonate CO_2 and the conversion factor of 2·27for only calcite, and 2·2 for a mixture of calcite and dolomite. No difficulty was faced for the satisfactory estimation of the carbonate contents of the Winterborne Kingston Borehole sediments, as they contain only one carbonate mineral, i.e. calcite. The abundances of calcite were computed using the carbonate CO_2 values obtained by the Infra-red gas analyser, which have been checked for precision as shown in Figure (2.3a & b). The values of CO_2 and calcite of the Winterborne Kingston Borehole sediments are tabulated in Appendix (2.1).

For the Warlingham Borehole sediments, which contain dolomite (ferroan) as the additional carbonate mineral, it was noticed that the amounts of carbonate CO_2 determined by the Infra-red gas analyser using Orthophosphoric acid, were much lower than the CO_2 values determined by other methods, including the calculated CO_2 concentrations obtained from CaO and MgO values, assuming that they represent the total carbonates, as is shown in Table (2.5). It seems that, due to the presence of dolomite, incomplete dissociation of carbonates took place. Therefore it was decided that the carbonate contents of these sediments may be determined as 'total carbonates', by the acid digestion method used by BELLAMY (1980) for the Kimmeridgian sediments, which contain similar dolomite (ferroan). The method was used after some modifications. A brief account of all the methods used is given below.

a) Total Carbonates in the Winterborne Kingston Borehole Sediments

i) Determination based on CO_2 values obtained by Infra-red gas Analyser

The amount of carbonate CO_2 for each sample was determined by

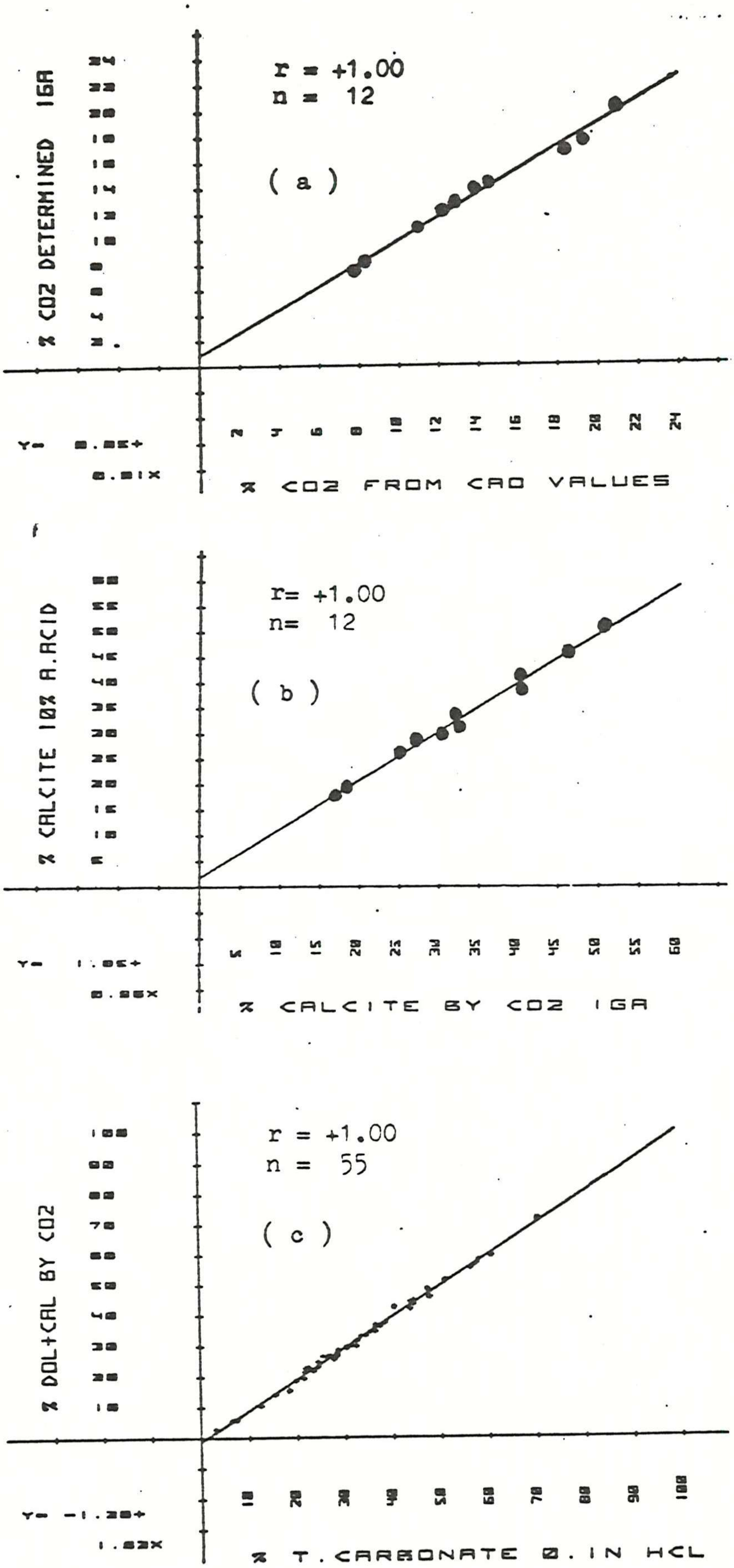
r = +1.00
n = 12
(a)
% CO2 DETERMINED IGA
2
4
6
8
10
12
14
16
18
20
22
24
% CO2 FROM CAO VALUES
Y= 0.05+
0.91X
r= +1.00
n= 12
(b)
% CALCITE 10% A.ACID
5
10
15
20
25
30
35
40
45
50
55
60
% CALCITE BY CO2 IGA
Y= 1.05+
0.95X
r = +1.00
n = 55
(c)
% DOL+CAL BY CO2
10
20
30
40
50
60
70
80
90
100
% T.CARBONATE 0.1N HCL
Y= -1.20+
1.02X

FIG.(2.3)

TABLE (2.5): Comparison of the Abundances of Carbonate CO_2 and Carbonates, determined by different methods in the sediments of two Boreholes

WARLINGHAM BOREHOLE SEDIMENTS

Sample No.	CO_2 from CaO + MgO	CO_2 by I.G.A.	CO_2 by 0·1N(HCl)	CO_2 by T.G.A.	Total carbonates from CO_2(I.G.A.)	Total carbonates from CO_2(T.G.A.)	Total carbonates 0·1N(HCl)
	%	%	%	%	%	%	%
BR-115	21·50	19·69	21·50	20·90	45·06	46·06	47·31
BR-123	19·68	14·80	19·70	19·20	31·48	42·24	43·31
BR-129	31·82	29·80	31·80	31·00	66·58	68·20	70·00
BR-199	11·89	7·78	11·90	11·60	16·00	25·52	26·16
BR-656	15·27	9·92	16·40	15·00	22·18	33·00	36·00
BR-826	16·20	11·72	16·40	15·40	26·38	33·88	36·00
BR-1220	11·68	7·44	12·10	11·00	16·78	24·20	26·60
BR-1811	14·00	11·25	14·15	13·10	24·87	28·80	32·00

/contd.over

TABLE (2.5) contd.

WINTERBORNE KINGSTON BOREHOLE SEDIMENTS

Sample No.	CO_2 from CaO	CO_2 by I.G.A.	CO_2 by 10% A/acid	Total carbonates from CO_2 (CaO)	Total carbonates from CO_2(I.G.A.)	Total carbonates from CO_2 (10% Acetic acid)
	%	%	%	%	%	%
WBK-8	20·85	20·20	20·72	45·87	45·90	45·60
WBK-9	23·58	22·34	23·04	51·88	50·70	50·70
WBK-10	18·39	17·03	17·77	40·46	39·70	39·10
WBK-12	19·30	17·73	18·54	42·64	40·30	40·80
WBK-23	13·94	13·93	14·86	30·67	31·70	32·70
WBK-28	10·99	10·99	11·95	24·18	25·00	26·30
WBK-30	13·91	13·93	14·64	30·60	31·70	32·20
WBK-32	12·32	12·05	13·00	27·13	27·30	28·60
WBK-37	14·38	14·18	14·43	31·64	31·70	31·75
WBK-46	12·95	12·80	13·50	28·49	29·70	29·70
WBK-54	8·14	8·01	8·73	17·91	18·20	19·20
WBK-58	7·81	7·62	8·20	17·18	17·30	18·05

the Infra-red gas analyser, as described under the heading of 'Determination of CO_2', and is tabulated in Appendix (2.1). The values of CO_2, determined by Infra-red gas analyser, were found satisfactory when compared with the CO_2 values of the same samples determined by other methods, as is shown in Table (2.5). A very strong positive correlation, highly significant at an 0·01% level, between the values of CO_2 obtained by Infra-red gas analyser and CaO values is shown in Figure (2.3a). Calcite being the only carbonate mineral present, in these sediments, it was assumed that the entire amount of carbonate CO_2 represents the amount of calcite. The abundances of calcite for each sample were calculated and are shown in Appendix (2.1). The estimation of the abundances of calcite was done according to the following:

$$\%\ \text{Calcite} = \%\ CO_2\ (\text{carbonate}) \times 2{\cdot}27.$$

Factor 2·27 is the conversion factor for CO_2 to calcite which is derived by dividing the molecular weight of $CaCO_3$(100) by the molecular weight of CO_2(44).

ii) Determination by Acid Digestion method (10% Acetic acid)

Acetic acid of 10% strength was used for the determination of carbonates, as proposed by MOLINA (1974) and applied by PAPAVASILIOU (1979). The results obtained by this method from 12 representative samples showed an excellent agreement with the carbonate values determined by other methods, including the CO_2 values determined by Infra-red gas analyser, which are shown in Table (2.5) and Figure (2.3b). Therefore, it was confirmed that values of carbonate CO_2 obtained by the Infra-red gas analyser are reasonably accurate, and the abundances of calcite estimated from these values are satisfactory. Figure (2.3b) shows a very strong positive correlation ($r = +1{\cdot}00$), highly significant at the 0·01% level, between the calcite abundances, estimated by 10% acetic acid, and CO_2 from Infra-red gas analyser, confirming the satisfactory estimation of carbonates.

b) Total Carbonates in the Warlingham Borehole sediments

i) Determination based on CO_2 values (I.G.A.)

The CO_2 values obtained by Infra-red gas analyser for these sediments were found to be much lower when compared with the CO_2 values determined by various other methods, as shown in Table (2.5). The abundances of carbonates estimated from these values were also found to be much lower, which is also shown in Table (2.5). It appears that Orthophosphoric acid, which completely dissociated carbonates in the Winterborne Kingston Borehole sediments, was not capable of dissociating thoroughly the carbonates of the Warlingham Borehole sediments, due to the presence of dolomite.

ii) Acid digestion method (10% Acetic acid)

The acid digestion method proposed by MOLINA (1974), and successfully used for the carbonate determination in the Winterborne Kingston Borehole sediments, was also found unfit for these sediments due to the presence of dolomite (ferroan). It appears that acetic acid of 10% strength was not strong enough to dissociate completely the entire contents of carbonates. This method was rejected as being unsuitable for these sediments.

iii) Acid digestion method (0·1N HCl)

The acid digestion method used by BELLAMY (1980) for the estimation of carbonates in the Kimmeridgian sediments, containing a similar type of dolomite (ferroan), was used with some modifications. The carbonate contents of 12 representative samples were determined by this method. The results showed an excellent agreement with the results obtained for the same samples by other methods, as shown in Table (2.5). Therefore the total carbonate contents of these sediments were determined by this method, and are tabulated in Appendix (2.2).

The details regarding the various steps involved, and the apparatus used in this method, are given below:

1) Filtration was done by the same apparatus as was used by MOLINA (1974).
2) Filtration disc of 3 porosity was used.
3) Tema-mill ground sample was dried for ½ an hour in an oven at 110°C temp.
4) Filter disc was washed and dried for 15 minutes in the same oven.
5) Filter disc was cooled in a desiccator and accurately weighed (A gms).

6) 0·5 gm. dried sample was weighed in a clean and dry beaker.
7) About 100 mls. of 0·1N HCl was added to the sample in the beaker.
8) The beaker was stirred by a glass rod and was left on a sand bath at 60°C overnight.
9) If all reaction was complete next day, the sample was filtered using a vacuum pump. If reaction was still evident, more hydrochloric acid (0·1N) HCl was added.
10) Finally the filter disc and residues were washed repeatedly by distilled water under the vacuum.
11) The washed filter disc, containing the residue, was left in an oven at 110°C temp. to be dried.
12) When dried, the filter disc, along with the residue, were carefully weighed (B gms.).
13) The loss in weight is the weight of carbonates removed, and it may be obtained by the difference of the two readings at steps (5) and (12), as is shown below:

$$A - B = C \text{ gm. (weight loss in 0·5 gm.)}$$

The contents of the total carbonates for each sample of the Warlingham Borehole sediments were determined by this method, and are tabulated in Appendix (2.2). From these carbonate values, the equivalent amounts of CO_2 were calculated by dividing the carbonate values by a factor of 2·2, and are tabulated in Appendix (2.2).

c) Determination of Calcite and Dolomite Abundances

The abundances of calcite and dolomite for each sample were calculated from the calcite/dolomite peak height ratios, already obtained by the X.R.D., and the amount of carbonate CO_2 obtained by converting the contents of total carbonates determined by the acid digestion method (0·1N, HCl), and both are tabulated in Appendix (2.2). The total carbonate content of each sample was divided by a conversion factor of 2·2, to convert it into an equivalent amount of CO_2. The conversion factor for CO_2 to calcite is 2·27 and for dolomite is 2·10. The Warlingham Borehole sediments contain calcite and dolomite - both minerals. Therefore it was decided that a conversion factor may be obtained by taking the average value of the two conversion factors.

The average value of the factors, being 2·18, was rounded up to 2·20. The abundances of calcite and dolomite in each sample were calculated as described below:

$$\text{Let } C = \%\ \text{calcite}$$

$$D = \%\ \text{dolomite}$$

$$\therefore C/D = R \text{ (known from the X.R.D.)}$$

OR

$$\frac{CaCO_3}{CaCO_3.MgCO_3} = R$$

OR

$$CaCO_3 + CaCO_3.MgCO_3 \longrightarrow 2\ CaO + MgO + 3CO_2$$

$$\longrightarrow X\ \%\ \text{of}\ CO_2.$$

$$\text{Since } C/D = \text{'R'} \quad - - - - - - - - - - (1)$$

$$(C \times \frac{44}{100}) + (D \times \frac{88}{184}) = X\ \%\ \text{of}\ CO_2 \quad - - - - - - (2)$$

$$\text{Since } C/D = \text{'R'}$$

$$\therefore C = R \times D$$

By substituting the value of C in equation (2), we get:

$$(R \times D \times \frac{44}{100}) + (D \times \frac{88}{184}) = X\ \%\ \text{of}\ CO_2$$

OR

$$(R \times D \times 0{\cdot}44) + (D \times 0{\cdot}48) = X\ \%\ \text{of}\ CO_2$$

OR

$$D(R \times 0{\cdot}44 + 0{\cdot}48) = X\ \%\ \text{of}\ CO_2$$

OR

$$D = \frac{X}{(R \times 0{\cdot}44 + 0{\cdot}48)}$$

OR

$$D = R \times 0{\cdot}44 + 0{\cdot}48$$

$$\therefore \text{Calcite (C)} = D \times R.$$

The values of the total carbonates determined by acid digestion method using 0·1N HCl, and the total of calcite and dolomite abundances calculated from the CO_2 values according to the above method, showed a very strong positive correlation (r = + 1·00), highly significant at an 0·01% level of significance, as is shown in Figure (2.3c). This confirms that the abundances of calcite and dolomite estimated for the Warlingham Borehole sediments are reasonably satisfactory.

2.I.7 Determination of Organic Carbon

The abundances of organic carbon in the sediments of both the boreholes were computed from the amounts of CO_2 representing the organic carbon present in the sediments. The CO_2 was determined by the difference of the total CO_2 and carbonate CO_2, both determined by the Infra-red gas analyser, and are tabulated in Appendices (2.1 and 2.2); for details see Determination of CO_2. The amounts of total CO_2, carbonate CO_2 and CO_2 representing organic carbon are also tabulated in Appendices (2.1 and 2.2).

The amount of organic carbon present in each sample was calculated according to the following method:

Let total CO_2 = C%

Let carbonate CO_2 = C1%

$\therefore$ CO_2 representing organic carbon = C - C1 = C2%

Therefore the abundance of organic carbon will be $\%C2 \times \frac{12{\cdot}01}{44}$

OR $\%C2 \times 0{\cdot}2729$.

The calculated abundances of organic carbon are shown in Appendices (2.1 and 2.2).

2.1.8 Determination of Pyrite Contents

The contents of pyrite of the sediments of both the boreholes were calculated from the amount of sulphur (S), as obtained from the Betaprobe, during the analysis of major elements (see analysis of major elements). Since pyrite is the only sulphide mineral present in these sediments, and detected in the X.R.D. runs of the random powder analysis of these sediments, it seems realistic to assume that the whole amount of sulphur of these sediments resides in pyrite. Having this view in mind, the abundance of pyrite in each sample was calculated and is tabulated in Appendices (3.1 & 3.2). The abundance was calculated as follows:

The pyrite % = % sulphur x 1·871.

The factor 1·871 was obtained by dividing the atomic weight of FeS_2 (119·9) by the atomic weight of S_2 (64·12).

$\therefore$ % pyrite = % sulphur x $\frac{119{\cdot}9}{64{\cdot}12}$ OR % pyrite = % S x 1·871.

The % of sulphur is already known for each sample.

2.I.9 Determination of Total Clays Content

The sediments of both the boreholes are composed mainly of minerals, e.g. quartz, calcite, dolomite, pyrite, organic carbon and total clays (illite, kaolinite, chlorite, smectite and mixed-layered minerals). The abundances of these minerals, with the exception of total clays, have already been calculated in parts per hundred, for each sample. Therefore the amount of 'total clays' present in each sample was obtained from the following equation:

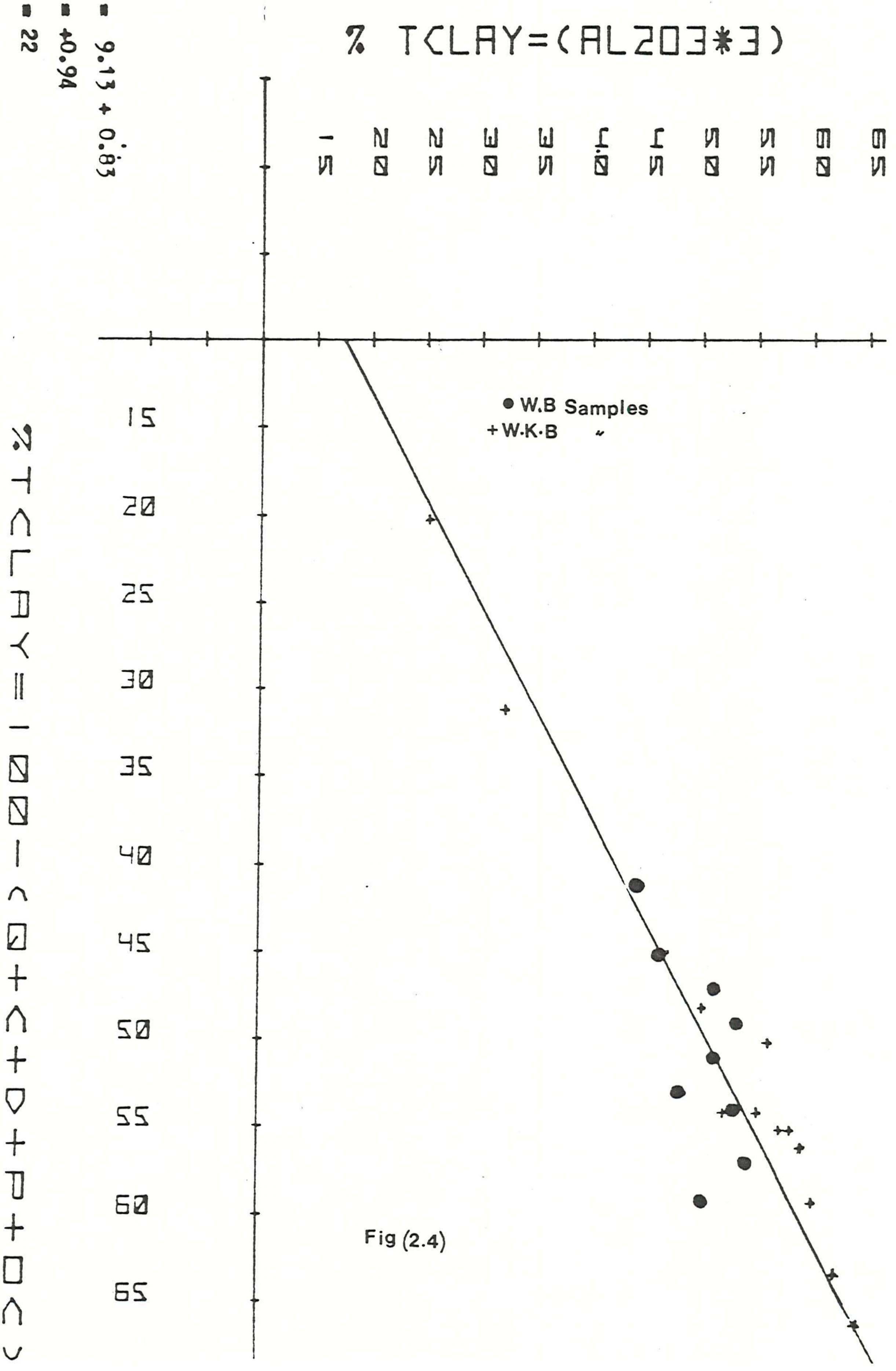
$$\%\ \text{Total clays} = 100 - (\text{quartz} + \text{calcite} + \text{dolomite} + \text{pyrite} + \text{organic carbon})$$

The accuracy of the estimation of total clay contents depending on the accuracy of the other mineral determinations, the mineral analysis of the bulk rock can only be regarded as semi-quantitative. A very rough check on the amount of total clays, determined in this way, can be done by comparing the calculated abundances of total clays obtained by multiplying the carbonate free values of Al_2O_3 by a factor of 3, as suggested by BÖSTROM (1972, 1974) and BÖSTROM et al. (1976). The abundances of total clays determined by the difference method,and calculated from the Al_2O_3 values, are plotted in Figure (2.4), which shows a very strong positive correlation ($r = + 0{\cdot}94$), highly significant at an 0·01% level of significance, between the abundances of the total clays determined and calculated values of total clays from the Al_2O_3 values. The abundances of total clays are tabulated in Appendix (3.1).

2.II Mineral Analysis of Clay Fraction ($< 2\mu$)

2.II a) Preparation of Oriented Slides

Oriented slides of clay fraction ($< 2\mu$) of each sample were prepared for the study of clay mineral species present in the sediments of the two boreholes. The clay fraction ($< 2\mu$) was separated from the whole rock by the processes of sedimentation. In this method rock powder, ground by hand in an agate mortar and pestle, was used. Mechanical grinding was avoided as it destroys the lattices of the clay minerals.



Y = 9.13 + 0.83

r = +0.94

n = 22

Fig (2.4)

About 1 gm. of the powdered sample was placed in a 100 ml. beaker. Acetic acid of 2% strength was added and the beaker was placed in the ultrasonic tank for 10-15 minutes; then it was left overnight so that the carbonate components are removed. The following day the liquid was decanted and the residue was washed with distilled water 3 to 4 times. Afterwards the beaker with washed residue was ¾ filled with distilled water and was put for 30 minutes into the ultrasonic tank again for complete disaggregation of the particles of the sample. To obtain the clay fraction ($< 2\mu$), the sample was allowed to sediment in the laboratory for four hours; during this period of sedimentation all the coarse particles settle down to the bottom of the beaker, leaving the clay sized particles in the suspension. The upper 5 cm. of this slurry was taken into a centrifuge tube, and the sample was centrifuged for about 10 minutes; during this phase all the clay sized particles ($< 2\mu$) settle down in the bottom of the tube, leaving clear water above. From this deposit of sediment four preparations were made by smearing the clay material onto glass slides. One slide was prepared after a special acid digestion treatment with hydrochloric acid (HCl), to destroy the chlorite. If kaolinite and chlorite both occur in one sample, removal of chlorite is necessary to obtain clear identification of the kaolinite. This was achieved, as mentioned above, by boiling the slurry in 1:1 hydrochloric acid for about 15 minutes. The acid treated slurry, after washing thoroughly in de-ionized water, was then smeared onto a glass slide in the usual way. All four slides prepared in this way were labelled as (N) normal, (H) heated, (G) glycolated, and (A/D) acid digested. The slide marked (G) was left in a desiccator containing ethylene glycol and placed in an oven at $\simeq 150^\circ$C temp. for one hour. The slide marked (H) was left in a furnace at a temperature of 450-500°C for two hours. The identification and estimation of the abundances of clay mineral species are facilitated by the above-mentioned treatments.

b) X-ray Diffractometry

All the samples, prepared as described above, were scanned on the Philip's PW 1010 X-ray Diffractometer on the X.R.D. settings mentioned below:

Divergence and scatter slits = ¼ degree
Receiving slits = 0·2 m.m.
Goniometer scanning speed = 1°, 2θ/minute
Recorder chart speed = 600 cms/hour
Time constant = 4

c) Identification of Clay Minerals

The clay minerals, identified in the sediments of the Warlingham Borehole, include illite, kaolinite, chlorite and mixed-layer (non-expanding). The sediments of the Winterborne Kingston Borehole contain the clay minerals: illite, kaolinite, chlorite and smectite (montmorillonite-illite). The identification of these minerals was done on the basis of their main (001) peak positions on the X-ray Diffractograms, which are shown in Table (2.6).

TABLE (2.6): Peak Positions of the Clay Minerals on the X.R.D. Diffractograms after certain treatments

Clay Mineral	Slide	Peak position, 2θ	Peak position in Å
ILLITE	N	8·84°, 2θ	9·99Å
	G	8·84°, 2θ	9·99Å
	H	8·84°, 2θ	9·99Å
KAOLINITE	N	12·4°, 2θ	7·13Å
	G	12·4°, 2θ	7 13Å
	H	Peak destroyed	
CHLORITE	N	6·2°, 2θ	14·24Å
	G	6·2°, 2θ	14·24Å
	H	6·4°, 2θ	13·80Å
MIXED-LAYER (non-expanding) (a mound was observed towards the 2θ lower angle)	N	From 8·0°, 2θ to 4·2°,2θ	11·04Å - 21·02Å
	G	No change	No change
SMECTITE (Montmorillonite+illite)	N	6·0°,2θ - 8·2°,2θ	14·72Å - 10·77Å
	G	5·18°, 2θ	17·04Å

Note: N = normal slide; G = glycolated slide; H = heated slide.

d) Estimation of Relative Abundances

The relative abundances of the clay mineral species were calculated by the method proposed by MATTER (1974), and satisfactorily used by PAPAVASILIOU (1979). For the correction of differences of the reflectivity of minerals certain factors were used, which are mentioned below:

Smectite peak area x $^1/_4$
Illite peak area x $^1/_1$
Mixed-layer peak area x $^1/_3$
Kaolinite peak area x $^1/_2$
Chlorite peak area x $^1/_2$

The kaolinite area was obtained on the acid digested slide, and then equalised to the glycolated slide, according to the calculations shown below:

$$\text{Kaolinite area(K)} = K_a \times \frac{I(g)}{I(a)} \quad - - - - \quad (1)$$

where K_a = area of kaolinite counted on the acid digested slide
$I(g)$= area of illite " " " glycolated slide
$I(a)$= area of illite " " " acid digested slide.

The area of chlorite was obtained by the difference of area of kaolinite as computed above (K), and the area of chlorite + kaolinite on the glycolated slide, at a peak position of 7Å, which is shown below:

$$K - Kg = \text{Ch. (area for chlorite).}$$

where K = computed area for kaolinite, mentioned above in (1)
Kg = area of kaolinite + chlorite, counted on the glycolated slide, at peak position of 7Å.

All areas of the clay minerals were counted on glycolated slides, and were summed and normalized to parts per hundred, and the abundances of the sediments of the two boreholes are tabulated for each sample in Appendices (7.1A and 7.2A).

e) Abundances of Clay Species in Bulk Rock

The abundances of the individual clay mineral species as part of the bulk rock were calculated by using the already known values of 'total clay' in per cent in the bulk rock, and the amounts of individual clay minerals, calculated in percentages in the ($< 2\,\mu$) fraction for each sample. The calculation was done according to the following:

The amount of total clay in bulk rock = A%
" " " clay mineral(b) in ($< 2\mu$) fraction = B%
∴ The amount of clay mineral(b) in bulk rock = $\frac{A}{100} \times B$.

As an example, the amounts of the individual clay minerals in the bulk rock of sample BR-115 have been calculated, using the data of its bulk and clay fraction ($< 2\mu$) mineralogy as under:

i) Minerals in bulk rock

	%
Quartz	= 16·00
Calcite	= 9·35
Dolomite	= 36·96
Pyrite	= 1·76
Organic carbon	= 0·27
Total clays	= 36·23
Total	=100·57

ii) Minerals in clay fraction ($< 2\mu$)

	%
Illite	= 58
Kaolinite	= 00
Chlorite	= 00
Mixed-layer	= 42
Total	100

		A/100		B		
% Illite in bulk rock	=	0·362	x	58	=	21·00
% Kaolinite " "	=	0·362	x	0	=	0·00
% Chlorite " "	=	0·362	x	0	=	0·00
% Mixed-layer " "	=	0·362	x	42	=	15·20
				Total	=	36·20

Where A represents the abundance of total clays calculated in bulk rock.
B " " " " individual clay minerals in the clay fraction ($< 2\mu$).

iii) Final bulk mineral composition of sample BR-115

	% Mineral
Quartz	= 16·00
Calcite	= 09·35
Dolomite	= 36·96
Pyrite	= 01·76

		% Mineral
Organic carbon	=	00·27
Illite	=	21·00
Kaolinite	=	00·00
Chlorite	=	00·00
Mixed-layer	=	15·20
Total	=	100·54

2.III Chemical Analysis

2.III.1 Analysis of Major Elements by Betaprobe

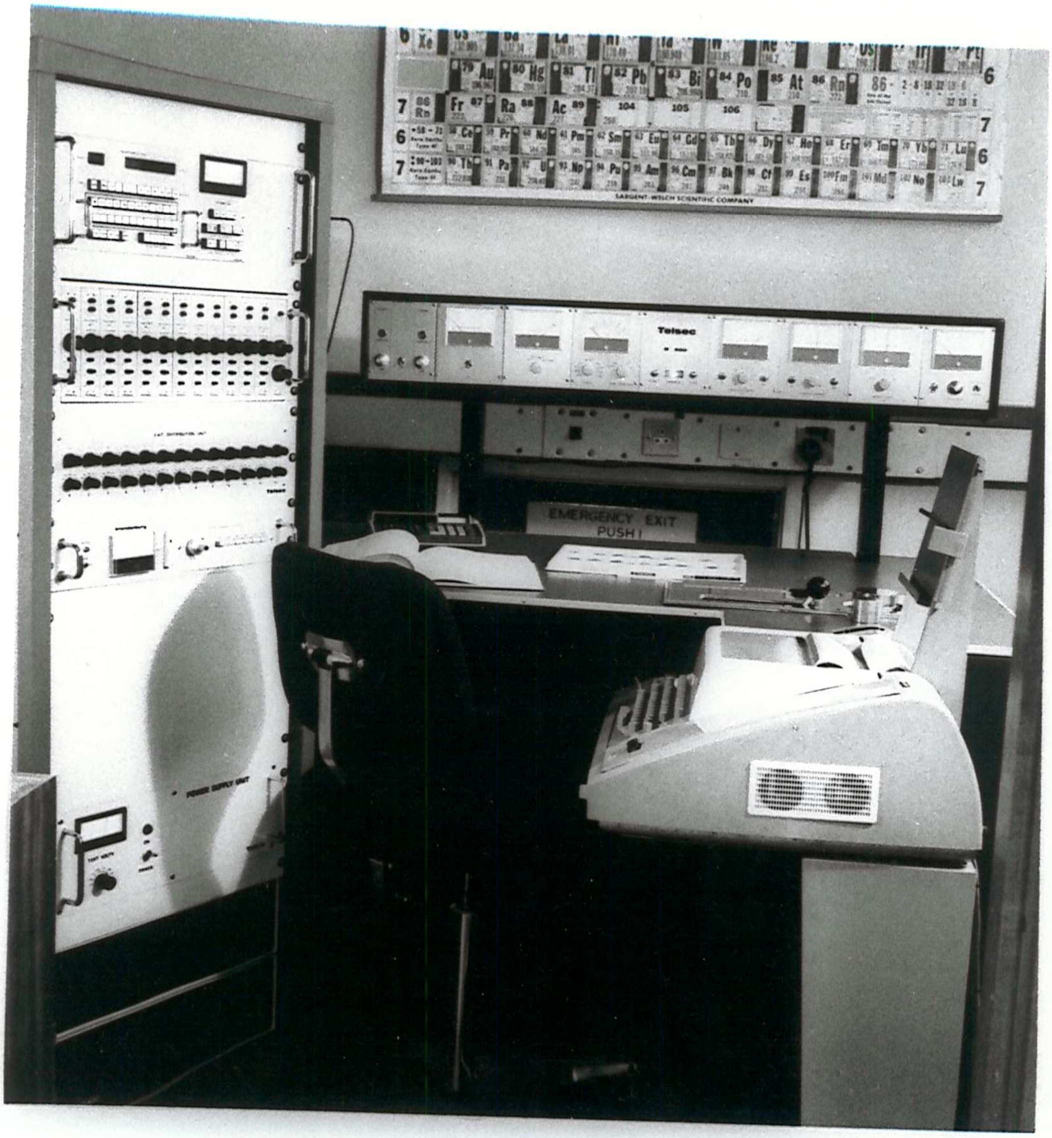
a) Betaprobe

A Telsec B-300 Betaprobe was used for the analysis of major elements, including phosphorus and sulphur. It is a 12-channel simultaneous X-ray Fluorescence Spectrometer with a Teletype printer giving a direct analysis print-out of concentrations of the elements, in per cent, present in the sample. The Spectrometer provides good analyses of light elements, e.g. Na, Mg, Al, Si, P, S, K, Ca, Ti and Fe, and some ultra-light elements, e.g. F, O, C, B, due to high X-ray intensities produced by direct excitation of an electron beam.

The characteristic X-radiation from each element present is detected by twelve pre-set crystal dispersion channels, each with its own gas flow proportional counters. The output from each channel is fed via a computer to the Teletype read-out. The computer holds calibration data for a series of different rock types, and thus an accurate analysis is achieved by a 20-second excitation period.

The Betaprobe (Telsec B-300) is shown in Plate (2·2); it differs from the conventional X.R.F. in many respects. The fluorescent radiation in the Betaprobe is excited by a beam of high energy electrons. The system of direct excitation by electrons is economical as well as very useful, as it produces very high intensities of characteristic X-radiation, at the expense of only a few watts power, which makes possible accurate analysis of the concentrations of light and ultra-light atomic number elements. For the analysis of the desired elements the sample can be prepared either as 'raw rock' or as a 'fluxed bead', using a small amount of the rock powder. In both cases graphite is added to the sample to make it conducting.

PLATE 2.2



a) TELSEC B-300 BETAPROBE

b) Settings of the Betaprobe

The requirements of power, gas and water to operate the Betaprobe are described below:

i) Electrical: 210/250 V. A.C. single phase 5A.

ii) Water : 50 litres/hour, at a maximum pressure of 50 p.s.i (for cooling the diffusion pump)

iii) Gas : 90% argon & 10% methane is required for the proportional counter. If elements like fluorine, oxygen, nitrogen, carbon and boron are included in the analytical programme, a separate supply of pure methane gas is also necessary.

c) Calibration

i) Raw Rocks: The Betaprobe was calibrated by running many international standards of sedimentary rocks to produce calibration plots for all elements. It was found necessary to produce two sets of calibration data - one for silicate sediments and one for carbonate-rich rocks. The different matrices evidently produced quite different mass absorption characteristics. The statistical details of the calibrations are given in Tables (2.7a and b).

ii) Fluxed Rocks: The Betaprobe was calibrated by running international standard rocks of all types. The statistical details of the calibration are given in Tables (2.7a and b).

TABLE (2.7a): Telsec B-300 Spectrometer - Element Calibration Statistics

			Carbonate Rocks (1D 9)		
	1 No.of Stds.	2 Mean(%)	3 Range(%)	4 Standard Error of Estimate(SEE) %	5* SEE as % of Mean
SiO_2	28	1.15	0.00 - 2.83	0.069	5.98
TiO_2	34	0.083	0.00 - 0.61	0.020	24.49
Al_2O_3	37	1.57	0.00 -16.00	0.062	3.92
Fe_2O_3	40	0.49	0.00 - 2.02	0.068	13.94
MgO	40	11.20	0.00 -21.59	0.627	5.60
CaO	40	38.50	13.30 -56.03	0.673	1.75
Na_2O					
K_2O	25	0.044	0.00 - 0.09	0.005	11.42
S					
P_2O_5	31	0.029	0.00 - 0.08	0.007	23.11

/contd.over

TABLE (2.7a contd.

SE of E (x) = $SD(x)\sqrt{1 - r^2}$

where r = correlation coefficient

SD(x) = standard deviation of element concentration values.

TABLE (2.7b): Telsec B-300 Spectrometer - Element Calibration Statistics

Sedimentary Rocks (1D 7)

	1 No.of Stds.	2 Mean (%)	3 Range (%)	4 Standard Error of Estimate (SEE)	5* SEE as % of Mean
SiO_2	30	51·21	28·29 - 65·39	% 1·99	3·88
TiO_2	24	0·739	0·35 - 1·06	0·033	4·41
Al_2O_3	27	16·19	7·24 - 23·58	0·804	4·97
Fe_2O_3	24	5·56	3·20 - 8·73	0·224	4·03
MgO	24	2·11	1·27 - 4·50	0·172	8·15
CaO	24	4·36	0·47 - 11·86	0·260	5·96
Na_2O	21	0·92	0·10 - 3·43	0·030	3·28
K_2O	30	3·36	0·74 - 7·93	0·046	1·36
S			0·033- 0·557		
P_2O_5	27	0·190	0·08 - 0·37	0·0067	3·53

****

SE of E (x) = $SD(x)\sqrt{1 - r^2}$

where r = correlation coefficient

SD(x) = standard deviation of element concentration values.

*(5) This is essentially an indication of 'coefficient of variation (CV)'. Values less than 5/6% are considered as entirely satisfactory. Values less than 15% may be considered as satisfactory. Values greater than 15% indicate problems in detection.

---

d) Sample Preparation

i) Raw Rock Sample

A Raw rock sample was prepared as follows:

1) 1·8 gm. of rock powder (1 hour dried at 110°C) was weighed

2) 0·2 gm. pure graphite (1 hour dried at 110°C) was added to the weighed rock powder.
3) The above mixture was ground in a 100 cc.capacity Tema mill for 15 minutes.
4) A small amount of the ground mixture was placed in the concave side of a lead disc, cleaned by acetone.
5) The sample top was covered with a cellulose sheet.
6) The disc was placed in a Press and a pressure of 10 tons was applied; the disc was left under pressure for about 3 minutes; gradually the pressure was released.
7) The disc was labelled and stored in a clean plastic tray in a desiccated box until a batch was ready for analysis.

(Note: If the amount of sample is not enough, half the amount of each sample and graphite may be used.)

ii) <u>Preparation of Fluxed Sample</u>

Fluxed samples were prepared when the amount of the sample was under one gram. The residues obtained by the leaching of samples with acetic acid and hydroxylamine-hydrochloride in most of the cases yielded samples under one gram. The chemicals used include lithium metaborate and pure graphite. The following are the various steps involved:

1) Lithium metaborate was dried by leaving it in a platinum crucible in a furnace at 600°C overnight.
2) Rock powder was dried, leaving it in an oven at 110°C for 1½ hours.
3) 0·4 gm. of rock powder was weighed in a clean platinum-gold alloy crucible (90% Pt, 10% Au).
4) 2·0 gm. of lithium metaborate was weighed in the same crucible.
5) The crucible was heated by Meker burner, the contents being retained in a fluxed state for 15 minutes. During heating, the lid of the crucible was kept half open for good oxidation.

6) The crucible was cooled in a desiccator for 15 minutes and then its weight was recorded and the 'loss on ignition' was calculated as a loss percentage.

7) The weight loss was made up by adding more lithium metaborate, bringing it to the original weight.

8) Again the contents of the crucible were heated on a burner to re-melt it for 10 minutes.

9) The crucible was cooled in a desiccator and the glass bead was removed.

10) The glass bead was weighed on a clean glazed paper. 10% of its weight of pure graphite was added to it.

11) The bead + graphite mixture was transferred to a clean 100 cc. Tema pot and was ground for 15 minutes.

12) The sample powder was put in a plastic sample bag and labelled. From this powder a disc was prepared in the usual way, and was run against the bead standards.

e) Detection Limits

The detection limits for all the elements analysed are given in Tables (2.7a and b).

f) Accuracy

The 'accuracy' of the determinations of each element has been determined as a standard error of the estimate (SEE), which has been extended to a type of coefficient variation. All statistical data are given in Tables (2.7a and b).

The abundances of the major elements were determined in the sediments of the Winterborne Kingston and Warlingham Boreholes, and are recorded in Appendices (4.1A) and (4.2A) respectively.

All analytical results of major elements are tabulated in Appendices (4.1A) and (4.2A).

2.III.2 Analysis of Trace Elements

2.1 Analysis of X-ray Fluorescence Spectrometer (X.R.F.)

a) X-ray Fluorescence Spectrometer (X.R.F.)

An automatic 24 channel Philips (PW-1212) X-ray Fluorescence

Spectrometer, with simultaneous punched tape and print-out facilities, was used for the analysis of trace elements (Mo, Nb, Zr, Y, Sr, Rb, Ti, Ni, Mn, Cr, V, U, Th, Pb, As, Zn, Cu, Ba, I,Ce and La) in bulk rock, clay and silt fraction samples. The analytical results of the bulk rock are tabulated in Appendices (4.1A and 4.2A). The goniometer of the X.R.F. can be set for 24 angular positions; 15 positions only in one cycle and the remaining 9 positions may be used in a second cycle of analysis if required. Different operating variables can be individually optimised for each angular position, including voltage, current, collimator, analysing crystal, detector, time and sample-spinner. 60 kV and 32 mA power supplies were usually used and a mixture of argon and methane gas was needed for the gas flow proportional cooler. The Philips PW-1212 X-ray Fluorescence Spectrometer is shown in Plate (2.3). The results of the analysis of trace elements in bulk rock of both the boreholes are tabulated in Appendices (4.1A) and (4.2A).

In X-ray spectroscopy the sample is irradiated with primary X-rays to produce secondary (fluorescent) radiation which, after collimation, is dispersed by an analysing crystal. The angle corresponding to a particular wave-length can be set on a goniometer and the intensity is recorded by counting with a suitable detector.

For optimum excitation and avoidance of unnecessary overlap problems, the trace elements were analysed on four separate programmes mentioned below:

1) Tungsten Tube Programmes:
    (i) (W-1) for Mo, Nb, Zr, Y, Sr, Rb, Ti
    (ii) (W-2) for Ni, Mn, Cr, V.

2) Molybdenum Tube Programme
    (MO-1) for U, Th, Pb, As, Zn, Cu.

3) Chromium Tube Programme
    (Cr-1) for Ba, I, Ce, La.

b) Sample Preparation

i) Washing of samples

All samples were obtained from the Borehole collection of I.G.S.

PLATE 2.3

PHILIP'S PW1212 X-RAY FLUORESCENCE
SPECTROMETER

The possibility of contamination with salts used in the drilling muds cannot be ruled out. Therefore, before grinding, all samples were washed as follows:

> 50 gms. of each sample was soaked in distilled water in a beaker of 250 mls. overnight. The following day the sample was centrifuged and the clear water separated by centrifuging was thrown away, and the centrifuge tube containing the washed sample was left in the cupboard for drying at a temperature of 110°C.

ii) Grinding the rock samples

After a couple of days, when the washed sample had completely dried in the cupboard, it was then loaded into the Tema-disc mill and was pulverised for 10 minutes. The Tema-mill is shown in Plate (2.2).

Ten minutes grinding of the rock produces less than 200 mesh particle size (SULAIMAN, 1972), an ideal grain size for chemical analysis. Between each rock-grinding the Tema-mill was cleaned by grinding broken glass for 3-4 minutes, followed by washing and drying.

iii) Pellet making

Pellets were prepared by taking approximately 10 gms of the sample powder in an agate pestle and mortar. To this powder 2-3 drops of a binder (2% aqueous solution of polyvinyl pyrrolidine) was added and thoroughly mixed with the help of the pestle. The damp paste thus produced was transferred into a loose-fitting cylinder placed in a small mould (COSGROVE, 1972a). The paste was tapped down so that it might attain the shape of the cylinder. The cylinder was then pulled out gently, and finely powdered boric acid was added to fill the space between the paste and the outer part of the mould. Afterwards more boric acid was added, covering the paste and filling the mould about ¾ full. A stainless steel plunger was inserted, and the paste (surrounded and covered by boric acid) was pressed at about 400-450 kg/sq.cm., for nearly three minutes, in a hydraulic press. The pressure was released slowly and the pellet was ready. The pellet was removed from the mould and kept in an air-tight container, which bears the mark of the sample number.

c) Precision and Detection Limits

The precision of the analysis of elements and detection limits are shown in Tables (2.8A-D). The operational conditions of the X.R.F., used during the analysis of all the programmes, have been described in Table (2.9).

All the determinations of elements were based on the previous extensive work of X.R.F. calibrations, carried out mainly by COSGROVE (1972). Regarding the calibration of the X.R.F. and the procedures of the sample preparations, however, the work of SULAIMAN (1972), BAQRI (1976), EL-SHAHAT (1977) and PAPAVASSILIOU (1979) may also be consulted.

d) X.R.F. Settings

Different settings on the X.R.F. for each tube programme were used, and are described in Tables (2.8A-D).

TABLE (2.8A): PW 1212 X-Ray Spectrometer - Tungsten One Programme (W-1) Element Calibration Statistics

Element	No.of stds.	Mean (ppm)	Standard Error of estimate (SEE) (ppm)	SEE as % of mean
Ti	36	4746	483	10
Rb	31	153	15	10
Sr	29	223	17	8
Y	24	51	9	17
Zr	31	185	21	11
Nb	19	18	3	17
Mo	9	33	6	17

****

$$\text{SE of E }(y) = \text{SD}(y)\sqrt{1 - r^2}$$

where r = correlation coefficient

SD(y) = standard deviation of element concentration values

/contd.over

TABLE (2.8A) contd.

PW 1212 X-Ray Spectrometer

Detection Limits for W.1 Programme

Ti	4 ppm
Rb	6 ppm
Sr	8 ppm
Y	5 ppm
Zr	5 ppm
Nb	5 ppm
Mo	4 ppm

Therefore any value below these limits should be recorded as n.d. = not detected.

****

$$\text{Detection Limit} = \frac{2\sqrt{2}}{m}\sqrt{\frac{Rb}{Tb}}$$

where m = slope in C/S/ppm
Rb = background in C/S
TB = time for background counts in secs.

TABLE(2.8 B): PW 1212 X-Ray Spectrometer - Tungsten Two Programme (W-2) Element Calibration Statistics

Element	No.of stds.	Mean (ppm)	Standard Error of estimate (SEE) (ppm)	SEE as % of mean
V	24	106	14	13
Cr	7	100	9	9
Mn	29	915	82	9
Ni	30	220	29	13
Ce	20	97	18	18
Ba	25	791	101	13

****

$$\text{SE of } E(y) = SD\,(y)\sqrt{1 - r^2}$$

where r = correlation coefficient
SD(y) = standard deviation of element concentration values.

/contd.over

TABLE (2.8B) contd.

PW 1212 X-Ray Spectrometer

Detection Limits for W.2 Programme

V	1 ppm
Cr	4 ppm
Mn	4 ppm
Ni	2 ppm
Ce	13 ppm
Ba	16 ppm

Therefore any value below these limits should be recorded as n.d. = not detected.

****

$$\text{Detection Limit} = \frac{2\sqrt{2}}{m}\sqrt{\frac{Rb}{Tb}}$$

where m = slope in C/S/ppm

Rb = background in C/S

Tb = time for background counts in secs.

TABLE (2.8C): PW 1212 Spectrometer:- Mo.1 Programme
Element Calibration Statistics

Element	No.of stds.	Mean (ppm)	Standard error of estimate (SEE) (ppm)	SEE as % of mean
U	13	29	4	14
Th	23	91	17	19
Pb	23	66	10	15
As	7	77	4	5
Zn	27	99	12	12
Cu	24	38	6	16

****

$$\text{SE of } E(y) = SD(y)\sqrt{1 - r^2}$$

where r = correlation coefficient

SD(y) = standard deviation of element concentration values.

/contd.over

TABLE (2.8C) contd.

PW 1212 Spectrometer

Detection Limits for Mo.1 Programme

U	5 ppm
Th	4 ppm
Pb	5 ppm
As	6 ppm
Zn	5 ppm
Cu	5 ppm

Therefore any value below these limits should be recorded as n.d. = not detected.

****

$$\text{Detection limit} = \frac{2\sqrt{2}}{m} \sqrt{\frac{Rb}{Tb}}$$

where m = slope in C/S/ppm
Rb = background in C/S
Tb = time for background counts in secs.

TABLE (2.8D): PW 1212 X-Ray Spectrometer - Chromium 1 Programme Element Calibration Statistics

Element	No.of stds.	Mean (ppm)	Standard Error of estimate (SEE) (ppm)	SEE as % of mean
Ba	28	597	64	11
Sc	19	17	1,8	11
I	5	39	2,2	6
Sn	7	132	2,7	2
Ce	20	92	21	23
La	32	62	16	25

****

$$\text{SE of E }(y) = SD(y)\sqrt{1 - r^2}$$

where r = correlation coefficient
SD(y) = standard deviation of element concentration values.

/contd.over

TABLE (2.8D) contd.

PW 1212 X-Ray Spectrometer

Detection Limits for Chromium 1 Programme

Ba	6 ppm
Sc	2 ppm
I	3 ppm
Sn	16 ppm
Ce	13 ppm
La	22 ppm

Any value below these limits should be recorded as n.d. = not detected.

$$\text{Detection limit} = \frac{2\sqrt{2}}{m}\sqrt{\frac{Rb}{Tb}}$$

where m = slope in C/S/ppm

Rb = background in C/S

Tb = time for background counts in secs.

TABLE (2.9): Operational Conditions for X.R.F. Determinations of Minor and Trace Elements

ELEMENT	LINE	CRYSTAL	PEAK 2θ	COLLIMATER	COUNTER	COUNTING TIME	TUBE	KV	mA	COUNTS
Mo	Kα	LiF220	29·05	F	S	40	W-1	95	20	FT
Nb	Kα	LiF220	30·58	F	S	40	W-1	95	20	FT
Zr	Kα	LiF220	32·25	F	S	40	W-1	95	20	FT
Y	Kα	LiF220	34·05	F	S	40	W-1	95	20	FT
Sr	Kα	LiF220	36·00	F	S	40	W-1	95	20	FT
Rb	Kα	LiF220	38·14	F	S	40	W-1	95	20	FT
Ti	Kα	LiF200	86·36	F	FL	40	W-1	60	32	FT
Cr	Kα	LiF200	69·16	F	FL	100	W-2	60	32	FT
Ni	Kα	LiF220	71·20	F	FL + S	40	W-2	60	32	FT
V	Kα	LiF200	76·70	F	FL	100	W-2	60	32	FT
Mn	Kα	LiF220	95·12	F	FL + S	40	W-2	60	32	FT
U	Lα	LiF220	37·23	F	S	40	Mo-1	95	20	FT
Th	Lα	LiF220	39·15	F	S	100	Mo-1	95	20	FT
Pb	Lα	LiF220	40·30	F	S	100	Mo-1	95	20	FT
As	Kα	LiF220	48·88	F	S	100	Mo-1	95	20	FT
Zn	Kα	LiF220	60·51	F	FL + S	40	Mo-1	95	20	FT
Cu	Kα	LiF220	65 52	F	FL + S	40	Mo-1	95	20	FT

/contd.over

TABLE (2.9) contd.

ELEMENT	LINE	CRYSTAL	PEAK 2θ	COLLIMATER	COUNTER	COUNTING TIME	TUBE	KV	mA	COUNTS
Ba	$L\alpha$	LiF200	87.05	F	FL	40	Cr-1	60	32	FT
Sc	$K\alpha$	LiF200	97.61	F	FL	100	Cr-1	60	32	FT
I	$L\alpha$	LiF200	102.83	F	FL	100	Cr-1	60	32	FT
Sn	$L\alpha$	LiF200	126.71	F	FL	100	Cr-1	60	32	FT
Ce	$L\alpha$	LiF220	128.15	F	FL	100	Cr-1	60	32	FT
La	$L\alpha$	LiF220	138.77	F	FL	100	Cr-1	60	32	FT

F = Fine; LiF200 = Lithium fluoride; FL = Flow; S = Scintillation; KV = Kilovolts; mA = Milliamperes; FT = Fixed Time.

2.2 Analysis of Atomic Absorption Spectrophotometry (A.A.S.)

a) Atomic Absorption Spectrophotometer (A.A.S.)

The Hilger Watts Atomspek H1550, Atomic Absorption Spectrophotometer (A.A.S.) was used for the analysis of major and trace elements (Al, Fe, Mg, Ca, Na, K and PB, Cu, Zn, Ni, Cr, Sr and Mn) in the leachates, obtained as a result of leaching selected samples with 1M-hydroxylamine hydrochloride 25% ($^{v}/v$) with acetic acid, during the study of the partitioning patterns of these elements in the sediments of the Oxford Clay. The same settings of the instrument were used which are recommended in the Rank Hilger Atomspek Handbook, which are also described in Table (2.10A). The Atomic Absorption Spectrometer is shown in Plate (2.4).

b) Preparation of Standards

Aqueous standards for each element were used for the analysis of the desired elements in the leachates. The aqueous standards were prepared using a solution of 1M-hydroxylamine hydrochloride 25% ($^{v}/v$) and acetic acid (mixed acid reducing agent) plus solution for each element from the stock solution of 1000 mg./lit. prepared according to BUCKLEY and CRANSTON (1971).

c) Precision and Accuracy

The precision and accuracy of the elements analysed by A.A.S. have been checked by PAPAVASILIOU (1979) and the results are reproduced in Table (F). He carried out extensive analyses of the major and trace elements in leachates and from deep sea sediments from the Indian Ocean, and compared these analyses with X.R.F. analyses for the same elements in the same samples, and found very satisfactory agreement. CHOWDHURY (1980) checked the accuracy of the determinations for Sr^{+2} and Mn^{+2} and also found them to be satisfactory, as is shown in the reproduced Table (D). The precision and accuracy of the results are given as standard deviation (S.D.) and coefficient of variation (C.V.) in Table (2.10B).

d) Calculation of the Results

The concentrations of the analysed elements were calculated by bracketing the unknowns with standards after the determination of the calibration curves for each element, as proposed by BUCKLEY and CRANSTON (1971).

PLATE 2.4

a) ATOMIC ABSORPTION SPECTROMETER (A.A.S.) H.W. ATOMSPEK H1550

b) TEFLON BOMB

TABLE (2.10A): Operational Conditions for A.A.S. Determinations for Some Major and Trace Elements

Element	Working range in g/ml.	Sensitivity in g/ml. for 1% absorption	Detection limits in g/ml.	Wave length in nm.
Si	20 - 500	2·00	0·50	251·60
Ti	30 - 500	3·00	0·50	364·30
Al	10 - 200	1·00	0·20	309·30
Fe	1 - 20	0·08	0·02	248·50
Mg	0·10 - 1·00	0·006	0·0006	285·20
Ca	0·50 - 10·00	0·05	0·005	422·70
* Na	0·50 - 5·00	0·02	0·002	589·00
* K[1]	0·50 - 5·00	0·02	0·002	766·50
* Li	0·20 - 4·00	0·02	0·002	670·80
Cr	1 - 20	0·05	0·01	357·90
Pb[2]	2 - 30	0·16	0·03	217·00
Cu	1 - 10	0·07	0·01	324·80
Zn	0·20 - 0·40	0·02	0·005	218·90
Mn	0·50 - 10·00	0·06	0·02	279·50
Ni	0·50 - 20·00	0·06	0·01	232·00

* Analysed by flame emission. Air/Acetylene flame was used in the determination of all elements except Si, Ti and Al, for which N_2O/Acetylene flame was used.

1. Interference from Na^+; standards were prepared and sodium added to the sample.
2. Background correction is necessary due to molecular absorption by Ca, Mg, K or Na. Thus the background absorption at the 220·3 nm resonance line was measured.

TABLE F

Comparison of chemical analyses of some rock and chemical standards derived by A.A.S., with their already established analyses

STANDARD	% Si	STANDARD	% Ti	STANDARD	%Al	STANDARD	% Fe
SY	A.27·82 F.30·50	SY	A.0·287 F.0·255	BCS	A. 4·50 F. 4·00	BCS 269	A.2·45 F.2·10
KPL	A.22·70 F.22·00	CGM	A.0·659 F.0·380	SY	A. 5·70 F. 4·47	MCM	A.1·61 F.1·30
CGM	A.26·56 F.28·70	TB	A.0·563 F.0·116	GR	A. 7·80 F. 8·13	KH	A.0·70 F.0·56
MCM	A.23·56 F.27·30			TB	A.10·87 F. 9·50	9gG	A.0·19 F.0·15
BCS 302	A. 9·36 F.11·00						
KH	A. 4·02 F. 4·00						

STANDARD	% Mg	STANDARD	% Ca	STANDARD	% Na	STANDARD	% K
Q_1	A. 8·00 F. 7·90	Q_1	A.40·00 F.39.50	SY	A.2·401 F.2·52	SY	A.22·80 F.22·00
Q_5	A. 1·60 F. 2·00	Q_2	A.20·00 F.19·50	L 15d	A. F.0·05		
		P_1	A.50·00 F.44·00				
		P_2	A.25·00 F.25·10				
		Q_5	A. 8·00 F. 8·50				

STANDARD	Zn ppm	STANDARD	Cr ppm	STANDARD	Mn ppm	STANDARD	Cu ppm
MCM	A. 37 F. 43	GR	A.126 F. 80	KPL	A. 710 F. 740	KPL	A.190 F.178
KPL	A.330 F.353	GH	A. 40 F. 42	MCM	A. 310 F. 300	CGM	A. 25 F. 40
CGM	A.120 F.128			CGM	A.1650 F.1120	MCM	A. 17 F. 35
				BMS	A. 830 F. 810	GR	A.370 F.373
				BCS 302	A.1625 F.1780		
				KH	A. 681 F. 790		

/contd.over

TABLE F contd.

STANDARD	Ni ppm	STANDARD	Pb ppm
CGM	A. 67 F. 80	MCM	A. 24 F. 45
MCM	A. 51 F. 65	KPL	A. 70 F.105
KPL	A.150 F.165	CGM	A. 18 F. 30

A = Actual (already existing well established analyses)

F = Found in the present study using A.A.S.

KPL, BMS, CGM, MCM = Southampton University, Geology Dept. rock standards.

Q_1, Q_2, Q_5, P_1, P_2 = Southampton University, Geology Dept. chemical standards.

GH, GR = French rock standards.

TB, KH = East German rock standards.

SY = U.S. Geol. Survey rock standards.

(Note: Table 'F' is reproduced from PAPAVASILIOU (1979).)

TABLE (2.10B): Precision of the Elements Analysis

Element	Standard Deviation	Coefficient of Variation	Standards Used Concentrations in mg/lit.
Si	0·320	5·40	400, 350, 300, 200, 100, 75, 50, 25
Ti	0·295	6·20	40, 20, 15, 7·5, 3, 1·5
Al	0·190	1·45	100, 75, 50, 37·5, 10
Fe	0·166	1·00	70, 50, 35, 17·5
Mg	0·25	2·80	50, 30, 15, 7·5, 5, 2·5
Ca	0·280	1·90	50, 30, 15, 7·5, 5, 2·5
Na	0·260	1·70	50, 30, 15, 7·5, 5 2·5
K	0·175	2·30	50, 30, 15, 7·5, 5, 2·5
Cr	0·326	3·60	1·00, 0·50, 0·25, 0·125, 0·01
Mn	0·130	4·20	5, 1·00, 0·50, 0·25, 0·1, 0·01
Ni	0·290	2·66	2·5, 2·00, 1·00, 0·50, 0·125, 0·01
Cu	0·178	3·90	0·75, 0·50, 0·25, 0·10, 0·05, 0·025, 0·01
Zn	0·14	1·85	2·5, 1·00, 0·5, 0·25, 0·125
Pb	0.22	7·26	2·5, 1·00, 0·5, 0·25, 0·125, 0·025
Sr	0·12	3·54	50, 30, 15, 7·5, 5, 2·5, 1·00, 0·50

TABLE D: Concentration of Sr^{+2} and Mn^{+2} in Sediments, analysed by A.A.S. and X.R.F.

Sample No.	Concentration of Sr^{+2}		Concentration of Mn^{+2}	
	Values determined by X.R.F.	Values determined by A.A.S.	Values determined by X.R.F.	Values determined by A.A.S.
SCB	1265 ppm	1282 ppm	310 ppm	284 ppm
WCAM	330 "	310 "	350 "	385 "
WCAM	314 "	378 "	470 "	437 "
BEO	610 "	545 "	585 "	626 "
BEB	283 "	330 "	755 "	790 "
DCO1	290 "	325 "	220 "	184 "
DCO2	343 "	360 "	186 "	210 "
DCNR	235 "	274 "	390 "	366 "
NDO	312 "	345 "	210 "	196 "
NDB	270 "	289 "	287 "	320 "
NDTC	288 "	312 "	345 "	331 "

(Note: Table 'D' is reproduced from CHOWDHURY, 1980.)

2.IV Acetic Acid Hydroxylamine Leaching

a) Method

The acetic acid-hydroxylamine leaching technique proposed by CHESTER and HUGHES (1967) was followed for the geochemical partitioning study of the selected bulk rock samples from the two borehole sediments of the Oxford clay. From each borehole collection, 12 representative samples were selected, which are shown in Table (2.11). CHESTER and HUGHES (op.cit.) noticed during their investigations that acid-reducing reagent (1M. hydroxylamine hydrochloride/25%($^v/v$) acetic acid) removed the $CaCO_3$,trace elements adsorbed onto mineral surfaces and ferro-manganese oxide phases. The remaining residue (unattacked) contained silicates, aluminosilicates,sulphates, sulphides, and metals tightly bound with organic material. Some of the residues, when run on the X.R.D., showed that dolomite was also leached to a significant degree.

The method used in the present study was as follows:

1) 2 gms. of the dry sample powder was weighed in a 'boat'.
2) The sample powder was transferred to a conical flask and 100 ml. solution of 1M. hydroxylamine hydrochloride/25%($^v/v$) acetic acid was added. The conical flask was left for four hours on a mechanical shaker.
3) The contents of the flask were washed into a pre-weighed (A gm.) centrifuge tube and later was centrifuged. The total weight now (B gms).
4) The liquid was poured off into a clean beaker.
5) Warm triple distilled water was added to the centrifuge tube, which again was centrifuged and the liquid was poured off into the beaker.
6) The centrifuge tube was then left for drying in a drying cupboard at 110°C temp.
7) When the contents had dried, the centrifuge tube was weighed. The weight of the residue and the dissolved material were calculated as follows:

weight of residue = combined weight (B) - weight of the empty tube (A)

TABLE (2.11): List of Samples leached by Hydroxylamine Hydrochloride from the Warlingham and Winterborne Kingston Borehole Sediments

Serial No.	Warlingham Borehole Sediments	Winterborne Kingston Borehole Sediments
1	BR-134	WBK-5
2	BR-278	WBK-15
3	BR-627	WBK-25
4	BR-826	WBK-28
5	BR-988	WBK-34
6	BR-1301	WBK-38
7	BR-1424	WBK-43
8	BR-1583	WBK-53
9	BR-1734	WBK-55
10	BR-1755	WBK-58
11		WBK-61
12		WBK-64

Note: 12 samples of each borehole were selected. During the leaching processes 2 samples from the Warlingham Borehole collection were lost.

= B gm - A gm = R gm (weight of residue)

weight of dissolved material = initial weight of sample - weight of the residue

= 2 gm - R gm = D gm

8) 2 mls. of 'Aristar' nitric acid (HNO_3) was pipetted into the beaker, containing the material leached by the acid-reducing reagents. This nitric acid (HNO_3) destroys the excess reducing agent.

9) The contents of the beaker were evaporated to dryness on a warm water bath.

10) The contents of the leached material (Step 9) were dissolved in 40 mls. of triple distilled water and made up to 250 mls. solution. This solution was analysed on A.A.S.using the aqueous standards, for the desired elements.

11) A blank solution was prepared using the same preparation method.

The leachate obtained, as above, was analysed on the A.A.S. using the aqueous standards prepared according to the same procedure as for the elements mentioned. All the standards were run at intervals during the analysis, to obtain the statistical data, such as standard deviation and coefficient of variance, which are summarized in Table (2.10A) in the description of analysis by Atomic Absorption Photospectrometer.

The chemical composition of the aqueous solution, of 250 ml. total volume, was obtained by reading the individual run of each element against the calibration curve.

b) Calculations

The actual concentration of the analysed elements in the dissolved material (i.e. non-lattice held or non-lithogenous) fraction can be calculated as under:

$$w = \frac{c \times v \times d}{y}$$

where w = the actual concentration of the element (i) in the (D gm) of the dissolved material.

c = the calculated concentration of the element (i) in the aqueous solution.

v = the volume of total solution, in this case 250 mls.

d = the specific weight of the solvent (i.e. H_2O) which is 1g/ml.

Having the data regarding the concentration of an element (i) in the total sediment, the calculation of the contributions made by the non-lattice held and lattice held (lithogenous) fractions was achieved as under:

1) A = contribution made by non-lattice held (non-lithogenous) fraction to total sediment, element (i) contents (in % or p.p.m.).

2) B = contribution made by the lattice held (lithogenous) fraction to total sediment, element (i) contents (in % or p.p.m.).

3) T = total element (i) (in % or p.p.m.) in sediment.

4) C = element (i) contents of the lattice-held (lithogenous) fraction (in % or p.p.m.).

5) K = element (i) content of the non-lattice held (non-lithogenous) fraction (in % or p.p.m.).

6) D = percentage of the dissolved material by acid-reducing agent.

7) F = percentage of the insoluble material by acid-reducing agent = 100-D.

Then:

1) $A = \frac{K \times D}{100}$

2) $B = T - A$

3) $C = \frac{B \times 100}{F}$ i.e. $C = \frac{(T - A) \times 100}{100-D}$

As the chemical composition of total sediment, the non-lattice held (non-lithogenous) fraction, and the percentages of insoluble and soluble materials are known, it is therefore possible to calculate A, B and C values. The above determinations and calculations are given for the sediments of both boreholes in the Appendices (6.1B & 6.2B) respectively.

PLATE 2.5

BINOS 1 INFRA RED GAS ANALYSER

2.V Determination of CO_2

The carbon dioxide (CO_2) was determined as 'total CO_2' and 'carbonate CO_2' for each sample of the two boreholes. Different methods of CO_2 determination were tried to select the most suitable one. It was noticed that carbonate CO_2, determined by the Infra-red gas analyser and the thermogravimetric balance, from the Warlingham Borehole samples, which contain calcite and dolomite (both minerals), was not in agreement. The values were found to be much lower than the values determined by the thermogravimetric balance and other methods, as are shown in Table (2.5). The reason for these low values may be that orthophosphoric acid used in the method might have failed to digest the entire amount of the carbonates, especially the dolomite.

The CO_2 values obtained by the thermogravimetric balance, and determined by the acid digestion method using 0·1N HCl, showed a very good agreement, as is shown in Figure (2.5a). These values also showed a very good agreement with the CO_2 values calculated from the CaO and MgO values obtained by the Betaprobe analysis, which are shown in Table (2.5b).

The CO_2 values obtained by the Infra-red gas analyser for the Winterborne Kingston sediments were found satisfactory, and therefore these values were used for the estimation of carbonate contents (calcite) of these sediments. The values of CO_2 used for the estimation of the abundances of calcite and dolomite, for the Warlingham Borehole sediments, were those obtained by the acid digestion method of 0.1N HCl. The values of CO_2 for both the boreholes' sediments are tabulated in the Appendices (2.1) and (2.2) respectively.

2.V.1 Determination of CO_2 by Infra-red Gas Analyser

a) Infra-red Gas Analyser

An infra-red gas analyser, shown in Plate (2.5) was used for the determination of both the combined CO_2 (carbonate CO_2 + organic carbon CO_2) and carbonate CO_2 separately. For the determination of combined CO_2 the Infra-red gas analyser was connected to a Pyrex tube, as shown in Plate (2.5), which passes through a thermostatically

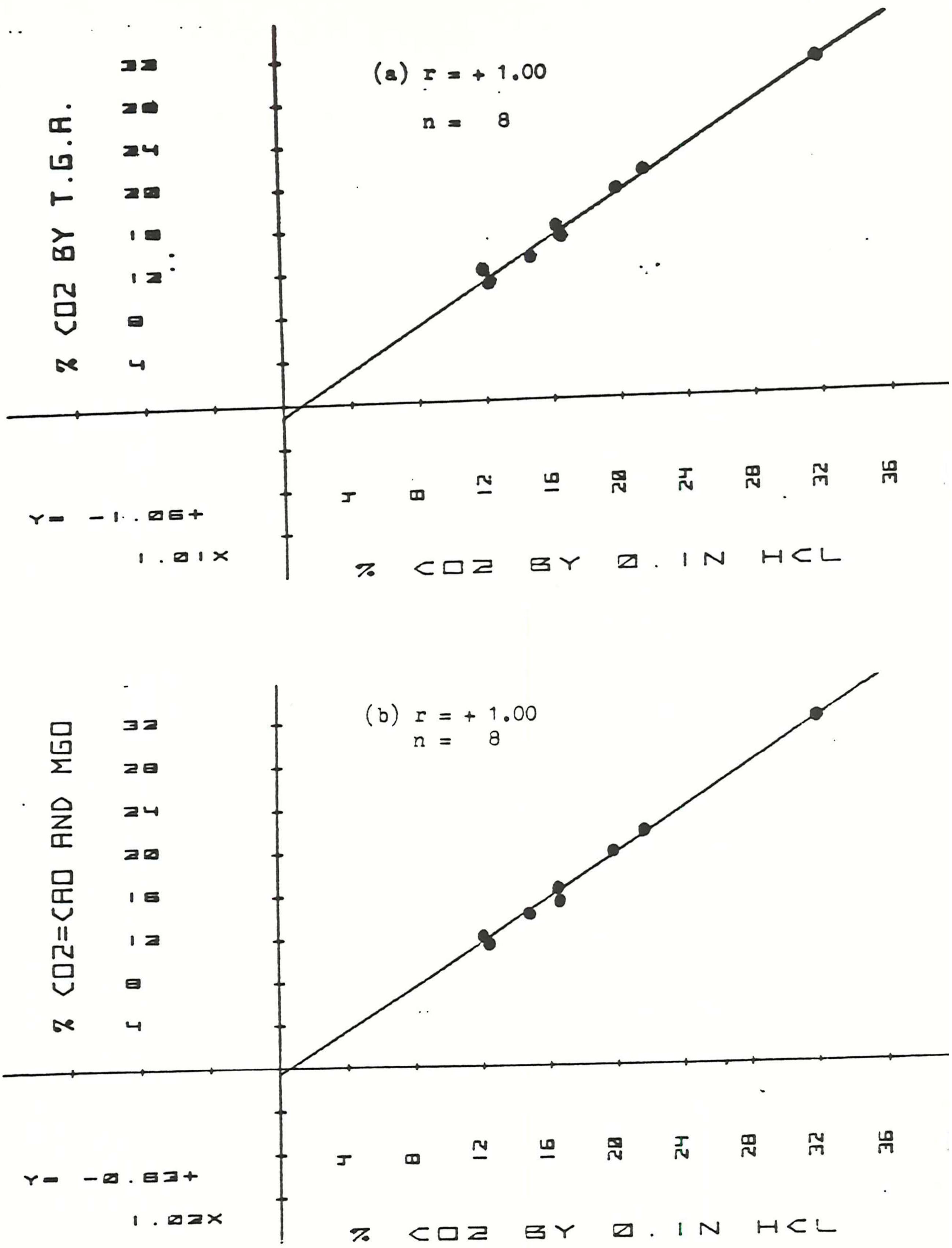

(a) r = + 1.00
n = 8
% CO2 BY T.G.A.
4 8 12 16 20 24 28 32
4 8 12 16 20 24 28 32 36
% CO2 BY Ø. IN HCL
Y= -1.06+
1.01X
(b) r = + 1.00
n = 8
% CO2=CAO AND MGO
4 8 12 16 20 24 28 32
4 8 12 16 20 24 28 32 36
% CO2 BY Ø. IN HCL
Y= -0.83+
1.02X

FIG.(2.5)

controlled tube furnace at a temperature of 850°C. Pure oxygen gas (200 mls/min.) was constantly flushed through the Pyrex tube in order to ensure the oxidation of all C-bearing material to CO_2. The sample, weighed in a silica boat fitted with a magnetic stem (as shown in Plate (2.5)), was pushed into the Pyrex tube with the help of a magnet in such a way that the sample entered the highest temperature part of the furnace. Simultaneously the red 'start' button on the volume meter box was pressed. The CO_2 produced from the C-bearing material filled the volume meter in about 8-9 minutes. The CO_2 so collected was measured by flushing through the 3,000 ppm CO_2 cell on the analyser, the response being recorded on the chart recorder simultaneously.

b) Calibration of the Gas Analyser

The Infra-red gas analyser was calibrated before the determination of any type of CO_2. The calibration was done by heating 0·01 gm of pure calcite (analar) as a standard in the silica boat, as described above. The standard was run three times to check precision, and every time the reading was recorded on the chart recorder. If the readings were essentially constant, the average of the three readings was taken as the final standard reading.

c) Determination of Combined CO_2

The combined CO_2 (carbonate CO_2 + organic carbon CO_2) was determined by heating up the weighed (0·01 gm) amount of the sample in the silica boat, in the furnace at 850°C temp., as explained above. The amount of CO_2 released from the sample and collected in the volume meter was measured and recorded on the chart recorder. The amount of CO_2 was calculated according to the following:

$$\% \, CO_2 = \frac{A}{B} \times 43 \cdot 97$$

where:

A = Reading of the sample as recorded on the chart.

B = Reading of the standard (obtained by averaging the three readings).

43·97 = Amount of CO_2 present in pure calcite.

d) Determination of Carbonate CO_2

The carbonate CO_2 of the samples containing only calcite was determined by the Infra-red gas analyser, after some modifications. The analyser was detached from the furnace and was connected with another Pyrex tube, fitted with a pipette filled with orthophosphoric acid. The Pyrex tube was heated by wrapping it with an electric coil; the temperature was maintained at 150°C throughout. Pure oxygen gas (150 mls/min.) was again flushed through the system.

The gas analyser was calibrated in the usual way. Pure calcite, the standard, was weighed (0·01 gm.) in an ordinary glass boat. The boat was pushed into the tube with the help of a magnet in such a way that its head containing the sample reached under the fitted pipette. Approximately 1 ml. of the orthophosphoric acid was dropped on the sample to dissociate the carbonate and produce CO_2. Within 8-9 minutes all carbonate CO_2 was released and filled the volume meter; it finally passed through the detector of the Infra-red gas analyser and was recorded on the chart. In the same way the samples were run and CO_2 was detected, and was finally calculated according to the calculations described under the heading of combined CO_2.

2.V.2 Determination of CO_2 by T.G.A.

A thermogravimetric balance (T.G.A.) was used to determine the CO_2 in some of the selected samples for comparing the values of CO_2 determined by other methods. The T.G.A. determines both CO_2 and H_2O as a result of the progressive loss of weight in %, caused by the increase of temperature from the room temperature to 1000°C. Sample powder (0·1 gm.) was used in this method. Pure oxygen gas was passed through the T.G.A. A graph was attached to the recorder on which the weight loss was recorded. The bulk of the CO_2 was expelled above 650°C. The amount of the expelled CO_2 recorded on the chart was finally calculated as a percentage. The values of the CO_2 determined by T.G.A. showed a very good agreement with the results obtained by other methods, as is shown in Table (2.5) and Figure (2.5a and b). The T.G.A. is shown in Plate (2.6).

PLATE 2.6

SHOWING THE THERMOGRAVIMETRIC ANALYZER AND
DIFFERENTIAL THERMAL ANALYZER

2.VI Determination of H_2O

a) Determination by Chemical Method

Water was determined as total water by chemical method (Penfield method) proposed by SHAPIRO and BRANNOCK (1962). The absorbed water (H_2O^-) was determined by weight loss at 110°C in a furnace. The lattice-held water (H_2O^+) was obtained by the difference of the two determinations. In the chemical method the sample was heated at about 1000°C in a Pyrex tube with sodium tungstate in it as a flux. The total water was expelled out of the sample and was condensed on a piece of filter paper, already weighed and placed in the upper part of the Pyrex tube. After heating, the tube was cooled by crushed ice filled in a polyethylene jacket which surrounded the tube. The arrangement of the apparatus is shown in Plate (2.7). The various steps were as under:

1) The tube having a 2 inch by 2 inch piece of the filter paper was weighed (A) and sealed by a rubber stopper.
2) 0·5 gm. of the sample powder + 1 gm. of sodium tungstate were weighed in an 18 m.m. by 150 m.m. Pyrex tube.
3) The filter paper piece was quickly transferred into the upper part of the Pyrex tube.
4) The Pyrex tube was inserted into the polyethylene cooling jacket, crushed ice was added to the jacket which kept covered that part of the tube enclosed by the jacket.
5) About 10-20 gms of NaCl were added to the crushed ice.
6) The cooling jacket, having the tube inserted in it, was placed at such a height as to allow its maximum heating, as is shown in Plate (2.7).
7) First the closed end of the tube was gently heated, then the rest of the tube was heated for 5 minutes at about 1000°C. A Fisher burner was used.
8) The tube was allowed to cool for one minute; its stopper was removed and, with the help of a small spatula, the walls of the tube were wiped vigorously with the piece of filter paper, which absorbed the derived water. It was quickly transferred into the weighing tube and its stopper was replaced immediately.

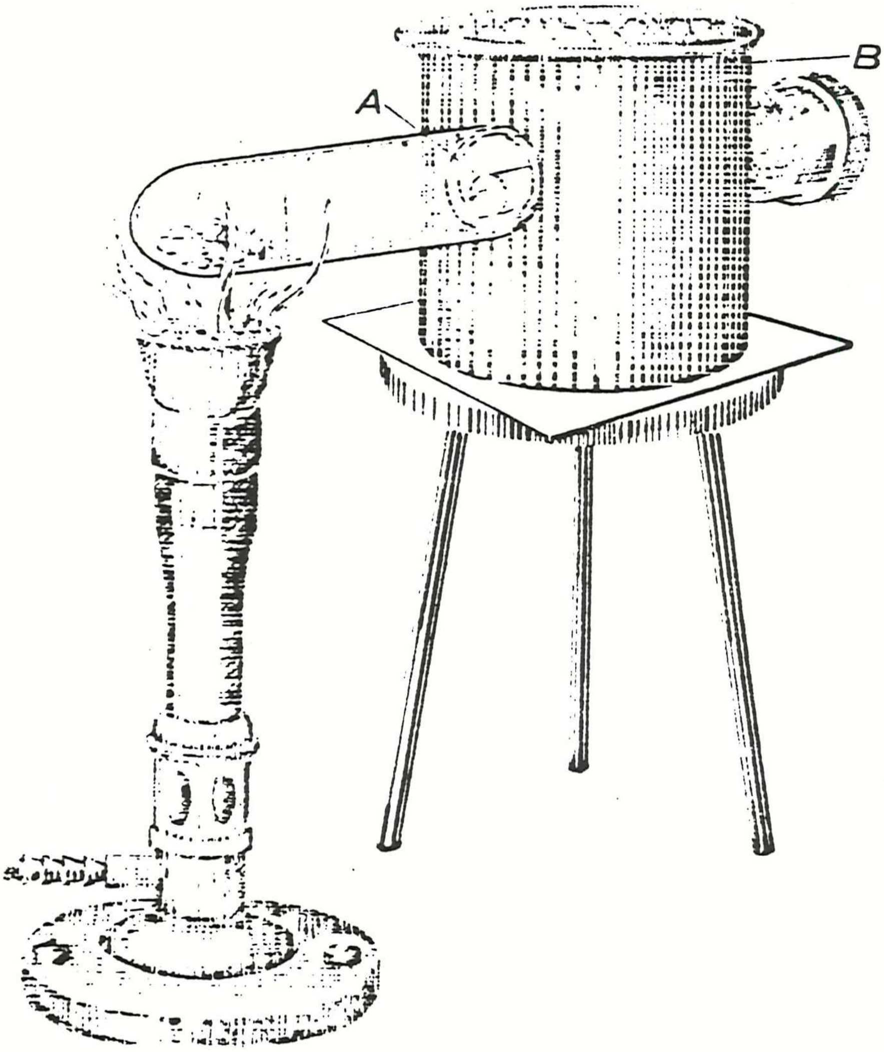


PLATE (2.7); Tube positon for water determination by chemical method.

A= coiled paper water absorbant.

B= Polyethylene continer with crushed ice.

9) The weighing tube containing the filter paper was weighed = (B gm.).

10) The weight of the total water was obtained by the difference of the two weights recorded, i.e. B - A = C gm.

11) The amount of lattice-held water (H_2O^+) was determined by subtracting the amount of absorbed water (H_2O^-), already obtained by the weight loss in the sample at 110°C, from the amount of total water (C) determined as above.

% of lattice-held water (H_2O^+) = C - absorbed water (H_2O^-)

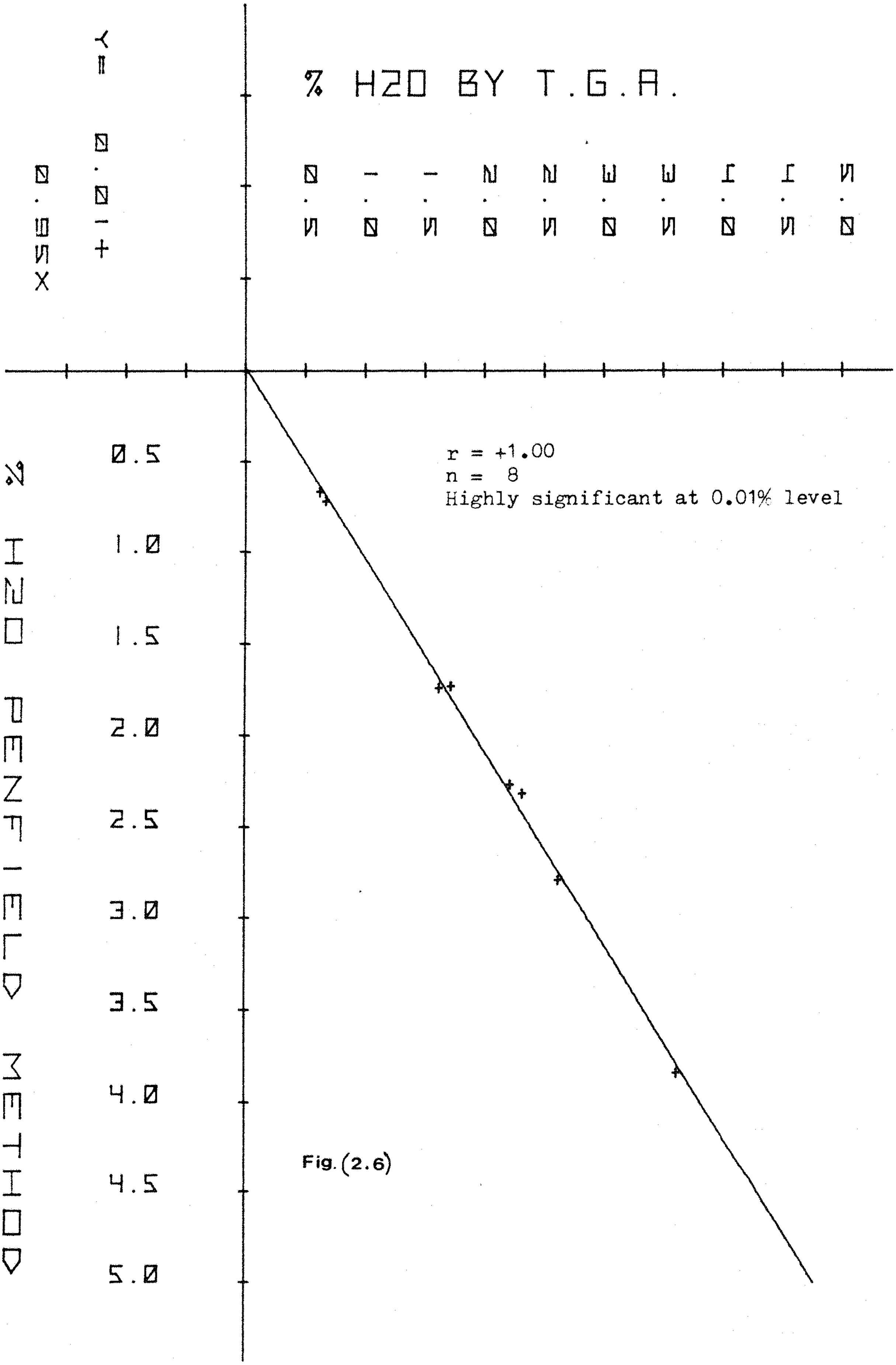
b) Determination of H_2O by T.G.A.

The thermogravimetric balance (T.G.A.), shown in Plate (2.7), had been used for the determination of water by many workers, including PAPAVASILIOU (1979), who used it for the determination of the water of the deep sea sediments of the Indian Ocean, and reported satisfactory results, which are reproduced in Table (K). This method is good in many ways: it gives satisfactory results and it needs a very small amount of the sample (0·1 gm). But it is very slow and, being slow, in one day only three or four samples can be analysed by this method.

The water determination is based on the loss of weight recorded due to continuous heating. The ignition of the sample begins from the room temperature and finishes at 1000°C temp. The progressive loss in weight percentage was recorded on a chart, which was due to an increase of temperature. The absorbed water (H_2O^-) was expelled between 25°C and 150°C temp. The lattice-held water (H_2O^+) was expelled between the temperature range of 150°C and 650°C.

Eight samples, which are shown in Table(2.12A), were selected from the Warlingham Borehole sediments for the determination of water by T.G.A. Water, in the same samples, was also determined by the chemical method to check the precision of the methods. The results of both the methods are tabulated in Table (2.12A). The graph, plotted by these results in Figure (2.6), shows a very reasonable agreement. The correlation coefficient value is (r = +1·00), which is highly significant at an 0·01% level.

The reproducibility of the chemical method was also checked



r = +1.00
n = 8
Highly significant at 0.01% level

Fig. (2.6)

TABLE K.

Precision of H_2O^+ determined by T.G.A.

	H_2O^+%
1	6·00
2	6·30
3	6·50
4	6·90
5	7·70
6	6·80
7	7·80
8	7·50
9	7·70
10	7·30
MEAN	7·05
VARIANCE	0·375
STANDARD DEVIATION	0·612
COEFFICIENT OF VARIATION	8·68%

Note: Table K is reproduced from PAPAVASILIOU, 1979.

TABLE (2.12A): Comparison of the results of H_2O^+, determined by different methods

Sample No.	H_2O^+ determined by T.G.A. %	H_2O^+ determined by Penfield Method %
BR-115	1·60	1·72
BR-123	2·30	2·30
BR-129	0·65	0·70
BR-199	1·70	1·71
BR-656	2·60	2·77
BR-826	2·20	2·25
BR-1220	3·60	3·82
BR-1811	0·60	0·65

TABLE (2.12B): Duplicate Analysis of H_2O^+ by Penfield Method

Sample No.	First Determination %	Second Determination %	Mean Values
WBK-8	1·8	2·0	1·9
WBK-16	3·4	3·6	3·5
WBK-34	5·4	5·2	5·3
WBK-47	7·8	7·6	7·7
WBK-54	6·9	7·0	6·95
WBK-61	6·4	6·6	6·50

by duplicate analysis of some of the samples and was found very good, as is shown in Table (2.12B). The amounts of H_2O^+, determined for both boreholes' sediments, are presented in the Appendices (2.1) and (2.2).

2.VII Determination of Ferrous Iron (Fe^{+2})

The rapid method of the determination of ferrous iron (Fe^{+2}) contents in silicate rocks, described by FRENCH and ADAMS (1972) was used to determine the contents of ferrous iron (Fe^{+2}) in the sediments of the Oxford Clay in the present investigations. The Fe^{+2} and Fe^{+3} contents are tabulated in Appendices (2.1) and (2.2). In this method, decomposition of the rock powder took place when it was boiled with a mixture of 40% m/v hydrofluoric acid (HF) and concentrated sulphuric acid (H_2SO_4) in a hot water bath. The whole procedure is briefly described below:

i) 0·25 gm of the rock powder was weighed in a polypropylene bottle.

ii) Equal volumes of 40% m/v (HF) and concentrated (H_2SO_4) were mixed in a polypropylene beaker.

iii) 10 mls of the mixture were added to the rock powder in the polypropylene bottle and its mouth was sealed.

iv) The bottle was left to 'float', upright or slightly tilted, in the boiling hot water tank for 5-10 minutes.

v) The bottle was removed; its contents were thoroughly washed with boric acid (saturated) solution in a 400 ml. beaker to complex out the excess HF.

vi) The ferrous iron (Fe^{+2}) was determined from this solution of decomposed rock by redox titration. A cerium sulphate ($Ce(SO_4)_2$) solution 0·05N and one drop of N-phenylanthranilic acid as an indicator were used in the titration.

The percentage of the FeO was calculated as under:

$$\%\ FeO = \text{mls of } Ce(SO_4)_2 \text{ used to titrate } Fe^{+2} + 1{\cdot}4362.$$

The Scanning Electron Microscope used in the present study is shown in Plate (2.8).

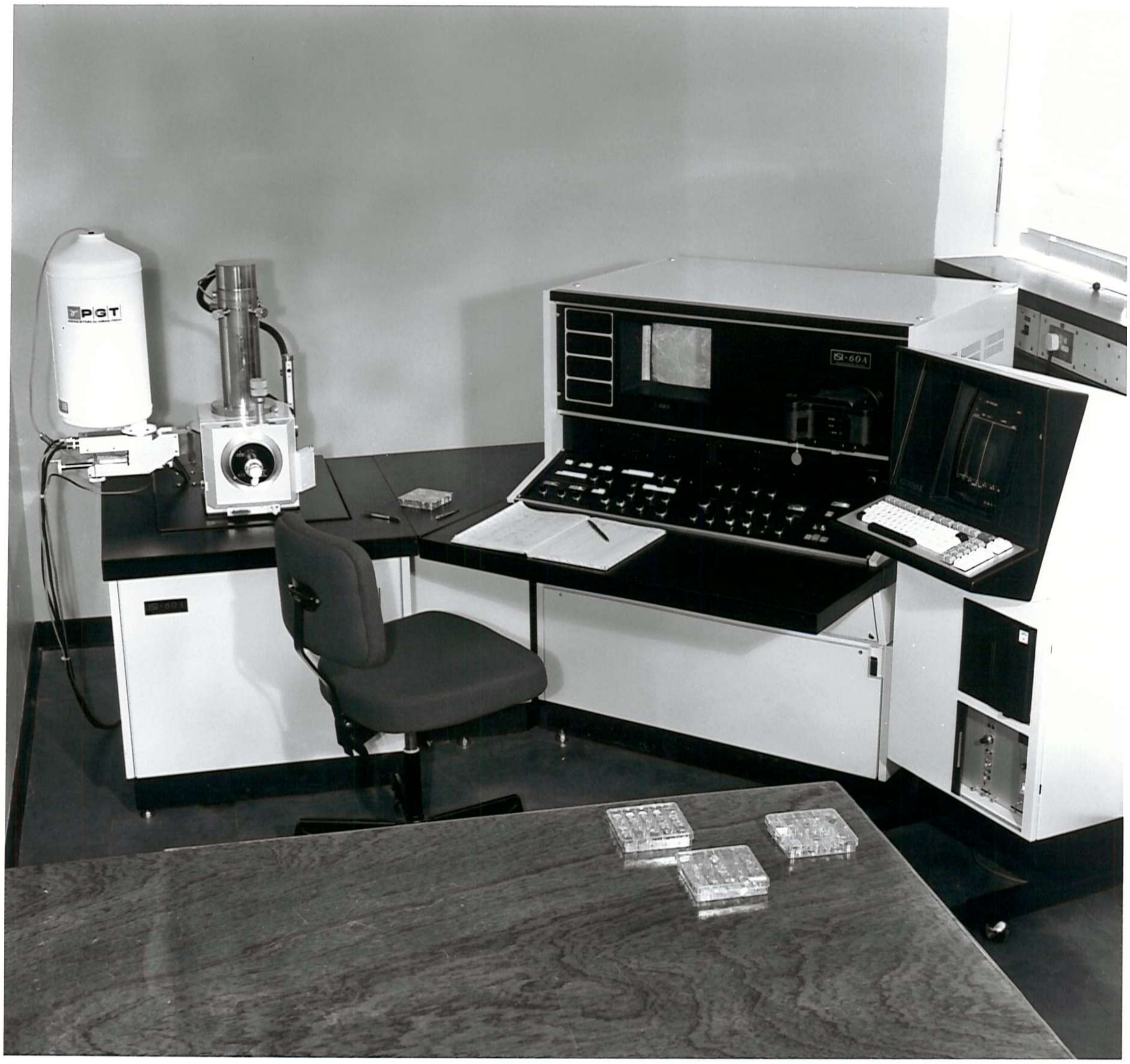


PLATE 2.8

SCANNING ELECTRON MICROSCOPE

CHAPTER THREE

MINERALOGY OF THE WHOLE ROCK

3.1 General Introduction

(a) Introduction

Mineral analysis of bulk rock samples of the (W.K.B.) and (W.B.) was achieved for all the samples by running random powder samples on the PW 1010 Philips X-ray Diffractometer. Details regarding sample preparation, identification of specific minerals and settings used on the X.R.D. are described in Chapter Two (see 2.I.1 to 3). The identification of specific minerals was done on the basis of the recognition of at least two characteristic d-spacings on the X.R.D. diffractogram. The characteristic d-spacings used in the present study were the same as those mentioned by BROWN (1961 & 1980). Many workers, including SCHULTZ (1964), JACKSON and FOOKES (1974), and PAPAVASILIOU (1979), have used these d-spacings. The characteristic peak positions used for each mineral are shown in 2°, θ and d.Å scales, as follows. Some of the non-clay minerals present in the studied sediments are shown in Plates (3.1 - 3.5).

Mineral	Peak position CuKα-radiation
Quartz	26·66°,2θ(3·34Å),20·85°,2θ(4·26Å)
Calcite	29·43°,2θ(3·03Å),39·43°,2θ(2·28Å)
Dolomite(ferroan)	30·84°,2θ(2·72Å),41·04°,2θ(2·19Å)
Pyrite	33·07°,2θ(2·70Å),37·10°,2θ(2·42Å
Feldspars	27·41°,2θ(3·22Å),27·93°,2θ(3·16Å)
Total Clays	19·91°,2θ(4·45Å).

The peak positions of each mineral are shown in Figure (3.1). The intensity of the peak of a mineral on the X-Ray diffractogram depends either on the proportion or the crystalline nature of the mineral. It means that if the proportion of a mineral is high and it is well crystallized, it will show strong characteristic peaks; otherwise the peak will be weak. Figure (3.1) shows much stronger peaks for minerals such as quartz, calcite, pyrite, total clays, being the commonly present major components in the studied sediments. The presence of feldspars was indicated by their characteristic peaks, but generally very weak in intensity, suggesting the presence of only small amounts (generally $<$ 5%).

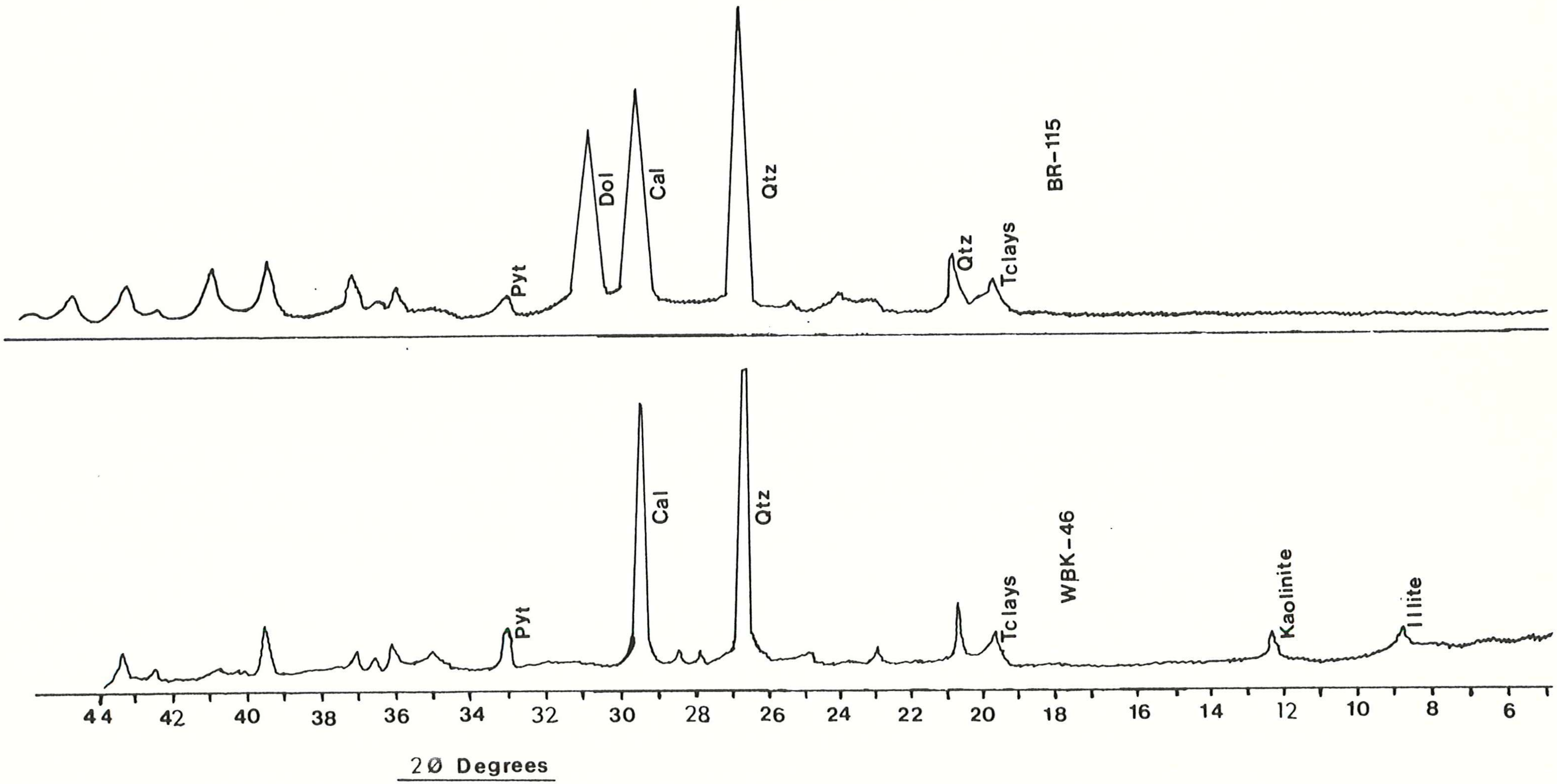


FIG.(3.1): X.R.D. trace of samples BR-115 and WBK-46, indicating the peak positions of main minerals identified in the Bulk rock samples of the studied sediments.

PLATE 3.1:

1. Pyrite Framboidal in BR-468
2. Pyrite Framboidal in BR-1326
3. Pyrite Octahedral Crystals in BR-468
4. Pyrite Octahedral Crystals in BR-958
5. Pyrite Framboidal in BR-958
6. Pyrite Framboidal in BR-958

Scale of the S.E.M. Photomicrograph

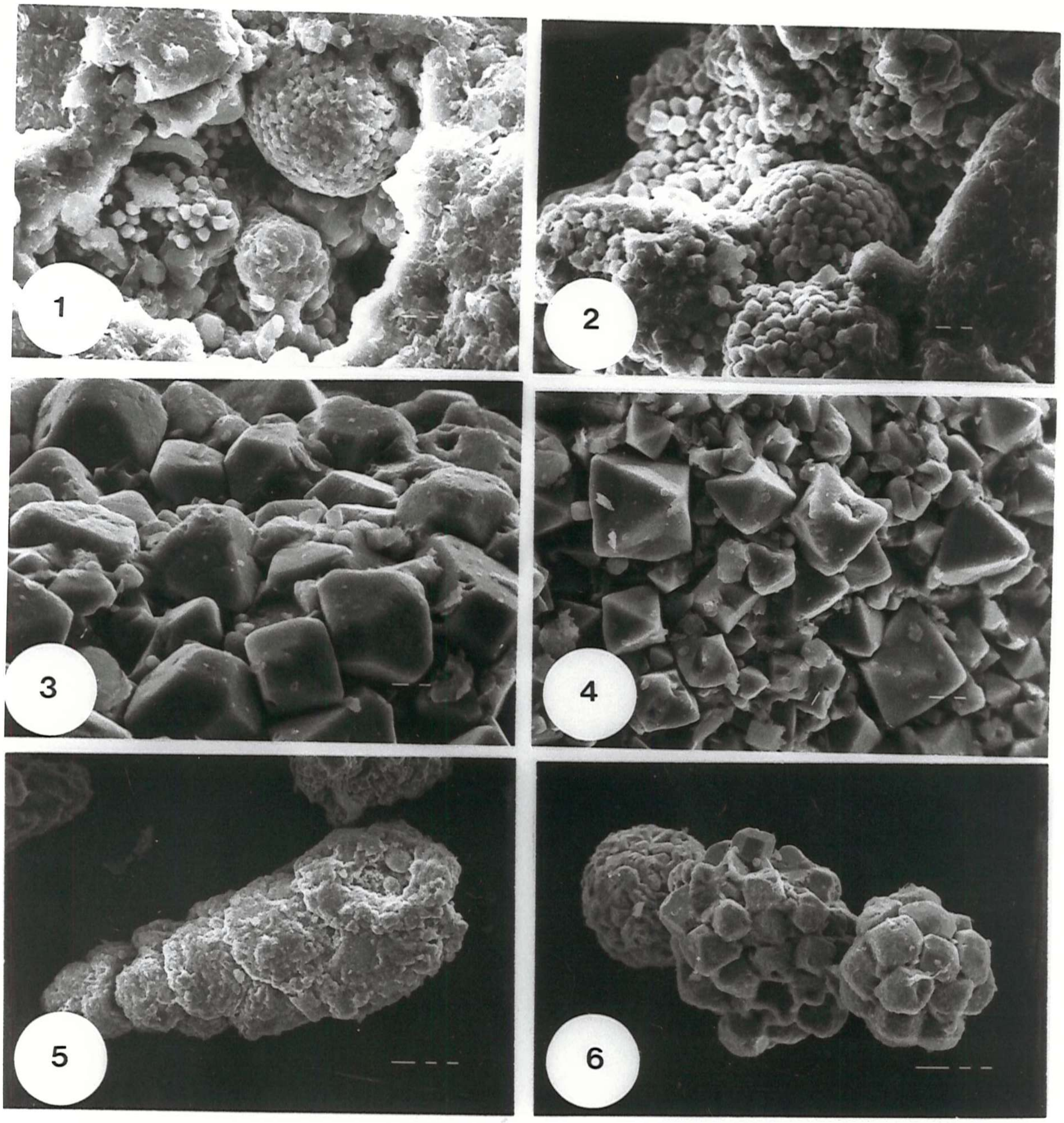
—— = 0.1 Micron

—— – = 1 "

—— – – = 10 "

—— – – – = 100 "

Note: The same scale is used for all the S.E.M. Photomicrographs.



PLATE—3.1

(b) Semi-Quantitative Estimation of Mineral Abundances

Initially the method proposed by SCHULTZ (1964), for the semi-quantitative analysis of minerals in sediments, was applied, but the results thus obtained were found to be unsatisfactory. The amounts of some of the minerals, such as pyrite, calcite and dolomite, were calculated from the chemical analysis results of S, CaO, MgO and CO_2. The chemically derived results of these minerals did not show good agreement with the estimates of these minerals by the application of SCHULTZ's (1964) method. The mineral abundances produced by SCHULTZ's (op.cit.) method can only be regarded as crude approximations because, in this method, neither an internal standard is used, nor the effects of mass-absorption are taken into consideration.

In the present study the semi-quantitative analysis of minerals present in the studied sediments has been done on the basis of 'independent' determinations of each mineral, by an experimentally determined suitable method described in Chapter Two. Sediments of both the boreholes (i.e. (W.K.B.) and (W.B.)) indicated the presence of common minerals such as quartz, calcite(pure), pyrite, total clays and feldspars (Na-bearing and K-feldspars). The only variation in the non-clay mineralogy in the sediments of the two boreholes is the presence of dolomite(ferroan) in the (W.B.) sediments. Descriptions of each mineral are as follows.

3.2 Descriptions of Minerals

(A) QUARTZ

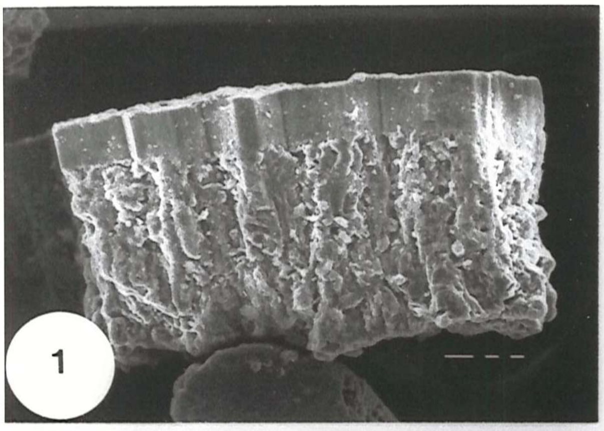
TABLE (3A)

	(W.K.B.)	(W.B.)
Range (individual samples)	17 to 28%	10 to 78%
Highest abundance:	23·64% (U.O.C.)	40·70% (K.F.)
Lowest abundance:	17·75% (L.O.C.)	18·00% (L.O.C.)
Average abundance:	20·92%	22·06%

Quartz is the ever present mineral in the studied sediments. The sediments of the (W.B.) contain higher average amounts of quartz as compared with (W.K.B.). The sediments of the (K.F.) of the (W.B.) show an exceptionally high amount of quartz, while the sediments of the (U.O.C.) in the (W.K.B.) show the highest concentration of quartz; these concentrations of quartz may be related to a near-shore type of deposition in the case of the (W.B.) and a rapid rate of sedimentation under shallow water conditions in the case of the (U.O.C.) of the

PLATE 3.2:

1. Heavy mineral in BR-468
2. " " " BR-468
3. " " " WBK-12
4. " " " BR-958
5. " " " BR-1326
6. " " " WBK-23



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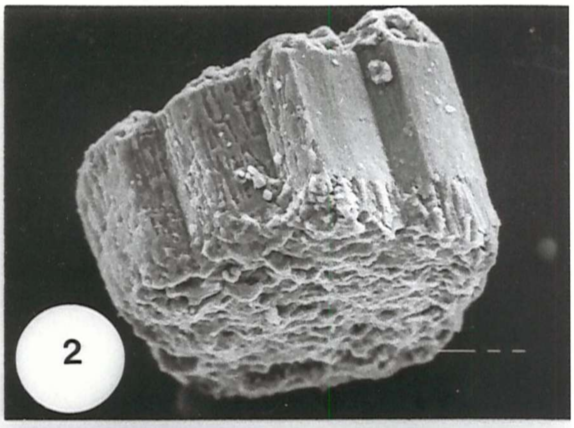

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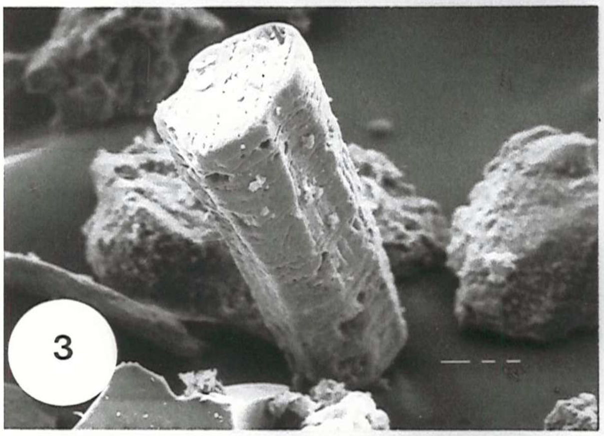

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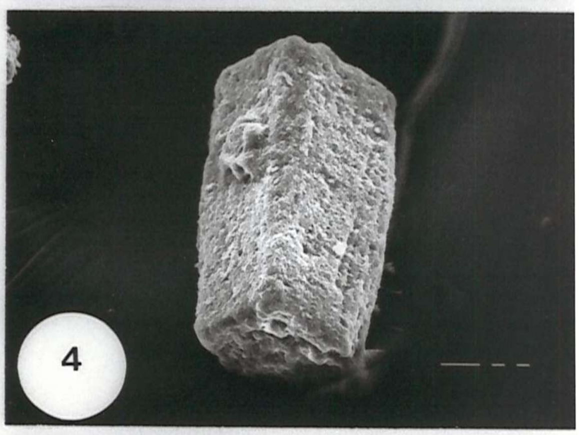

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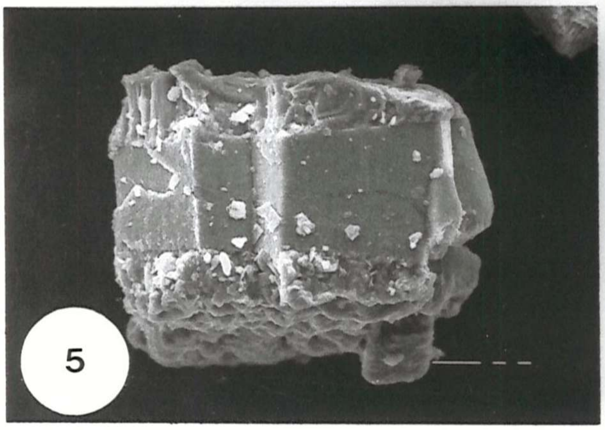

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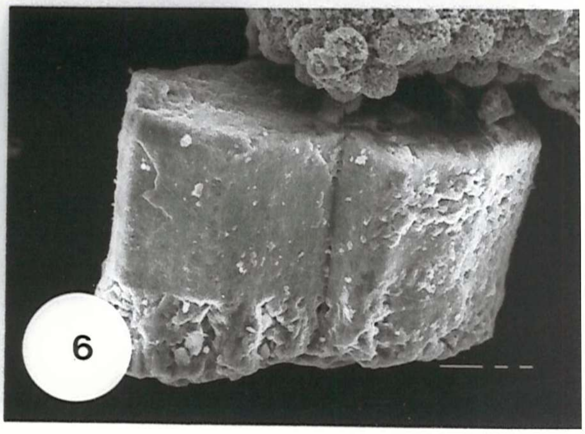


6

PLATE—3·2

(W.K.B.) sediments. According to RONOV (1965), near-shore sediments contain higher amounts of quartz. The grains of quartz in the (W.B.) sediments are finer and more rounded as compared with those of the (W.K.B.) sediments, suggesting that the detritus of the Oxford Clay sediments at the (W.B.) site was dominantly contributed by recycled material. The grains of quartz in the (W.K.B.) sediments are coarse and angular, suggesting that they did not experience many cycles of sedimentation, and did not travel over a long distance.

(B) CALCITE

TABLE (3B)

	(W.K.B.)	(W.B.)
Range (individual samples)	15 to 55%	0 to 58·20%
Highest abundance:	39·35% (U.O.C.)	26·86% (U.O.C.)
Lowest abundance:	17·25% (L.O.C.)	9·83% (K.F.)
Average abundance	29·66%	22·52%

Calcite showed higher average contents in the (W.K.B.) sediments than in the (W.B.) sediments. The highest concentration of calcite in the sediments of both the boreholes is present in the (U.O.C.), and the lowest in the (L.O.C.) in the (W.K.B.), and in the (W.B.) in the sediments of the (K.F.), as shown in Table (3B). Calcite in both the borehole sediments is low-Mg calcite, as is indicated by the characteristic peak positions at 3·03Å ($29{\cdot}43^{o}$,2θ) and 2·28Å ($39{\cdot}43^{o}$,2θ). The abundance of calcite in the case of the (W.K.B.) sediments was calculated directly from the amount of carbonate CO_2, independently determined by the infra-red gas analyser; calcite being the only carbonate mineral in these sediments. For the sediments of the (W.B.), the abundance of calcite was calculated by using the values of dolomite already calculated, and the calcite/dolomite ratios determined by X.R.D., which are shown in Appendix (2.2).

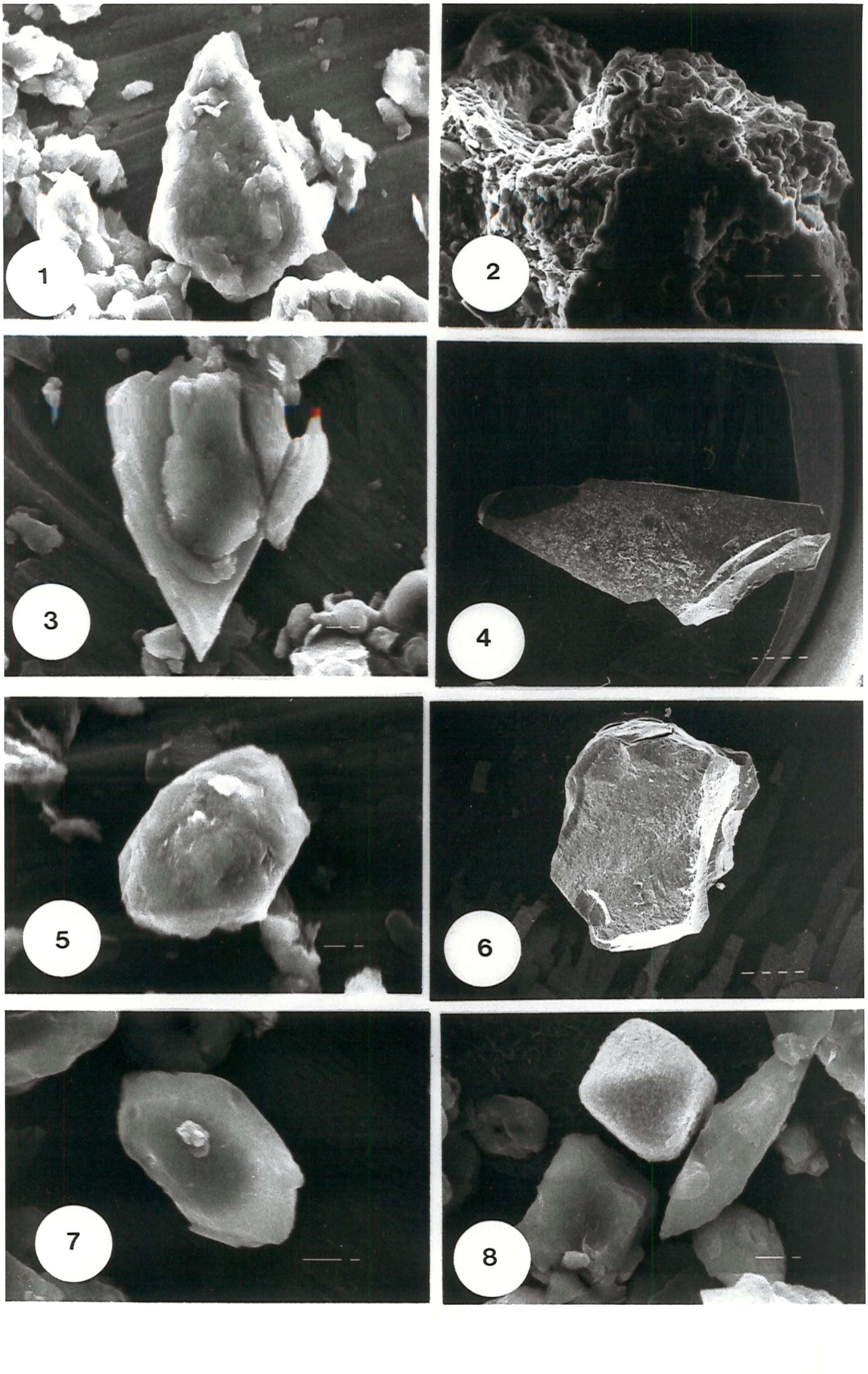
(C) PYRITE

TABLE (3C)

	(W.K.B.)	(W.B.)
Range (individual samples)	1·30 to 6·80%	0·24 to 12·70%
Highest abundance:	3·90% (L.O.C.)	3·03% (K.F.)
Lowest abundance:	2·25% (U.O.C.)	1·04% (U.O.C.)
Average abundance:	2·82%	1·67%

PLATE 3.3:

1. Angular fragment of Quartz in WBK-12
2. Silica precipitated (?) in WBK-12
3. Angular fragment of Quartz in WBK-21
4. Chert in WBK-23
5. Sub-angular Quartz in BR-468
6. Chert in WBK-23
7. Quartz crystal in BR-1326
8. Pyrite and Quartz in WBK-25



PLATE— 3.3

The presence of pyrite in the studied sediments was detected by its characteristic peaks at 2·70Å (33·07°,2θ) and 2·42Å (37·10°,2θ). The abundance of pyrite in each sample was calculated as described in Chapter Two (see I.1.8(b)), by using the amounts of sulphur determined for each sample by Betaprobe, during the chemical analysis of the major elements. The X.R.D diffractograms of all the samples of the studied sediments indicated the presence of pyrite as the only sulphide mineral present in these sediments.

The sediments of the (W.K.B.) indicated higher average value of pyrite over the (W.B.) sediments, as shown in Table (3C), suggesting that much stronger reducing conditions existed in the (W.K.B.) sediments at the time of their deposition. The highest concentration of pyrite in the (W.K.B.) sediments is present in the (L.O.C.), and in the (W.B.) sediments in the (K.F.), as shown in Table (3C). These enrichments of pyrite suggest that in the case of the (W.K.B.), the much stronger reducing conditions during the time of the deposition of (L.O.C.) may be related to deeper water conditions, and in the case of the (W.B.) the stronger reducing conditions that existed in the sediments of (K.F.) may be related to the rapid rate of sedimentation which is inferred from the highest concentrations of quartz and kaolinite in these sediments, as shown in Table (4.2A).

(D) ORGANIC CARBON:

TABLE (3D)

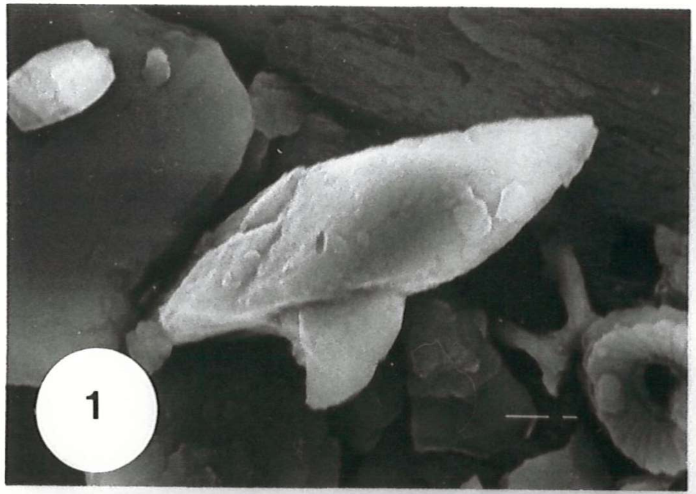
	(W.K.B.)	(W.B.)
Range (individual samples)	1 to 5%	0 to 11·35%
Highest abundance:	4·32% (L.O.C.)	3·93% (L.O.C.)
Lowest abundance:	1·50% (U.O.C.)	0·57% (U.O.C.)
Average abundance:	2·40%	1·66%

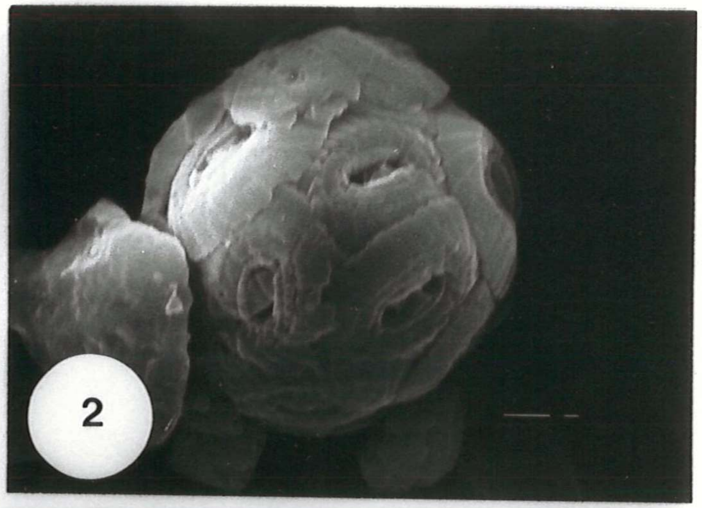
The abundances of organic carbon were calculated from the amount of CO_2, representing the contents of organic carbon in the studied sediments. The amount of CO_2 was obtained by the difference of the total CO_2 and the carbonate CO_2 values, both determined independently by the Infra-red gas analyser. The estimation of the abundance of organic carbon was done according to the method described in Chapter Two (see I.1.7(b)).

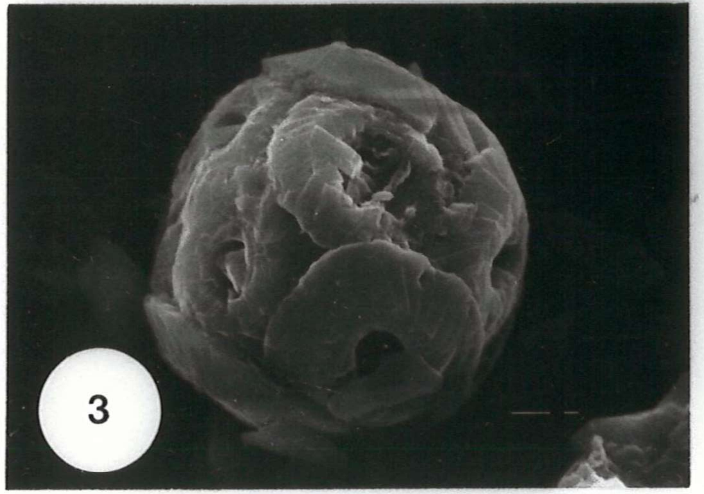
The higher concentration of organic carbon is present in the (W.K.B.) sediments. It supports further the views expressed earlier regarding the existence of stronger reducing conditions in these

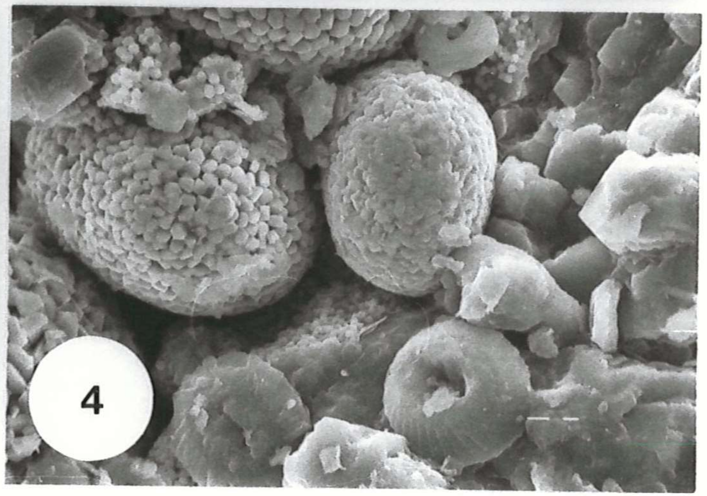
PLATE 3.4:

1. Coccolith and Quartz in BR-468
2. Coccoliths in BR-958
3. Coccoliths in BR-1326
4. Coccoliths and Framboidal Pyrite in BR-1326









PLATE– 3.4

sediments as compared with those of the (W.B.).

The highest concentration of organic carbon in both the boreholes is present in the sediments of the (L.O.C.), and the lowest in the (U.O.C.), as shown in Table (3D). But the sediments of (L.O.C.) of the (W.K.B.) show an enhanced value when compared with the (L.O.C.) sediments of the (W.B.).

(E) DOLOMITE:

TABLE (3E)

	(W.K.B.)	(W.B.)
Range (individual samples)	NIL	0 to 36·80%
Highest abundance:	NIL	10·82% (U.O.C.)
Lowest abundance:	NIL	1·45% (K.F.)
Average abundance:	NIL	6·57%

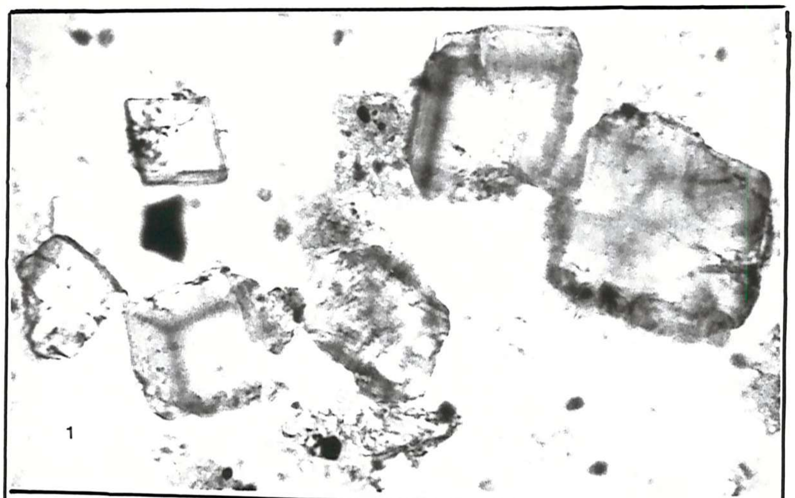
Dolomite (ferroan) is present only in the sediments of the (W.B.) samples. It was identified by its characteristic peak positions on the X.R.D. diffractograms at 2·72Å (30·84°,2θ) and 2·19Å (41·04°,2θ). BELLAMY (1980) also identified ferroan dolomite at the same peak positions in the Kimmeridgian sediments from the Dorset coast. The abundances of dolomite (ferroan) were calculated by using the values of the ratios of calcite/dolomite, which are shown in Appendix (2.2), and the amounts of CO_2 determined by the acid (HCl 1:1) digestion method which are also tabulated in Appendix (2.2). The acid digestion method (HCl 1:1) was used because dolomite (ferroan) does not dissociate completely by the attack of 'orthophosphoric' acid, used for the determination of carbonate CO_2 by the 'Infra-red' gas analyser, and,as a consequence of this, a lower amount of CO_2 was being measured leading to lower amounts of dolomite.

Dolomite showed its highest and lowest abundances associated with the highest and lowest concentrations of calcite and mixed-layer minerals respectively in the sediments of the (U.O.C.) and (K.F.). These associations indicate the strong relationship between these three phases. Mixed-layer minerals may be related to dolomite on genetic grounds; they might have contributed Mg^{+2} for the formation of dolomite.

PLATE 3.5:

1. Dolomite rhombohedral crystals in a smeared slide, BR-115. Magnification 640X
2. Dolomite rhombohedral crystals in a smeared slide, BR-123. Magnification 640X
3. Dolomite rhombohedral crystals in a smeared slide, BR-1326. Magnification 640X
4. Calcite crystal in WBK-12, S.E.M. Photomicrograph
5. Calcite crystal in WBK-23, S.E M. Photomicrograph

Scale same as other micrographs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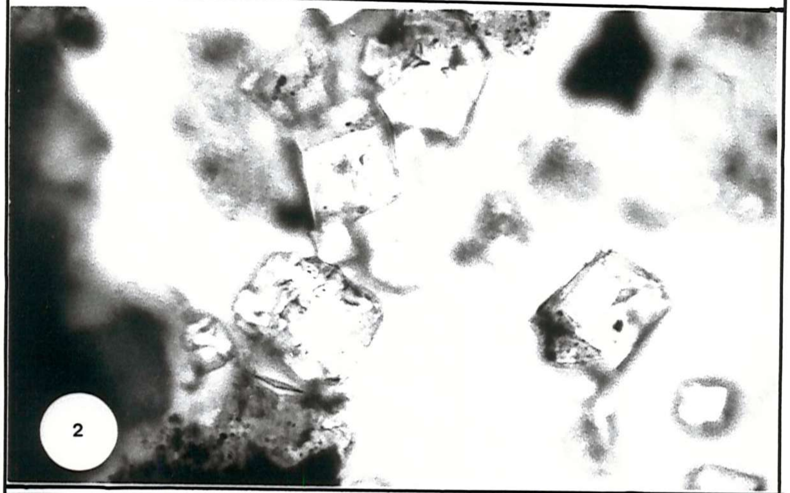
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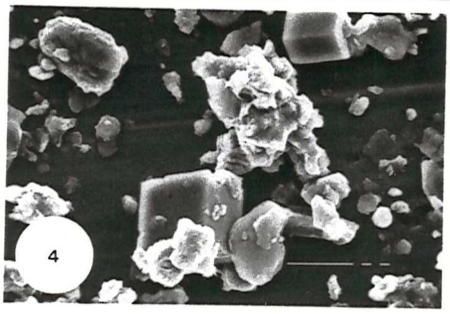
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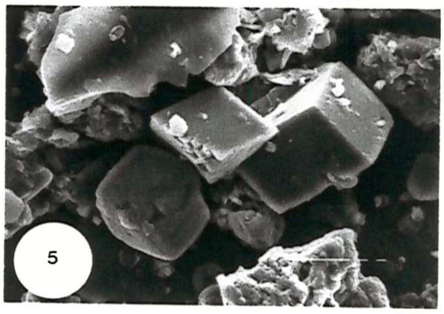
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PLATE– 3·5

(F) TOTAL CLAYS:

TABLE (3F)

	(W.K.B.)	(W.B.)
Range (individual samples)	21 to 61%	18·34 to 76·11%
Highest abundance:	56·50% (K.F.)	54·43% (L.O.C.)
Lowest abundance:	33·00% (U.O.C.)	40·29% (U.O.C.)
Average abundance:	44·18%	45·51%

The presence of 'total clays' in the studied sediments was measured by its diagnostic peak position at 19·90°,2θ (4·45Å), on the X.R.D. diffractogram. The total clays are composed of clay minerals such as illite, kaolinite, chlorite and smectite/mixed-layer minerals. The amount of total clays was calculated by the difference method (COSGROVE, 1973), i.e. [%Total clays = 100 - (QTZ+CAL+DOL+PYT+CORG)]. The abundances of clays thus calculated were found to be reasonably satisfactory, as described in Chapter Two (see 2.I.a).

The sediments of the (W.K.B.) showed the highest and lowest concentrations of the total clays in the (K.F.) and (U.O.C.) sediments respectively, while the sediments of the (W.B.) showed such concentrations in the (L.O.C.) and the (U.O.C.) sediments respectively. These trends indicate shallowing deposition of the Oxford Clay sediments during the time of the Upper Oxford Clay in the sediments of both boreholes. The sediments of the (U.O.C.) of both the boreholes show an antipathetic relationship between total clays and total carbonates. The average content of total clays in the (W.B.) sediments is slightly higher as compared with the (W.K.B.) sediments, as shown in Table (3F). It may give some clue as to the influence of recycled material on the detritus of the (W.B.) sediments.

(G) FELDSPARS:

Feldspars (e.g. Na-bearing and K-bearing), in minor amounts, are present in the sediments of both the boreholes. Their presence was indicated by weak peaks at 27·41°,2θ (3·22Å) and 27·93, 2θ (3·16Å). Abundances of feldspars were not estimated - being in such small amounts ($<$5%).

3.3 Correlations

The correlation coefficient matrices for the (W.K.B.) and (W.B.) sediments are given in Tables (3.2a & 3.2b), and the summaries of statistics in Tables (3.1a & 3.1b) respectively. Groups of minerals indicating highly significant levels (i.e. 99·99% and 95%) of correlation (±) are shown in Figure (3.2). It is evident from this Figure that in both the borehole sediments there exists a very strong positive correlation (significant at the 99·99% level) between pyrite, C_{org}, total clays and depth in the borehole. These correlations are obvious and confirm that reducing conditions existed within the sediments of both boreholes. Minerals such as quartz, smectite and calcite in the (W.K.B.) sediments displayed a very strong negative correlation, significant at the 99·99% level, with depth, and a very strong positive correlation among themselves. These correlations suggest a decrease in the abundances of these minerals with the increase of depth in the borehole, and also a strong genetic inter-relationship. In the sediments of the (W.B.) there exists a strong negative correlation (significant at the 99·99% level) of minerals such as dolomite, calcite, mixed-layer mineral and total carbonate minerals, with depth. Mixed-layer minerals showed a very strong positive correlation with dolomite ($r = +0{\cdot}816$; significant at 99·99% level), and a less strong positive correlation with calcite ($r = +0{\cdot}211$), significant at the 95% level. These correlation trends of mixed-layer minerals clearly indicate that there exists a much stronger genetic relationship between the mixed-layer clays and dolomite than between dolomite and calcite.

3.4 Stratigraphic Variations of Minerals

The stratigraphic distribution of the minerals studied in the present sediments is shown in Figures (3.3 & 3.4) respectively. The sediments of the (W.K.B.) show, in Figure (3.3) the enriched values of minerals such as quartz, calcite and smectite in the (U.O.C.), and the enrichment of detrital minerals such as kaolinite, illite and chlorite, associated with pyrite and C_{org} towards the deeper parts of the borehole. The sediments of the (W.B.) show, in Figure (3.4), the enriched abundances of minerals such as calcite, dolomite, mixed-layer minerals and illite in the (U.O.C.) sediments. It also shows much enhanced abundances

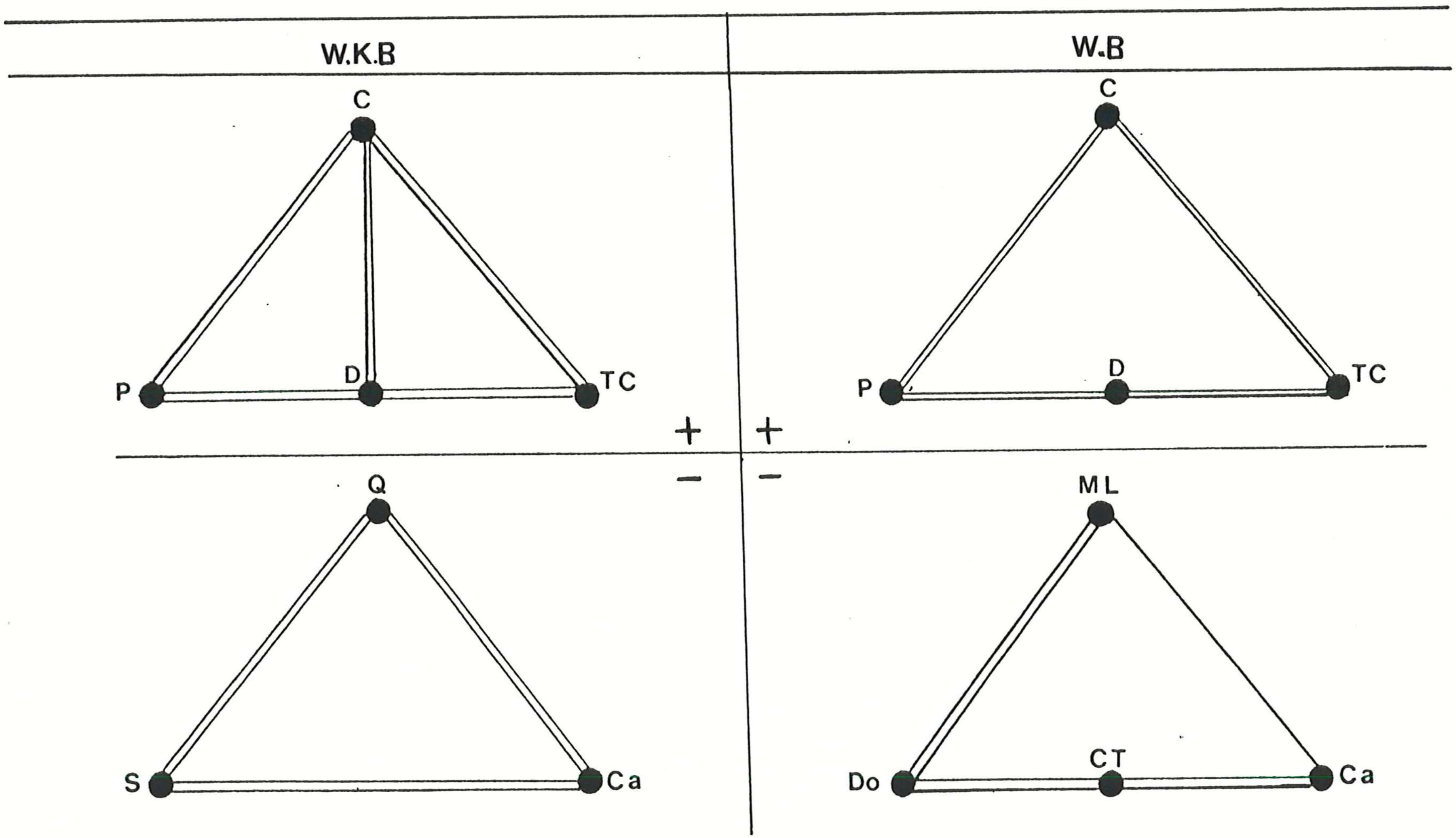


FIG.(3.2): Groups of Correlating Minerals in Bulk Rock and their relationships with depth in the Boreholes.

Note: C = Corg, P = Pyrite, D = Depth in borehole, TC = Total clays, ML = Mixed-layer minerals, Ca = Calcite, Do = Dolomite, CT = Total carbonates, S = Smectite, Q = Quartz.

// indicates 99·99% level of significance of correlation.
/ " 95·00% " " " " "

TABLE (3.1a): Summary of statistics of the bulk rock minerals in the (W.K.B.) sediments

MINERALS	MEAN	VARIANCE	S.DEVIATION	S.E. OF MEAN	SKEWNESS	KURTOSIS
QUARTZ	20·92063	9·88521	3·14408	0·39612	0·3380	-0·4241
ORGANIC CARBON	2·40444	1·55407	1·24662	0·15706	0·7838 **	-0·3878
PYRITE	2·82381	1·19475	1·09304	0·13771	1·2057 ***	1·8369 **
CALCITE	29·66508	103·11521	10·15457	1·27936	0·4110	-0·6567
TOTAL CLAYS	44·18095	116·12092	10·77594	1·35764	-0·3838	-1·0471

Number of cases = 63

Significance levels = * = 5%
** = 1%
*** = 0·1%
**** = 0·01%

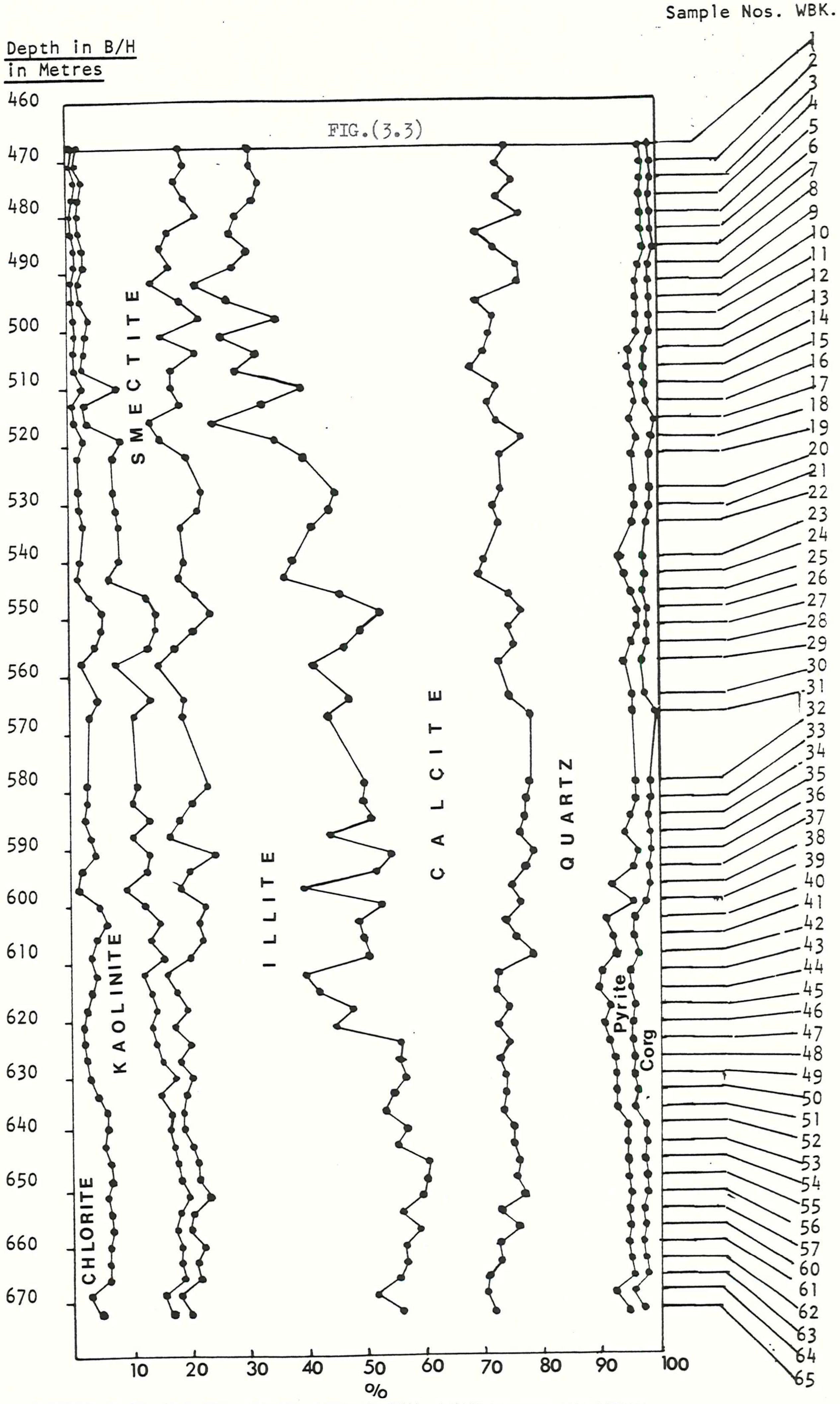
TABLE (3.1b): Summary of statistics of the bulk rock minerals in the (W.B.) sediments.

MINERALS	MEAN	VARIANCE	S.DEVIATION	S.E. OF MEAN	SKEWNESS	KURTOSIS
QUARTZ	22·0640	116·11	10·776	1·2201	3·173 ****	11·96 ****
ORGANIC CARBON	1·6659	3·3047	1·8179	0·20583	2·686 ****	9·999 ****
PYRITE	1·6719	2·4530	1·5662	0·17734	4·876 ****	32·13 ****
CALCITE	22·5170	128·54	11·338	1·2837	0·5586 *	1·438 **
DOLOMITE	6·5724	57·846	7·6057	0·86117	2·521 ****	6·368 ****
TOTAL CLAYS	45·5140	146·42	12·100	1·3701	-0·4772	0·6405

Number of cases = 78

Significance levels:
* = 5%
** = 1%
*** = 0·1%
**** = 0·01%

FIG.(3.3)



OXFORD CLAY AND KELLAWAYS MINERALOGY, WINTERBORN KINGSTON of purely detrital minerals such as quartz and kaolinite, associated with authigenic mineral pyrite, in the deeper parts of the borehole.

3.5 Discussion

(a) Winterborne Kingston Borehole Sediments

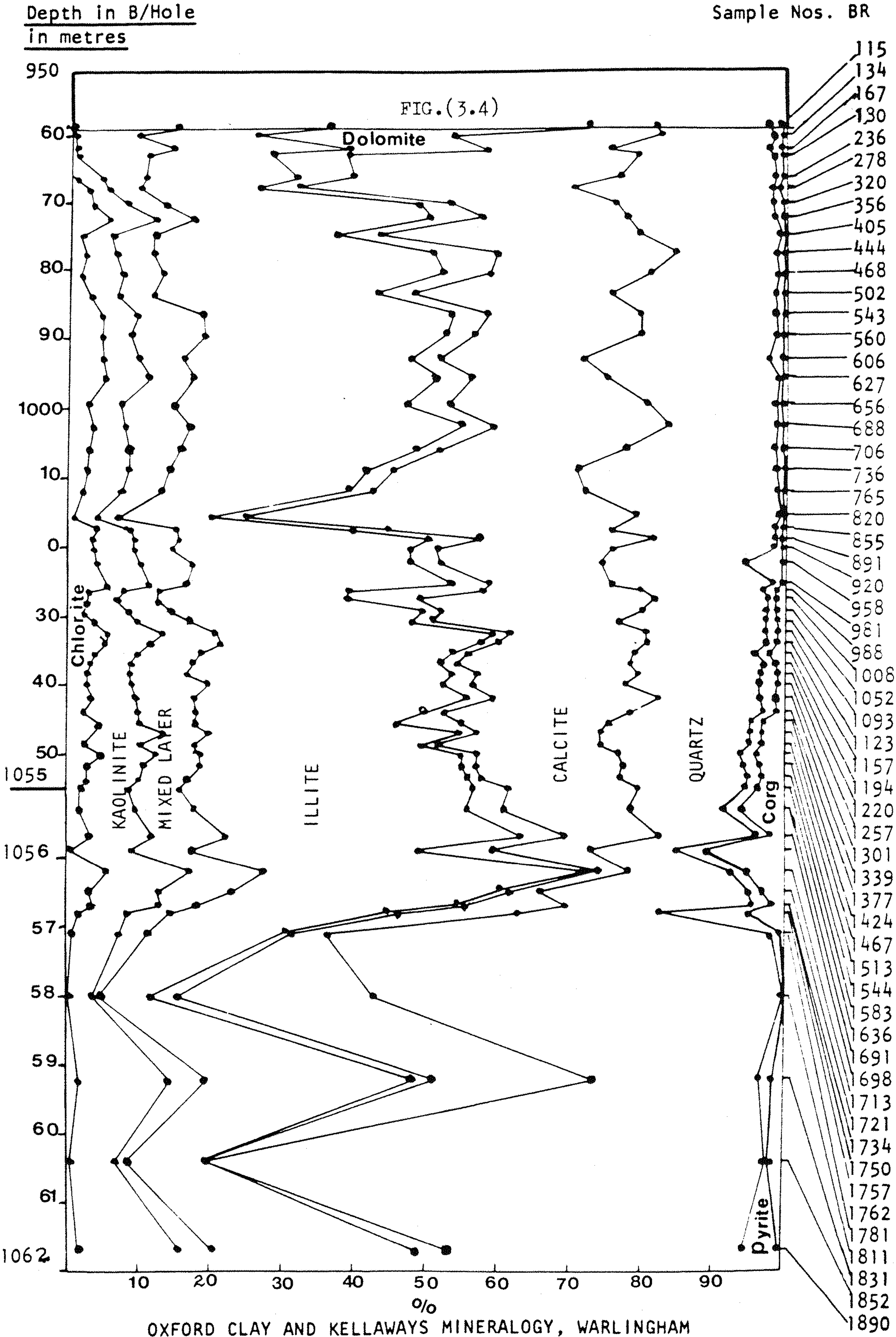
The relationships demonstrated by minerals, shown in the correlation coefficient matrix (Table 3.2a) and Figures (3.2 & 3.3), suggest as follows:

(i) The strong positive correlations of depth with total clays, organic carbon, illite, kaolinite, chlorite and pyrite, and strong negative correlations with calcite, smectite; both correlations being significant at 99·99% levels, indicate the sympathetic and antipathetic relationships between these phases and depth.

(ii) The very strong positive correlation of C_{org}, significant at 99·99% levels, with typically detrital mineral kaolinite ($r=+0{\cdot}68$) and total clays ($r = +0{\cdot}527$), and its very strong negative correlation with smectite ($r = -0{\cdot}65$) and calcite ($r = -0{\cdot}587$), both significant at the 99·99% levels, tend to suggest a detrital origin for the organic carbon.

(iii) Pyrite showed a strong positive correlation with C_{org} ($r = +0{\cdot}518$), kaolinite ($r = +0{\cdot}414$) and depth ($r = +0{\cdot}45$), all correlations being significant at the 99·99% levels, indicating a strong relationship between these components. The concentration of kaolinite and C_{org} presumably created reducing conditions for the formation of pyrite in the Lower Oxford Clay sediments. The reducing conditions may be the result of high biogenic activity or a high rate of sedimentation, or both. BLOXAM and THOMAS (1969) and SPEARS (1964) used ratios of quartz/organic carbon, quartz/Zr, quartz/combined SiO_2, as a measure of sorting or rate of sedimentation. These ratios were calculated for the different divisions of the Oxford Clay and Kellaways Formations in the studied sediments, and are tabulated in Table (4.1C). From this Table, it is evident that the highest values of these ratios exist in the sediments of the (U.O.C.), and the lowest in the sediments of the (K.F.). It suggests a high rate of sedimentation during the deposition of the

FIG.(3.4)



OXFORD CLAY AND KELLAWAYS MINERALOGY, WARLINGHAM

TABLE (3.2a): Correlation Coefficients matrix of the bulk rock minerals in the (W.K B.) sediments

	DEPTH	QTZ	CORG	PYT	CAL	TCLAY	ILL	KAOL	CHLR	SMECT
DEPTH	1 0000									
QTZ	-0·5598	1·0000								
CORG	0·6779	-0·4858	1·0000							
PYT	0·4554	-0·5627	0·5186	1·0000						
CAL	-0·8976	0·4146	-0·5876	-0·2197	1·0000					
TCLAY	0·8842	-0·5694	0·5270	0·2100	-0·9722	1·0000				
ILL	0·9162	-0·5877	0·5705	0·2731	-0·9565	0·9148	1·0000			
KAOL	0·9348	-0·6353	0·6818	0·4145	-0·9148	0·9261	0·9463	1·0000		
CHLR	0·7896	-0·4548	0·4135	0·1586	-0·8054	0·8272	0·8268	0·7594	1·0000	
SMECT	-0·8897	0·5900	-0·6532	-0·4572	0·7820	-0·7866	-0·8799	-0·9042	-0·7847	1·0000

Note: For 60 degrees of freedom the values of correlation coefficients for 99·99% and 95% levels are:

99·99% level $r = \geq \pm 0{\cdot}32$

95% " $r = \geq \pm 0{\cdot}25$

(U.O.C.)and a slow rate for the (K.F.) sediments. But the sediments of the (L.O.C.) in comparison with the sediments of the (K.F.) display higher values of the ratios mentioned above. It suggests that the rate of sedimentation during the deposition of the (L.O.C.) was comparatively higher than that for the sediments of the (K.F.). Only the quartz/C_{org} ratio is lowest. The (L.O.C.) is rich in organic carbon, the majority of which is believed to be detrital. The abundant amounts of allochthonous organic matter lowers the quartz/C_{org} ratio. Therefore the use of this ratio in such cases may give faulty results.

(iv) The very strong positive correlation ($r = +0{\cdot}78$) shown by calcite with smectite suggests a common (non-detrital) origin for both minerals. Both minerals show, in Table (3.2a), very strong negative correlation, significant at the 99·99% levels, with typical detrital components such as kaolinite, illite, chlorite and total clays. These correlation trends confirm that both minerals, i.e. calcite and smectite, are non-clastic (authigenic?) in origin.

(v) The positive correlation of quartz with smectite ($r = +0{\cdot}59$) and with calcite ($r = +0{\cdot}44$), both being significant at the 99·99% levels, suggests some genetic relationship between these components. There exists a strong antipathetic relationship of smectite and calcite with depth in the borehole. Quartz also shows a decreasing trend with depth, but not so distinct as that displayed by calcite and smectite, as shown in Figure (3.3). The similarity in distribution of these minerals may be related to their origin. CHOWDHURY (1980) reported authigenic smectite in the 'mud-rocks' of the Corallian from the Dorset coast. It is distinctly possible that some of the smectite present in the Oxford Clay sediments may be of authigenic origin. Biogenous or diagenetically precipitated silica,such as opaline-silica and cristobalite etc. in sediments, has been reported by many workers including CALVERT (1966), EMERY (1960), CALVERT and PRICE (1971). CHOWDHURY (1980) mentioned the possibility of the occurrence of diagenetic silica in the Corallian sediments from the Dorset coast, associated with smectite of authigenic origin. Therefore, it is possible that the observed association between smectite and quartz in the present study may be of a similar nature to that of Corallian

TABLE (3.2b): Correlation Coefficients matrix of the bulk rock minerals in the (W.B.) sediments

	DEPTH	QTZ	CORG	PYT	CAL	DOL	TCLAY	ILL	KAOL	CHLR	M/LYER
DEPTH	1·0000										
QTZ	0·2462	1·0000									
CORG	0·5855	-0·1549	1·0000								
PYT	0·3244	-0·0812	0·4456	1·0000							
CAL	-0·4198	-0·3530	-0·4102	-0·2623	1·0000						
DOL	-0·6308	-0·2402	-0·2302	-0·1169	0·0314	1·0000					
TCLAY	0·4399	-0·3747	0·4589	0·1949	-0·5470	-0·3944	1·0000				
ILL	-0·2150	-0·3973	-0·0375	-0·0636	0·1604	-0·0836	0·2694	1·0000			
KAOL	0·7356	0·6207	0·2734	0·1470	-0·3139	-0·6679	0·1010	-0·3133	1·0000		
CHLR	0·2075	-0·1086	-0·0050	-0·0562	-0·0408	-0·4794	0·4453	0·0744	0·0908	1·0000	
M/LYER	-0·6256	-0·3195	-0·2259	-0·0779	0·2116	0·8165	-0·3830	-0·2528	-0·7750	-0·4777	1·0000

Note: For 76 degrees of freedom the values of correlation coefficients for 99·99% and 95% levels are as follows:

99·99% $r = \geqslant \pm 0{\cdot}29$

95% $r = \geqslant \pm 0{\cdot}20$

mud-rocks. Some of the quartz in the present sediments may be of diagenetic origin, having been derived from 'cristobalite', an opaline-silica (metastable phase of silica), in turn of volcanic origin.

(b) Warlingham Borehole Sediments

The sediments of the Oxford Clay and Kellaways Formations from the (W.B.) also demonstrated some specific relationships between minerals and depth, which are discussed as follows:

(i) The strong positive correlations of depth with kaolinite (r = +0·73), C_{org} (r = +0·585), total clays (r = +0·439) and pyrite (r = +0·324), and its medium strong positive correlation with quartz (r = +0·246), suggest that abundances of kaolinite, C_{org} and pyrite are related strongly and sympathetically with depth; these trends are shown in Figure (3.4). The very strong negative correlations of depth with dolomite (r = -0·6308), calcite (r = -0·419) and mixed-layer minerals (r = -0·625) on the one hand suggest a decrease in the contents of these non-detrital components with the increase of depth in the borehole and, on the other hand, indicate that the detrital components were more abundantly supplied to the basin of deposition at the time of sedimentation of the older (deeper) sediments (i.e. K.F.).

(ii) Quartz in these sediments showed only one very strong positive correlation. This is with the detrital component kaolinite (r = +0·62; significant at the 99·99% level). It also showed very strong negative correlation with calcite (r = -0·35; significant at the 99·99% level). These correlations confirm that the (W.B.) sediments contain only detrital quartz.

(iii) Dolomite showed a very strong positive correlation (r = +0·816; significant at the 99·99% level) with mixed-layer minerals, which are strongly and negatively correlated with depth, quartz, total clays, kaolinite and chlorite; all correlations are significant at the 99.99% level. These associations suggest that there exists a strong relationship between dolomite and the mixed-layer minerals. There is a strong possibility that the present mixed-layer (non-expanding) minerals in the (W.B.) sediments, initially, were like smectite (expanding) as present in the (W.K.B.) sediments. The assumed smectite was degraded due to the effect of some natural processes and provided Mg^{+2} for the formation of dolomite. Some Mg^{+2} could have been provided in this way; the rest resulting from entrapped (interstitial) sea-water. Both mixed-layer mineral, i.e. the non-expanding type in the (W.B.), and the expanding type in the (W.K.B.), exhibited the same trend in their concentrations, being highest in the (U.O.C.) and lowest in the (K.F.) sediments. The very weak positive correlation of dolomite with calcite (r = +0.0314) suggests that dolomite originated as an independent phase in the present sediments and is not the alteration product of calcite.

(iv) Pyrite showed a very strong positive correlation with C_{org} (r = +0·44), depth (r = +0·32), suggesting that organic carbon in the (W.B.) sediments also played some role in the generation of reducing conditions, as has been described for the (W.K.B.) sediments. The highest abundances of pyrite (1·94%) and C_{org}(3·93%) are present in the (L.O.C.) sediments, and indicate that much stronger reducing conditions existed at the time of deposition of these sediments. The relationship of pyrite with kaolinite (r = +0·147) and total clays (r = +0·19) is very weak, but suggests that, on the whole, these detrital components also assisted in the creation of reducing conditions.

(v) The very strong positive correlation of C_{org} with depth (r = +0·585) and total clays (r = +0·458), both being significant at the 99·99% level, suggests that some amount of C_{org} of detrital origin is also associated. This relationship is further confirmed by a medium strong positive correlation of C_{org} with kaolinite(r = +0·27; significant at the 95% level).

3.6 Provenance of the Studied Sediments

The association of minerals such as quartz, kaolinite, illite and chlorite in the sediments of the (W.K.B.) suggests that the provenance most likely was in igneous and metamorphic rocks which, after weathering, produced the detritus for the (W.K.B.) sediments. The presence of clay minerals, e.g. illite and kaolinite in abundant amounts, suggests a significant contribution by the weathering of acid igneous rocks. The enrichment of the (K.F.) sediments in the contents of chlorite, as shown in Figure (3.3), does suggest the dominant contribution from a metamorphic terrain. The Cornubian Massif and the Armorican Massif (CHOWDHURY, 1980), shown in Figure (1.5), are the most probable provenances of these sediments. The sand fraction of these sediments studied under a binocular microscope showed the presence of fragments of acidic igneous rocks, angular to sub-angular grains of quartz of coarse to fine grain size, confirming that the described Massifs were the provenances for these rocks. The presence of smectite (authigenic?) suggests the availability of some volcanoclastic material for its formation. CHOWDHURY (1980) reported the presence of smectite, associated with recognisable volcanic components, in the Lower Calcareous Grit Group Sediments from the Dorset coast. He suggested that 'air-fall' volcanic ash from a North Sea volcanic source was the origin of smectite in his sediments. A similar material and source is considered responsible for the origin of smectite in the Oxford Clay sediments from the (W.K.B.).

The enriched abundances of minerals such as illite (65.63%), quartz (22·06%), and the depleted abundances of minerals such as kaolinite (12·33%) and chlorite (5·36%) in the (W.B.) sediments, over their counterparts in the (W.K.B.) sediments, suggest that the provenance for the (W.B.) sediments was different from that of the (W.K.B.) sediments. The degraded nature of the illite, indicated by the poor degree of crystallinity of illite and enriched abundances of components such as quartz, degraded illite, mixed-layer (non-expanding) minerals and total clays in the (W.B.) sediments, strongly support a provenance composed of re-cycled material for the (W.B.) sediments. Enriched values of certain elements in the bulk rock and clay fraction ($< 2\mu$) samples of the (W.B.) sediments, mentioned elsewhere in the present thesis, provide additional evidence regarding the re-cycled sedimentary material as being the most probable source for the formation of the (W.B.) sediments.

It is suggested that the sediments of the (W.B.) were dominantly contributed by the sedimentary rocks existing in the East Anglian Massif (KENT, 1980). All the three mentioned 'Massifs' were present at the time of deposition of the studied sediments; their geographic positions are shown in Figure (1.5).

3.7 Origin of Non-Detrital Minerals

The studied sediments contain calcite, pyrite, dolomite and smectite among the non-detrital components. The non-detrital nature of calcite and pyrite is well-known; in addition to this, all these minerals indicated very strong negative correlations, significant at the 99·99% level, with typically known detrital components such as kaolinite, chlorite, illite, quartz, total clays and also with some typical detrital elements such as Zr, Nb, Cr, Ti, Si and Al, etc.

The occurrence of dolomite in minor amounts (up to 3%) in the Oxford Clay sediments has been reported by JACKSON (1972) and JACKSON and FOOKES (1974) from the English Midlands, but no explanation regarding its origin has been given. HUDSON and PALFRAMAN (1969), DUFF (1975) and HUDSON (1978) have explained the origin of pyrite and calcite in the Oxford Clay sediments, based on most authenticated information. Therefore in the present study only a brief account will be given on the origin of these two minerals, which is as follows:

(a) Pyrite:

Pyrite is an authigenic sulphide of iron (FeS_2). It is usually present in the organic-rich fine-grained sediments deposited under marine environments. Many workers, including KAPLAN *et al.* (1963), BERNER (1970 & 1971), GARDENER (1973), SWEENEY *et al.* (1973) and PRICE (1976) have mentioned the presence and traced the origin of pyrite present in the sediments studied by them. Most of these workers agree regarding the processes of the pyrite formation and the kinetic factors affecting the processes. It is commonly known that the formation of pyrite proceeds in environments where the essential conditions such as low Eh, availability of iron and HS^- or H_2S are met. The condition of low Eh is produced by the decomposition of organic matter as a result of attack by anaerobic bacteria. Iron is provided by clay minerals, either retained in their structural positions or as Fe-oxides/hydroxides, adsorbed onto the surfaces of the clay minerals. Other iron-bearing minerals such as fine-grained limonitic goethite and hematite also contribute to the marine environments some amount of the iron required for the formation of pyrite. The source of sulphur is the organic matter, as mentioned by KUMMEL (1948). The source of H_2S is the abundant amount of sulphates present in sea-water which, on bacterial decomposition, is reduced to HS^- or H_2S. BERNER (1971) stated that dissolved sulphate is the principal source of sulphur in most of the sediments for the genesis of pyrite. According to KAPLAN et al. (1963), the organic sulphur content of the marine organisms averages only about 1% by dry weight. It means that if the organic sulphur only were to have been the major source of the pyrite in marine sediments, then more than 100% organic matter would have been required by many of the sediments containing rich abundances of pyrite. GARRELS and CHRIST (1965) mentioned the necessary range of Eh ($\leq$ -0·20) and pH (7-8) for the stability of pyrite in an anoxic environment.

The occurrence of pyrite in the Lower Oxford Clay sediments has been reported by RUTTEN (1956), HUDSON and PALFRAMAN (1969), JACKSON (1972), JACKSON and FOOKES (1974), DUFF (1975), HUDSON (1978) and BELLAMY (1980). These authors have suggested the various possible sources of sulphur and iron, and have explained the mode of formation of pyrite. RUTTEN (op.cit.) postulated that phytoplankton blooms are responsible for the formation of pyrite. DUFF (1975) mentioned that pyrite in the sediments of (L.O.C.) is produced by the post-depositional preservative changes. HUDSON and PALFRAMAN (1969) proposed three possible sources for the sulphide ions, for the formation of pyrite, which include (i) decomposition of proteins in the trapped organic matter of fossils and sediments; (ii) the reduction of sulphate of the sea-water trapped within the sediments, presumably by the bacteria; (iii) the bacterial reduction of sulphate from the overlying water, taking place at the interface or within diffusional contact with it.

The environments under which the sediments of the Oxford Clay and Kellaways Formations were deposited at the sites of the two boreholes at present under discussion appear to be favourable for the genesis of sulphide minerals such as pyrite. All the essential conditions required in marine environments for the genesis of pyrite, described earlier, were definitely present in the environments at the Winterborne Kingston and Warlingham sites. The studied sediments contain appreciable abundances of organic carbon, iron-containing clay minerals, Fe-oxides/hydroxides coated on clay minerals, carbonate-minerals and concentration of phosphorus, all of which indicate the occurrence of the essential conditions required for the genesis of pyrite in these sediments, during the time of their deposition.

It is therefore concluded that reducing conditions existed, probably within the freshly deposited sediments, and also at the sediment and sea-water interface, at the sites of the (W.K.B.) and (W.B.). Clay minerals, particularly illite, chlorite and smectite, provided the iron present in the octahedral sheet and inter-layer positions, and also adsorbed onto the grains of these clays as Fe-oxides/hydroxides. Sulphur was provided by the organic organisms, and mainly by the reduction of dissolved sulphate in the sea-water by the action of anaerobic bacteria. In the sediments of the (W.B.), strong reducing conditions were created during the time of deposition of the (K.F.) sediments, probably due to a greater input of detrital components,which presumably increased the rate of sedimentation and caused the entrapment of organisms within the freshly deposited sediments; which ultimately led to the abundant genesis of pyrite in these sediments.

(b) Calcite:

The calcite present in the sediments of the Oxford Clay and Kellaways Formations in both the boreholes is pure calcite (i.e. low Mg), as indicated by its characteristic peak positions at $29{\cdot}43^{\circ}$,2θ($3{\cdot}03$Å), $39{\cdot}43^{\circ}$,2θ($2{\cdot}28$Å) and $43{\cdot}24^{\circ}$,2θ($2{\cdot}09$Å) on the X-ray diffractograms. Calcite is present as the second most abundant mineral. HUDSON and PALFRAMAN (1969) studied the preservation of calcitic shells in the Lower Oxford Clay at Woodham brick-pit. HUDSON (1978) described the origin of the concretions, based on isotopic studies, in Lower Oxford Clay from the Midlands in England. He mentioned the mechanism of the formation of concretions, source of the carbon, and the probable temperature (13-16°C) at which the formation took place. BELLAMY (1980) described the calcite mineralogy and geochemistry of nodules from the Lower Oxford Clay from Dorset and many areas in the Midlands in England. He mentioned that Oxford Clay nodules from Dorset contain 94·05% $CaCO_3$, 5·33% MgO, 0·57% $FeCO_3$, 0·04% $MnCO_3$ and 529 p.p.m. of Sr.

The origin of carbonate minerals such as calcite, aragonite and dolomite, in sediments and sedimentary rocks, has been described in great detail by many workers, and there exists a voluminous bibliography on various aspects of the origin of the above-mentioned minerals. The essential physico-chemical conditions and the constraints which favour the precipitation, dissolution, crystallization and diagenetic alteration of the carbonate minerals are very well explained by many authors, including DEER et al. (1962), DEGENS (1965), BERNER (1971), BLATT et al. (1972), BASS et al. (1973), ALLEGER and MICHARD (1974), MILLIMAN (1974), BATHURST (1975), ANDERSON and LAURENCE (1976), and KRAUSKOPF (1979).

DEGENS (1965) stated that commonly found carbonates in sediments include the anhydrous Ca-Mg carbonates such as calcite, aragonite and dolomite. Dolomite is the double carbonate of Ca and Mg, and is rhombohedral, while calcite and aragonite are the polymorphic forms of $CaCO_3$; calcite is rhombohedral and aragonite is orthorhombic. Aragonite, being a metastable phase, with the passage of geological time, changes to more stable phases such as calcite and dolomite. MILLIMAN (1974), KITANO and HOOD (1965), BROOKS et al. (1950) and KINSMAN and HOLLAND (1969) stated that low-Mg concentration within the precipitating liquids, low pH and low temperature, are conducive for the precipitation of calcite. KRAUSKOPF (1979) stated that, in marine environments, the precipitation of $CaCO_3$ is favoured where the water is warm and the CO_2 is being lost through evaporation or photosynthesis, as on the shallow banks off Florida and the Bahamas. He further mentioned that cold water and an abundance of CO_2 promotes the dissolution of $CaCO_3$. The scarcity of calcareous shells in parts of the deep ocean below about 4,000 metres may be due to the presence of cold masses of CO_2-saturated water. ALLEGRE and MICHARD (1974) also mentioned that abundant amounts of $CaCO_3$ ($> 80\%$) occur to a depth of 3,500 metres and very low contents of $CaCO_3$ ($< 5\%$) below a depth of 3,500 metres.

Precipitation of $CaCO_3$ may take place either inorganically or through the agency of organisms. Organisms may accomplish the precipitation either in the building-up of their shells or incidentally as they remove CO_2 from the water, or during decay if they supply alkaline material to the water (KRAUSKOPF, 1979). DEGENS (1965) also mentioned that $CaCO_3$ deposition under marine conditions appears to be governed largely by the activities of organisms that deposit calcite, aragonite or both, during their life cycle. KRAUSKOPF (1979) went on to mention that sea-water is approximately saturated with $CaCO_3$. BLATT et al. (1972) stated that an increase in pH, in the depositional environments, favours the formation of calcite. BASS et al. (1973) mentioned that the precipitation of calcite at low temperature in a CO_2-rich environment proceeds when the pore water and fracture fluids become supersaturated with respect to calcite. BERNER (1971) mentioned that a widespread precipitation of $CaCO_3$

takes place in areas of shallow water, such as continental shelves. RILEY and CHESTER (1979) mentioned that Coccolithopuorids have a test of jointed or separated circular, elliptical or angular calcitic plates termed coccoliths, rhabdoliths, etc. After the death of these organisms, these tests usually disintegrate into these plates, which may be preserved as calcite in sediments. According to these authors, calcite and aragonite are both significantly soluble in sea-water. Factors influencing the dissolution rate of $CaCO_3$ described by RILEY and CHESTER (op.cit.) include (i) depth of water; (ii) rate of deposition of total sediments (carbonates + non-carbonates); (iii) the physico-chemical conditions (e.g. partial pressure of CO_2, temperature and the hydrostatic pressure); (iv) rate of removal of dissolved calcium, which affects the solubility equilibrium of the carbonates (calcium carbonate solubility increases with both, i.e. the total hydrostatic pressure and CO_2 partial pressure, PYTKOWICZ, 1967).

Most of the factors mentioned above were present in one form or another in the environments under which the deposition of the sediments of the Oxford Clay and Kellaways Formations took place. According to HUDSON (1975), concretions were precipitated from the solution that had dissolved marine fossil carbonates. HUDSON (1978) mentioned that abundant aragonite was available and still is available in the Oxford Clay sediments, and this is capable of precipitating a low-Mg calcite. BARNARD (1952 & 1953) and CORDEY (1962) described the presence of foraminifera in the Oxford Clay sediments. ROOD et al. (1971) described the coccoliths present in the Oxford Clay; some of the coccoliths seen in the studied sediments are shown in Plate (3.4). DUFF (1975) described the faunal assemblage of the Lower Oxford Clay.

It is therefore concluded that the calcite present in the studied sediments was largely precipitated from virtually $CaCO_3$-saturated sea-water (KRAUSKOPF, 1979). In addition, living organisms of both macro and micro nature, abundantly thriving in the environments of the deposition of Oxford Clay, might have significantly contributed $CaCO_3$ present in the shells of invertebrate fauna, tests of foraminifera and plates of coccoliths. Some of the calcite may be a product of the conversion of 'aragonite', the most unstable phase and commonly present in the environments, as mentioned by HUDSON (1978). Aragonitic material in the Oxford Clay sediments from the Warlingham Borehole has been reported by CALLOMON and COPE (1971).

(c) Dolomite:

Dolomite is one of the most common minerals extensively found in strata of all geological ages from the Pre-Cambrian to Cenozoic (KRAUSKOPF, 1979). Dolomite may be of primary origin (i.e. direct precipitation from sea-water above the depositional inter-face), or secondary in origin - all other modes of occurrence. Mineral dolomite is a double carbonate of magnesium and calcium (i.e. $CaMg(CO_3)_2$). The structure contains CO_3^{2-} anions and regularly alternating cations Ca^{+2} and Mg^{+2}; the regular alternation of cations Ca^{+2} and Mg^{+2} is of vital importance in the structure of dolomite, and differentiates dolomite from a magnesian calcite.

Dolomite in the sediments at present under investigation was found only in the Warlingham Borehole sediments, associated with calcite and mixed-layer (non-expanding) clay mineral. The occurrence of dolomite in the Oxford Clay is not new; JACKSON (1972) and JACKSON and FOOKES (1974), during their studies of Lower Oxford Clay sediments, mentioned the occurrence of minor amounts (up to 3%) in the samples from the Lower Oxford Clay collected from Calvert and Whittlesey from the English Midlands. SIDDIQUI (1979) reported dolomite in the Oxford Clay sediments during a petrographic study of Jurassic sediments in the Worlaby E-borehole. However, the occurrence of dolomite in southern England (i.e. Warlingham) reported by the present author is new, because none of the early workers such as JACKSON (1972), JACKSON and FOOKES (1974) and RUSSELL (1979), who studied the Oxford Clay from Dorset, have reported the presence of any dolomite. JACKSON (op.cit.), JACKSON and FOOKES (op.cit.) have only mentioned the occurrence of magnesian calcite in the Oxford Clay from the Chickerell brick-pit, near Weymouth.

Dolomite in the (W.B.) sediments displayed certain trends with depth in the borehole and other minerals, as shown in Figure (3.4). Its highest concentration associated with the highest abundances of calcite, mixed-layer minerals and lowest amounts of organic carbon is present in the (U.O.C.), and the lowest concentration associated with the lowest abundances of calcite, mixed-layer minerals and significantly higher amounts of $C_{org.}$ in the (K.F.) sediments, as shown in Table (4.2B). Samples from BR-115 to BR-199, which belong to the transitional zone between the Oxford Clay and the overlying Corallian sediments of shallow water environments, show exceptionally high values of dolomite abundances, ranging from 10·30% to 36·80%, as shown in Appendix (3.2). A drastic drop in the contents of dolomite from sample BR-211 towards the deeper part in the borehole is evident in Appendix (3.2). The only exception is in samples BR-988 and BR-1721; these two samples showed significantly higher amounts of dolomite, as compared with other samples from the deeper parts in the borehole. Sample BR-988 contains 20·56% dolomite, associated with 23·03% calcite, 1·52% C_{org} and 4·22% mixed-layer minerals, while BR-1721 contains 10·44% dolomite, associated with 13·59% calcite, 8·23% mixed-layer minerals, and the highest amount of C_{org}, i.e. 11·53%. All the trends observed and described suggest various relationships with dolomite and its origin.

Dolomite, at present under discussion, is associated with clays as disseminated fine grains and crystals, not visible to the naked eye, but clearly identifiable in smeared slides and thin sections under the microscope. Some of the perfect rhombohedra of the dolomite are shown in Plate (3.5). It is a ferroan dolomite, as indicated by its characteristic d-spacings on the X-ray diffractogram at $30{\cdot}86^{\circ}, 2\theta (2{\cdot}72\text{Å})$ and $41{\cdot}04^{\circ}, 2\theta (2{\cdot}19\text{Å})$, and a significant amount of Fe present in the lattice structure, as demonstrated by the chemical formula calculated for the two samples. The chemical formulae of the two samples, i.e. BR-115 and BR-123, were calculated from the known concentrations of Mg, Ca and Fe, determined in the leachates of these samples, obtained by dissolving them in HCl(0·1N) and measuring their concentrations by A.A.S. In calculating the formula of dolomite which is mixed with calcite, it is necessary to have a knowledge of the proportions of CaO in the dolomite and calcite phases. BELLAMY (1980) reported a chemical formula ($Ca_{52}Mg_{45}Fe_{3}$) for Kimmeridgian dolomite (determined on the pure mineral) which is very closely similar to the dolomite encountered in the Oxford Clay. Therefore in the present calculation, the Ca value of Ca_{52} was assumed, giving the following formulae for the two Oxford Clay samples:

BR-115: $Ca_{52}Mg_{40}Fe_{8}$

BR-123: $Ca_{52}Mg_{41}Fe_{7}$

Both dolomite formulae show enriched values of Fe and reduced values of Mg over the Kimmeridgian dolomite. According to MURATA et al. (1972) and FRITZ and JACKSON (1972), respectively the diagenetic ferroan and non-ferroan dolomite contains 48-58 mole % of $CaCO_3$ and late diagenetic dolomite contains 51-56 mole % of $CaCO_3$.

Many workers have attempted to explain the mechanisms of the formation of primary and secondary dolomite. According to KRAUSKOPF (1979), it is the most 'stubborn' question in carbonate geochemistry. PETERSON et al. (1966) stated that "mineral dolomite is a geological enigma". INGERSON (1962) expressed the conclusion that the "dolomite problem revolves mainly about the abundance of dolomite in ancient sedimentary rocks". BERNER (1971, pp.148-155) stated that the "formation of sedimentary dolomite is one of the great unsolved problems of sedimentary petrology". From these statements it becomes clear that to explain the origin of dolomite in sediments is not an easy task; one needs some sophisticated information such as isotopic data and possibly the maturity of the sediments as inferred by the maturity of the organic matter associated with it. The present author lacks these data, and therefore the interpretations given here are based only on the apparent trends exhibited by dolomite, sub-surface geology and tectonic controls.

In order to get some insight, to be able to explain the origin of dolomite in the studied sediments, the works of many geoscientists were consulted and some of them are mentioned here. They include BISSELL et al. (1958), ZEN (1959), DEGENS et al. (1964), KHALE (1965), PETERSON et al. (1966), BERNER (1966 and 1971), DREVER (1971), FOLK and LAND (1975), IRWIN and CURTIS (1977), KRAUSKOPF (1979), IRWIN (1980), ZENGER and DUNHAM (1980), GAINES (1980), MATTES and MOUNTJOY (1980), LAND (1980), CARPENTER (1980), LUMSDEN and CHIMAHUSKY (1980) and BAKER and KASTNER (1981). These authors have explained all possible constraints essential for the formation of dolomite, and available in nature, such as the thermodynamic conditions, transformation of carbonate minerals (e.g. aragonite and magnesian calcite), source of magnesium, role of clay minerals as magnesium source, catalysts, membrane and centre of nucleation for dolomitization. They have also mentioned the role of reduction of sulphate ions for providing the influx of Mg^{+2} ions into carbonate muds, if the Mg^{+2} is combined with SO_4^{-2} in sea-water. A brief account of the related published work is as follows.

BISSELL et al. (1958) stated that diagenetic dolomitization is effective when the calcium carbonate is metastable and is in a realm conducive to replacement. According to these authors Mg^{+2} ions are available in solutions and they occur in certain conditions in the crystal structure of calcite in warm sea-water and, being in a metastable state, this carbonate allows diagenetic change. These authors further mentioned that aragonite - the most metastable phase - can change to dolomite if the Mg^{+2} ions are available during diagenesis. These authors further stated that the influx of Mg^{+2} from the bottom waters into the sediments is possible as a result of decomposition of organic matter by bacteria, with generation of CO_2. As a result of this process, first the alkalinity ($\lneqq HCO_3^- + CO_3^{-2}$) would rapidly increase and then would decrease with the loss of CO_2 from the interstitial water of the sediment; with increasing alkalinity, dolomite could reach saturation state and precipitate.

MATTES and MOUNTJOY (1980), during a study of dolomitization in the Upper Devonian rocks in Alberta, mentioned that deep burial diagenesis provides all the necessary conditions for the formation of dolomite. With the increase of depth, temperature increases and helps to promote the rate of dolomitization. The organic-rich acids present at depth may assist in the mechanism of dolomitization. According to GULLIKSON et al. (1961) and KITANO and HOOD (1965), organic acids present in the sub-surface fluids and brines may enhance dolomite formation at depth. They promote the entry of magnesium into calcite lattices and may promote dolomite formation in a similar fashion, i.e. by dehydrating magnesium through the formation of magnesium/organic acid complexes. MATTES and MOUNTJOY (1980) proposed that the source of fluids for the dolomite in the Miette build-up in Alberta was the shale basin surrounding the Miette build-up.

MAGRA (1976) and KAHLE (1965) stated that, in thick compacting shale sequences, the net direction of water movement is vertically upwards. MATTES and MOUNTJOY (op.cit.) stated that the Mg^{+2} for dolomitization at the Miette build-up was largely derived from the formation fluids.

LAND (1980) stated that large concentration of iron in dolomites seems to be common in association with late phases from the saline formation waters and not with early phases, generally produced under oxidizing conditions. CARPENTER (1980) mentioned that dolomite associated with sandstones generally appears to be more calcic and ferroan than that associated with carbonate rocks. He further stated that water-producing depths should be between 1000 and 5000 metres. According to him these depths ensure a lengthy residence time for water within the rock; it also provides high enough temperature, which increases the probability that rock and water have come to equilibrium.

GEORGE (1977) reported that dolomite cement co-existing in Hosston Formation in central Mississippi contains 56 mole % of $CaCO_3$ and 17 mole % of $FeCO_3$. FOX (1979) mentioned that dolomite cement in Nugget Sandstone in south-western Wyoming is equally calcic and contains 11 mole % of $FeCO_3$.

The descriptions given in the foregoing paragraphs make it clear that sub-surface factors such as formation waters, organic acids, and the general structural controls, play a vital and significant role in the processes related to the dolomitization and formation of diagenetic dolomites in sediments during the burial diagenesis. Therefore it seems reasonable to take into consideration the well established major events of tectonism which caused subsidence and subsequent uplifts (see ARKELL, 1933) in the geological past in southern England. A reconstruction of the palaeo-topographic features of the Oxfordian times in the geological past was essential in order to understand these events. Therefore stratigraphic data obtained from a number of deep boreholes in southern England published in I.G.S. publications was used to reconstruct the probable palaeo-topography that existed during the Oxfordian times, as shown in Figure (1.5), which also shows the locations of some of the boreholes and the palaeo-topographic features and structural controls which have affected the geology of the area (MOORE, 1982, personal communications) during the Oxfordian times. WORSSAM <u>et al.</u> (1971) mentioned the presence of a series of minor faults in the Warlingham Borehole, which are shown in Figure (3.5). These facts suggest the occurrence of a monoclinal structure in the Warlingham area.

For the formation of a diagenetic dolomite in sediments, a somewhat elevated temperature and high Mg^{+2}/Ca^{+2} ratio is required. These conditions may be produced by the pressure of the overburden of sediments and the sub-surface fluids, either in the same sediments in which dolomite is found or in the sediments in the adjacent areas. HANE <u>et al</u>. (1980) stated that the sub-surface temperature was between 40° and 50°C at a depth of 1000 metres in the sediments of southern England. In order to

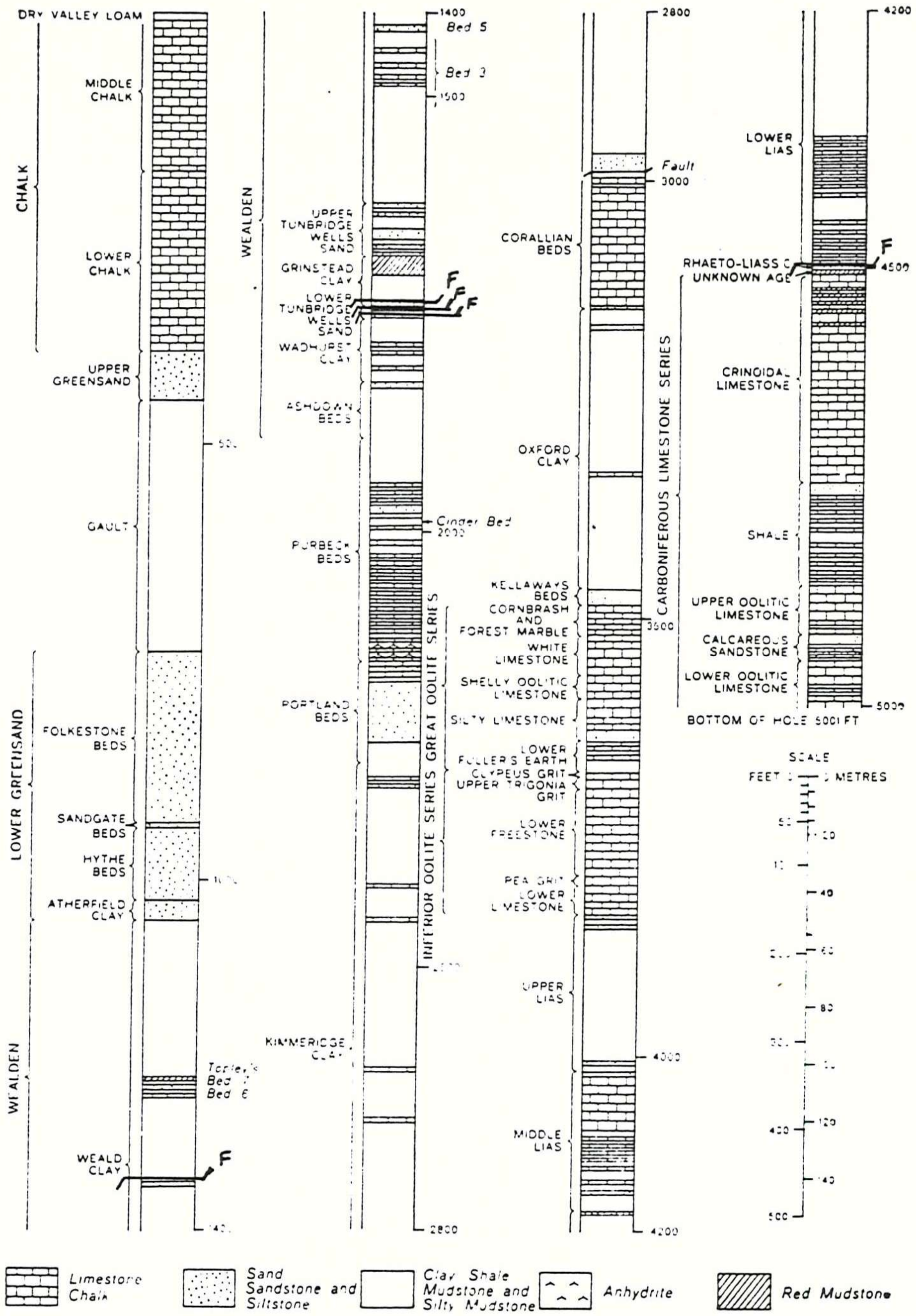


FIG.(3.5). Has been reproduced from WORSSAM and IVIMY-COOK (1971).Faults positions are marked as mentioned by WORSSAM and IVIMY-COOK(op.cit).Faults described at depths of 1725ft.,1728ft.,and 1767ft.,could not be marked in the Log being very closely located.

have some idea regarding the temperature of the Oxford Clay sediments at Warlingham, the overburden was calculated based on the information on borehole data published by the I.G.S.; it hardly exceeds 1123 metres. According to HUNT (1979), this much overburden on Oxford Clay sediments was neither sufficient to cause any diagenetic change in the existing clay minerals, nor was it capable of producing a temperature higher than 50°C. As a matter of interest, COLTER and HAVARD (1981) mentioned the maturity of the Oxford Clay at a depth of approximately 3000 metres in Wytch Farm oil-field in Dorset. This information suggests that the Oxford Clay sediments at Warlingham under 1123 metres overburden were unable to acquire maturity. However, the sediments to the south of Warlingham (for example, at Cowden $>$ 2000 metres thick) in the adjoining Wealden Trough, being much thicker can produce comparatively much higher temperatures up to 100°C. USDOWSKI (1968) mentioned that the average position of equilibrium between calcite and dolomite in the system $Ca^{+2} - Mg^{+2} - CO_3^{-2} - SO_4^{-2} - Cl_2^{-2} - H_2O$ occurs at 80°C and 18 mole % Mg^{+2} ($Mg^{+2}/Ca^{+2} \sim 0{\cdot}13$).

The thick sequence of sediments in the Wealden Trough, according to CARPENTER (1980), may contain formation waters with a lengthy time of residence in sediments. The topographic features of the Warlingham and adjoining areas shown in Figure (1.5) strongly suggest the possibility of a derivation of formation waters (phraetic water) northward from the south. The thick sequence of sediments in the Wealden Trough created high pressures which might have squeezed waters into the less compressed sediments in the Warlingham area. The older sediments, i.e. the Inferior Oolite and Kellaways, being sufficiently porous, might have facilitated the upward flow of fluids (KAHLE, 1965) being supplied from the adjacent sediments to the sediments at the Warlingham site. These fluids were probably rich in Mg^{+2} concentration (BISSELL et al., 1958). MATTES and MOUNTJOY (1980) mentioned that sub-surface fluids commonly have a Mg^{+2}/Ca^{+2} ratio in the range of 0·15 to 0·60 (USDOWSKI, 1968). According to these authors the Alberta sub-surface fluids contain 24 mole% Mg^{+2} ($Mg^{+2}/Ca^{+2} \sim 0{\cdot}19$), which gave rise to the formation of microcrystalline scattered micron-sized clear subhedral crystals of dolomite in the sediments of the Miette build-up, which show a strong resemblance to the subhedral crystals of dolomite in Oxford Clay, shown in Plate (3.5). These authors further stated that, with the increase of temperature, the requirement of Mg^{+2} in solution to attain dolomite stability diminishes.

According to USDOWSKI (1968), the average position of equilibrium between calcite and dolomite at 80°C in the system Ca^{+2} - Mg^{+2} - CO_3^{-2} - SO_4^{-2} - Cl_2^{-2} - H_2O occurs at approximately 18 mole % Mg^{+2}($Mg^{+2}/Ca^{+2} \sim 0{\cdot}13$). MATTES and MOUNTJOY (op.cit.) mentioned that deeply buried sediments contain, at increased temperature, a high and stable Mg^{+2}/Ca^{+2} pore-fluid ratio. It is very possible that the proposed fluids in the case of Warlingham sediments, supplied by the deeply buried sediments of the Wealden Trough, brought similar high stable Mg^{+2}/Ca^{+2} ratio pore-fluids at higher temperatures into the Oxford Clay sediments and thus brought about the formation of dolomite in these sediments. MATTES and MOUNTJOY (1980) mentioned that the micro-sized crystals of dolomite in the Miette build-up contain between 41 and 44 mole % $MgCO_3$. The dolomite in the Oxford Clay also showed 40 and 41 mole % $MgCO_3$ for the two samples. The concentration trends of dolomite with depth in the borehole indicate the lowest abundance in the (K.F.) and highest in the (U.O.C.), which may reflect the controls of the upward flow of fluids and its concentration in the (U.O.C.) sediments. It strongly supports the proposed theory of the upward moving fluids as a source of Mg^{+2} for the formation of dolomite.

The discussions given in the foregoing pages lead to the following conclusions:

(1) The dolomite in the studied sediments is diagenetic in origin (LAND, 1980; MURATA et al., 1972; FRITZ and JACKSON, 1972).

(2) The Mg^{+2} was probably largely supplied by phreatic waters from the thick sedimentary sequence in the adjoining Wealden Trough.

(3) Mixed-layer minerals also might have contributed some Mg^{+2}, either from their lattice position or adsorbed onto their surfaces.

(4) The highest concentration of dolomite in the (U.O.C.) sediments may be due to upward movement of pore fluids, which may cause the increased concentration of dolomite, as suggested by KAHLE (1965).

(5) Some Mg^{+2} may have been provided due to the preferential exchange of K^{+} over Mg^{+2} at exchange sites in clays. It is possible that either this mechanism or the exchange of Ca^{+2} for Mg^{+2} is responsible for the increase of Mg^{+2} in the Upper Oxford Clay, which contains the highest abundances of illite and mixed-layer minerals. The Mg^{+2} concentration shown in Table (7.1A5), noticed in the structural formula of illite for sample BR-468 from the (U.O.C.) in the (W.B.) sediments might be due to the ion exchange mechanism, as mentioned

above.

(6) A very weak genetic relationship exists between dolomite and calcite in the studied sediments, as indicated by a weak positive correlation of the two phases.

(7) Organic carbon might have played some role, in specific cases only, in the supply of Mg^{+2} for the formation of dolomite, as indicated by the sympathetic relationships of C_{org} and dolomite in samples BR-988 and BR-1721, both shown in Appendix (3.2).

An attempt has been made to explain the possible mechanism of dolomite formation in the studied sediments, based on the theory of upward migrating warm phreatic waters. It is suggested that, in order to confirm this theory, more work should be done based on isotopic data and the maturity of organic carbon.

3.8 Conclusions

On the basis of the correlation coefficients, vertical variation and mineral associations, described in the foregoing pages, the conclusions drawn are as follows:

(1) Detrital components such as total clays (illite, kaolinite and chlorite), quartz and organic carbon, have shown enrichment with depth; indicating a greater input of these components at the time of deposition of the sediments of Lower Oxford Clay and Kellaways Formation.

(2) The major part of organic carbon seems to be of detrital origin. It displayed similar trends to those of other detrital components, such as quartz and kaolinite. Terrestrial plants might have contributed a significant proportion to the organic carbon.

(3) Pyrite showed enriched abundances in the (W.K.B.), being the sediments laid down under much stronger reducing conditions than those of the (W.B.). Framboidal pyrite in the (W.B.) sediments is shown in Plate (3.1).

(4) Smectite in the (W.K.B.) sediments seems to be authigenic in origin (air-fall volcanic ash). Mixed-layer minerals in the (W.B.) sediments are probably detrital in origin.

(5) Calcite in the sediments of both boreholes is pure calcite, and was authigenically precipitated.

(6) Dolomite (ferroan) is present only in the (W.B.) samples. It is diagenetic and most probably was formed by phreatic waters supplied by the thick sequence of sediments from the adjacent Wealden Trough sediments.

(7) Some quartz in the (W.K.B.) sediments may be diagenetic in origin. The sediments of the (W.B.) contain only detrital quartz.

(8) Quartz grains in the (W.K.B.) sediments are coarser than those in the (W.B.) sediments, and are not well rounded, as shown in Plate (3.3); and indicate that neither have been transported from distant areas, nor have suffered many cycles of erosion and sedimentation.

(9) The rate of deposition of the sediments, at the time of deposition of the Upper Oxford Clay, was probably high. Either the site of deposition was near the source or the input of sediments was very rapid, which may be due to humid climate or due to tectonism, as mentioned in Chapter One.

(10) The provenance for the (W.K.B.) sediments most probably was to the west of the site of deposition, i.e. the Cornubian Massif. The Armorican Massif to the south might also have contributed significantly. The Cornubian Massif is dominantly composed of igneous and low-grade metamorphic rocks.

(11) The provenance for the (W.B.) sediments most probably was the 'East Anglian Massif' dominantly composed of Palaeozoic sedimentary rocks.

(12) The abundances of non-clay minerals, calculated in the present study, seem to be realistic and satisfactory. They show good agreement in Table (3.3) with the published abundances.

TABLE(3.3): Comparison of the abundances of bulk minerals in the Lower Oxford Clay, in the studied sediments, with those reported by other workers

MINERALS	(1)	(2)	(3)
QUARTZ	24	18	17
CALCITE (P)[5]	01	24	18
CALCITE (M)[6]	02	00	00
DOLOMITE	00	00	04
PYRITE	05	04	02
ORGANIC CARBON	06	04	04
TOTAL CLAYS	57	50	54
PLAGIOCLASE	03	n.d.	n.d.
K. FELDSPAR	02	n.d.	n.d.
GYPSUM(4)	01	00	00
JAROSITE(4)	03	00	00

Note: (1) Average mineral abundances as reported by JACKSON and FOOKES (1974) from Chickerell brick-pit, Dorset.

(2) Average mineral abundances as reported in present study in the Winterborne Kingston Borehole sediments, Dorset.

(3) Average mineral abundances as reported in present study in the Warlingham Borehole sediments, Surrey.

(4) Gypsum and Jarosite, being the products of weathering, have not been encountered in the studied samples, being borehole samples.

(5) Calcite Pure.

(6) Calcite Magnesian.

CHAPTER FOUR

GEOCHEMICAL STUDIES OF THE WHOLE ROCK

Introduction

Major elements, including Si, Ti, Al, Fe(total iron), Mg, Ca, Na, K, S and P, were analysed as oxides % in 63 and 78 samples of the Oxford Clay and Kellaways Formations from the Winterborne Kingston and Warlingham Boreholes, respectively. The samples were prepared as 'raw rock' samples and were analysed by Telsec B-300 Betaprobe, already calibrated by the standards of sedimentary rocks. In addition to these elements, other chemical components, e.g. CO_2, H_2O^+, H_2O^-, Fe^{+2} and organic carbon, were also determined for each sample by following the standard analytical techniques, which are described in Chapter Two (see Chemical Analysis). The results of the chemical analysis of the sediments of both boreholes, with sample numbers and the depth in the borehole, are tabulated in the Appendices (4.1A and 4.2A).

All chemical data, including the concentrations of major, minor and trace elements, CO_2, H_2O^+, Fe^{+2}, Fe^{+3} and organic carbon, of each borehole was punched onto computer cards for processing the data on the University Computer, ICL-2900. The data bearing cards were used for various statistical analyses, e.g. bivariant correlation, R-mode factor analysis. The bivarient correlation programme used was written by CLAYTON (1970); it produced a summary of statistics of the data fed in, a correlation coefficient matrix (r), and regression equations for the Y and X axes respectively. The R-mode factor analysis programme used was that of MATHER (1970), modified by CLAYTON (1970). Briefly, R-mode factor analysis deals with the study of the inter-relationships between variables. Applications and theoretical background of the R-mode factor analysis are described in detail by JÖRESKOG et al. (1976). The R-mode factor analysis programme used extracts the desired number of factors and gives the correlation of R-mode factors.

The summary of the statistics of the data of the two borehole samples and the correlation coefficient (r) matrices are tabulated in the Appendices (4.1B, 4 .2B and 4.1C, 4.2C) respectively. The distribution of major elements, their correlations with other components and geochemical behaviour are described separately for the sediments of each borehole, as follows.

4.1 Geochemistry of Major Elements of the Winterborne Kingston Borehole Sediments

a) Silicon

Silicon occurs in two most common modes of occurrence in these sediments. It occurs as free silica in the form of quartz and as combined silica, mainly located in the clay minerals; occasionally in minor amounts in feldspars. The silica content of the Winterborne Kingston Borehole sediments varies from 25·8 to 47·8%. The average content of 63 samples, on an absolute basis, is 38·97%, and on a carbonate free basis is 55·9%, as is shown in Table (4.3). The highest and lowest concentrations of silica, on a carbonate free basis, are shown by the Upper Oxford Clay (60·14%) and the Lower Oxford Clay (49·29%) respectively, as is shown in Table (4.1A).

The combined silica value can be obtained by deducting the X.R.D. determined amount of free silica, i.e. quartz, from the total amount of silica determined in the bulk-rock by the Betaprobe. The free silica abundance of these sediments varies from 13·6 to 28%. The highest concentration of quartz (23·6%) occurs in the Upper Oxford Clay sediments, as is shown in Table (4.1B). It occurs mainly as angular to sub-hedral grains, suggesting less transportation of these sediments. Chert clasts have also been seen in these sediments.

COUTURE (1977) suggested that the presence of biogenous silica in sediments is indicated by a high Si/Al ratio (4·2) and the presence of terrigenous sediments is indicated by a low Si/Al ratio. The Upper Oxford Clay sediments show the highest Si/Al ratio (4·84), as is shown in Table (4.1C), suggesting the presence of some biogenous/diagenetically precipitated silica in these sediments. The Si/Al ratio in other parts of the Oxford Clay and Kellaways sediments is low, as is shown in Table (4.1C); it ranges from 2·9 - 3·3, suggesting the domination of terrigenous or detrital components in these sediments. The major detrital component of these sediments is clay (illite + kaolinite + chlorite), its highest concentration being in the Lower Oxford Clay (50·3%)

and the Kellaways sediments (56·5%), as is shown in Table (4.1B); supporting the view that in these sediments the silica is also detrital and that the only sediments which may contain biogenous/ diagenetic silica belong to the Upper Oxford Clay. It is worth mentioning here that the Upper Oxford Clay has the highest concentration of smectite (45·2%), as is shown in Table (4.1B); which is probably authigenically produced.

SPEARS (1964) used the free silica/combined silica ratio as a measure of rate of sedimentation. This ratio for the Upper Oxford Clay sediments, as shown in Table (4.1C), is highest (1·84); indicating the comparatively higher rate of sedimentation for these sediments. SPEARS (op.cit.) also used the free silica/Zr ratio as a measure of sorting and rate of sedimentation. The free silica/Zr ratio of the Upper Oxford Clay is also highest (1555·26), which is shown in Table (4.1C), and it supports the views expressed above. The concentration of the detrital components such as quartz (23·6%) and Zr (251 p.p.m.) in the Upper Oxford Clay sediments, which are also shown in Tables (4.1A and 4.1B), further confirms the views expressed above. RONOV (1965) noticed that near-shore sediments contain higher quartz than the basin sediments. The distribution of quartz in these sediments shows its minimum concentration (17·7%) in the Lower Oxford Clay, which is shown in Table (4.1B), indicating that deepest basin conditions existed at the time of deposition of these sediments. The maximum concentration (4·32%) of organic carbon, which is shown in Table (4.1B), in the Lower Oxford Clay also suggests deepest water conditions for the deposition of these sediments.

The correlation coefficient matrix shown in Appendix (4.1C) indicates a very strong positive correlation of silicon, significant at the 0·01% level, with typically lithophile and detrital elements, e.g. Al, Ti, Na, K, Mg, Rb, V, Cr, Ce, Th and Zr. The same correlation coefficient matrix shows very strong positive and negative correlations of silicon, highly significant at the 0·01% level, with depth and detrital component total clays (illite, kaolinite, chlorite), and also with non-detrital components, e.g. Ca, P, Mn, Sr, CO_2, calcite and smectite. These correlations

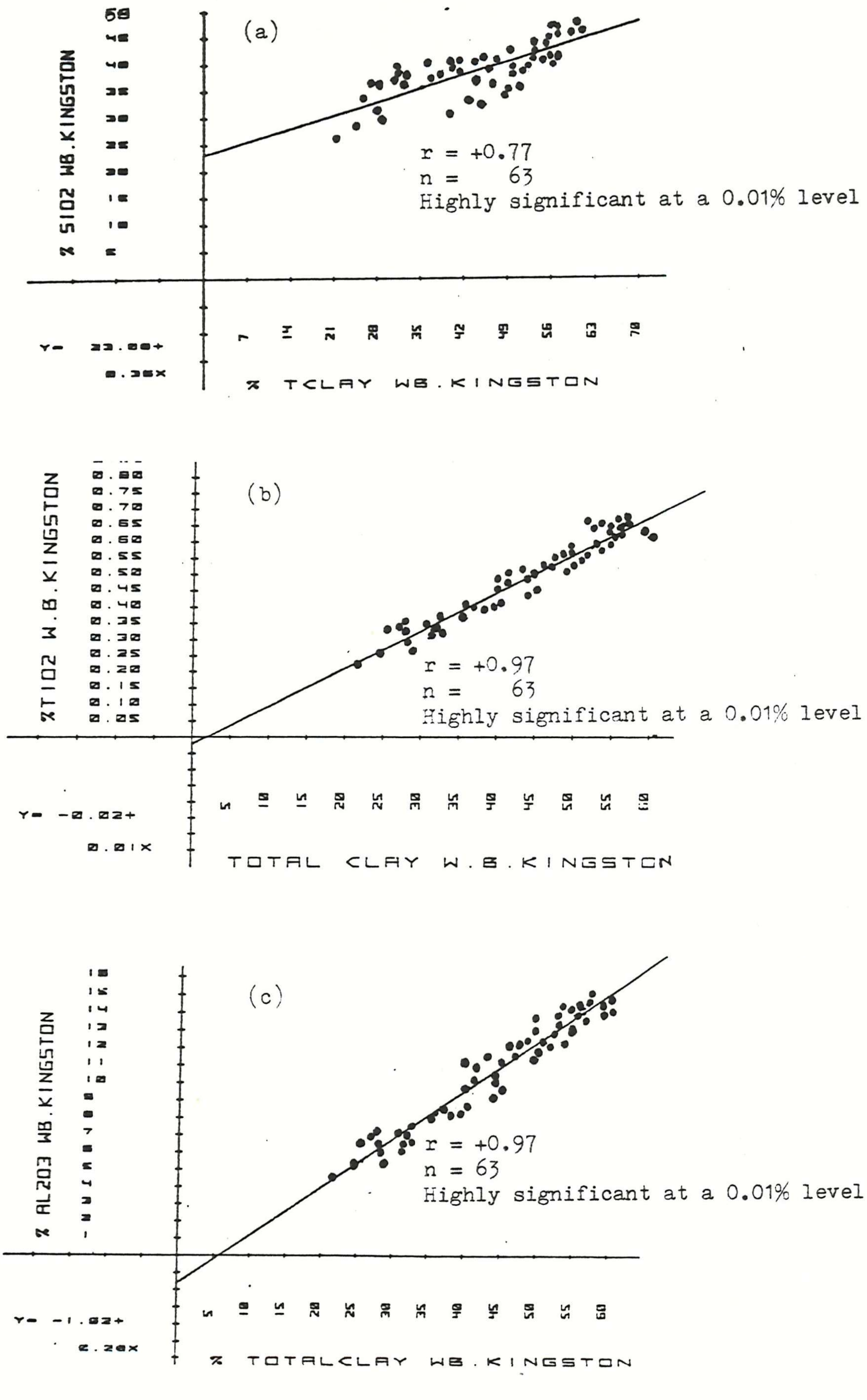

(a)
% SIO2 WB.KINGSTON
50
r = +0.77
n = 63
Highly significant at a 0.01% level
Y= 23.00+
0.36X
7
14
21
28
35
42
49
56
63
70
% TCLAY WB.KINGSTON
(b)
%TIO2 W.B.KINGSTON
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
r = +0.97
n = 63
Highly significant at a 0.01% level
Y= -0.02+
0.01X
5
10
15
20
25
30
35
40
45
50
55
60
TOTAL CLAY W.B.KINGSTON
(c)
% AL2O3 WB.KINGSTON
r = +0.97
n = 63
Highly significant at a 0.01% level
Y= -1.02+
0.28X
5
10
15
20
25
30
35
40
45
50
55
60
% TOTALCLAY WB.KINGSTON

FIG.(4.1)

strongly indicate that silica occurs mainly as combined silica in clay minerals, and free silica in quartz in these sediments. This conclusion is further confirmed by the positive correlation of silica with combined silica ($r = +0{\cdot}95$) and total clays ($r = +0{\cdot}75$), highly significant at an 0·01 level. The strong association of silica with clays is very well illustrated by the Figure (4.1a). This figure shows an intercept of a value of 23·08%, indicating that 23·08% of SiO_2 is not associated with clays. The excessive amount (23·08%) of SiO_2 may be present as mineral quartz, which is abundantly present in every sample. The average value of quartz in these sediments is 20·92%, which is very close to the value of the intercept and therefore justifies the occurrence of the excessive amount of SiO_2.

The abundance of silica in these sediments, see Table (4.3), shows a good agreement with the abundance of silica in sediments and shales reported by other workers.

b) Titanium

The sediments of the Winterborne Kingston Borehole contain variable amounts of TiO_2, which varies from 0·22 - 0·68%. The average contents of 63 samples on an absolute basis and on a carbonate free basis are 0·49% and 0·69% respectively; both average values are shown in Table (4.3). The distribution of TiO_2 in the succession of the Oxford Clay and Kellaways Formations is variable. It showed its lowest (0·59%) and highest (0·77%) concentrations in the Upper Oxford Clay and Kellaways sediments respectively, as is shown in Table (4.1A). There is a gradual increase in the contents of TiO_2, kaolinite and total clays, as is shown in Tables (4.1A) and (4.1B) respectively. The TiO_2 showed a very strong positive correlation with kaolinite ($r = +0{\cdot}84$) and total clays ($r = +0{\cdot}97$); both correlations are highly significant at the 0·01% level of significance. It shows that a strong relationship exists between TiO_2, kaolinite and total clays.

Titanium in sedimentary rocks may occur in heavy minerals such as ilmenite, rutile, anatase, brookite and sphene etc. According to DEGENS (1965), the bulk of TiO_2 in sediments is incorporated in the clay fraction. Its presence in the clay fraction may be due to the interaction of clay minerals with amorphous or finely dispersed crystalline titanium oxide or titanium dioxide (hydrated), released during the weathering. Titanium is thus not only adsorbed onto the clay particles, but occurs in the form of finely disseminated cryptocrystalline TiO_2 needles of one of the polymorphs of TiO_2 (rutile, anatase and brookite). Rutile has been reported from many shale deposits, and anatase from 'Carboniferous fire-clays' in Great Britain (DEGENS, 1965; p.91). SULAIMAN (1972) also reported the presence of rutile in the 'Namurian argillites' of Ireland.

Titanium has been used to indicate the changes in the grain size of the sediments, climatic conditions and also for tracing the provenance of the sediments. SPEARS and KANARIS-SOTIRIOU (1975) used the TiO_2/Al_2O_3 ratio as an indicator of grain size. According to these authors the ratio increases from mudstone - siltstone - sandstone. In the Oxford Clay sediments the highest and lowest TiO_2/Al_2O_3 ratios exist in the Upper Oxford Clay (0·048) and the Lower Oxford Clay (0·044) sediments respectively, suggesting that the sediments of the Lower Oxford Clay are composed of the finest particles and may be classified as mudstones; and the sediments of the Upper Oxford Clay are composed of coarser particles and are more silty. The distribution of detrital components, such as quartz, total clays and Zr, and variations of TiO_2/Al_2O_3 ratios for the stratigraphic succession, are shown in Tables (4.1A, 4.1B and 4.1C); all these support the views expressed above.

COUTER (1977) mentioned that montmorillonite with a high Ti/Al ratio is lowest in acid rocks and highest in basic rocks (see data KRAUSKOPF, 1979). The Upper Oxford Clay sediments showed the maximum concentration of smectite (45·16%) and the highest value of the TiO_2/Al_2O_3 ratio (0·048). This relationship, according to COUTER (op.cit.), suggests that smectite of the Upper Oxford Clay sediments is the alteration product of volcanic material. The variations of mineral abundances and the TiO_2/Al_2O_3 ratios are given in Tables (4.1B and 4.1C).

The TiO_2/Al_2O_3 ratio has been considered as a measure of climate. MIGDISOV (1960) suggested that clays of a humid climate generally contain higher amounts of Ti and Al. The highest concentrations of TiO_2 (0·77%) and Al_2O_3 (17·17%) are present in the Kellaways and the Lower Oxford Clay sediments, as shown in Table (4.1A), which indicate a change in the climatic conditions. EL-SHAHAT (1979) suggested that the higher concentration of Ti in the 'Durlstone Formation' is an indicator of higher rainfall. CHOWDHURY (1980) reported higher concentrations of Ti and Al in the 'Upper Calcareous Grit Group' mud-rocks, and considered it due to the change in climate from tropical-arid to more humid. The Ti/Zr ratio has been considered as an indicator of provenance of the sediments. The Ti/Zr ratios for the different parts of the Oxford Clay and Kellaways Formations sediments are shown in Table (4.1C). The lowest value of Ti/Zr ratio exists in the Upper Oxford Clay sediments, indicating a different provenance for these sediments.

The correlation coefficient matrix in Appendix (4.1C) shows a very strong positive correlation of TiO_2, significant at the 0·01% level with depth, Al, K, Mg, Na, Si, V, Cr, Ni, Th, Cu, Rb, Ce, Nb and total clays. These relationships suggest that TiO_2 occurs with total clays, a conclusion confirmed by Figure (4.1b), in which TiO_2 values are plotted against the abundances of total clays for 62 samples. The graph shows the value of correlation coefficient ($r = +0{\cdot}97$) significant (at an 0·01% level). The hydroxylamine hydrochloride and acetic acid leaching study also supports this view. Carbonate corrected values of TiO_2 have been compared with the TiO_2 concentration in the leached residue; in most of the cases both results agree. TiO_2 also occurs in the form of 'anatase', as can be seen from the prominent anatase peak at $25{\cdot}37^{\circ},2\theta$ in the X.R.D. Diffractogram, which is shown in Figure (4.1d). The sample, before running on the X.R.D., was heated for ½ hour at 600°C, as suggested by BRINDLEY et al. (1947), to destroy the kaolinite, in order to get the anatase peak. SULAIMAN (1972) followed this technique and identified anatase in the Namurian argellite. The abundance of TiO_2 in the Winterborne Kingston Borehole sediments is compared with the TiO_2 abundances reported by other workers, in Table (4.3).

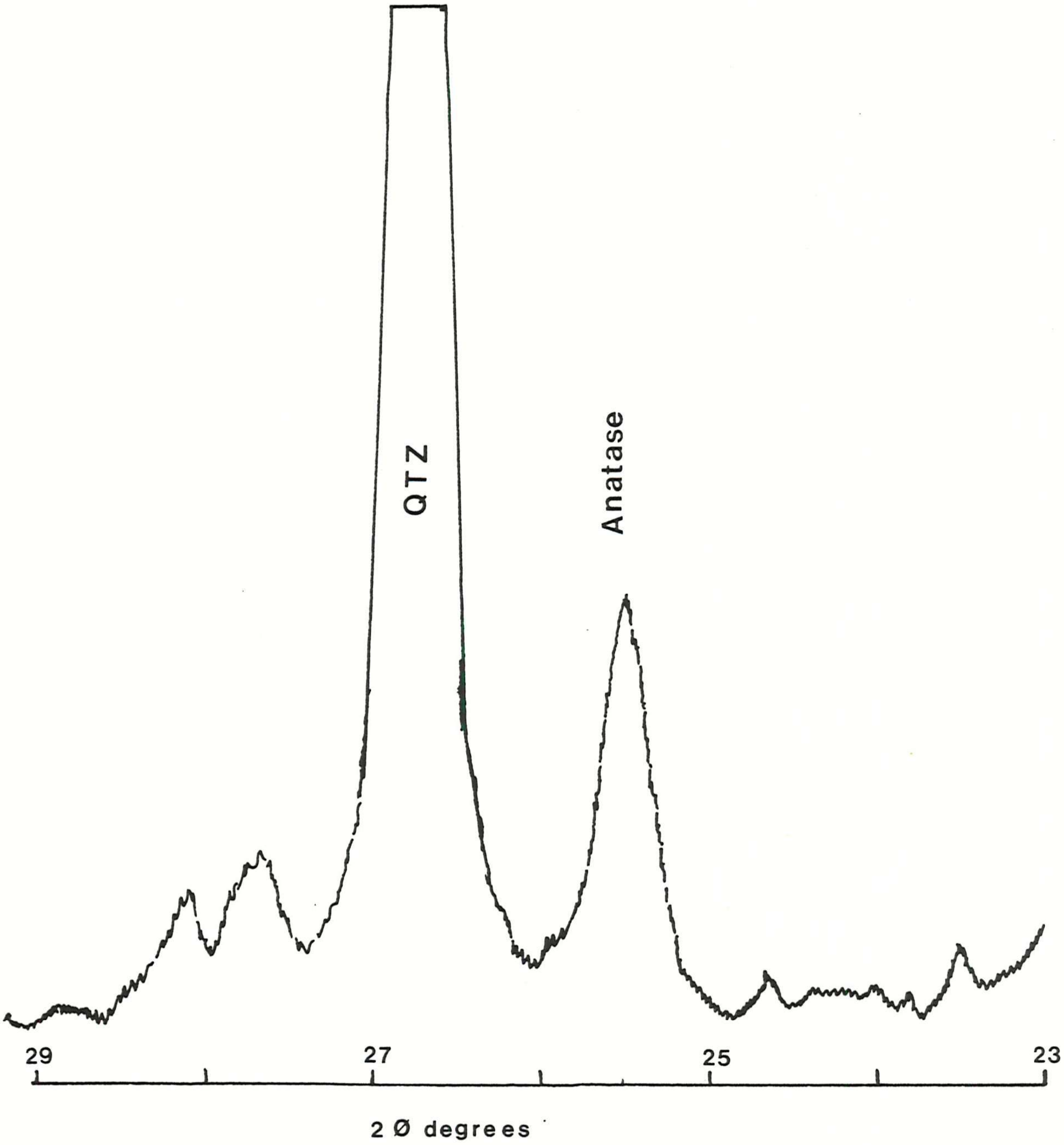


FIG.(4.1d): Anatase peak at 25·4°,2θ in sample WBK-63. Before running on X.R.D. the sample was heated for ½ hour at 600°C to destroy kaolinite, as suggested by BRINDLEY et al. (1947).

c) Aluminium

The alumina contents of the Winterborne Kingston Borehole sediments varies from 4·55% to 15·08%. The average contents of Al_2O_3 of 63 samples on an absolute basis and a carbonate free basis are 10·73% and 15·26% respectively; both values are shown in Table (4.3). The abundance of Al_2O_3 is variable in the sequence of the sediments. The lowest concentration (7·53%) is in the Upper Oxford Clay sediments and the highest concentration is shown by the Lower Oxford Clay sediments (14·21%). The distribution of Al_2O_3 in the sediments is shown in Table (4.1A); it seems to be controlled by the contents of total clays and also species of the clay minerals. Montmorillonite generally contains a lesser amount of Al in comparison with illite and kaolinite. The depleted amount (7·53%) of Al_2O_3 in the sediments of the Upper Oxford Clay is the result of the highest and lowest concentrations of smectite (15·02%) and total clays (33·3%) respectively.

As the content of Al_2O_3 in sediments indicates the abundance of the total clays, the expected good agreement between the calculated abundances of total clays, shown in Table (4.1B), and the concentrations of Al_2O_3, shown in Table (4.1A), is found. The sediments of the Kellaways Formation show the highest abundances of total clays (56·5%) and Al_2O_3 (17·16%). The abundances of Al_2O_3 and total clays in different parts of the Oxford Clay and Kellaways Formations are shown in Tables (4.1A) and (4.1B) respectively.

The lowest and highest values of the Al_2O_3/SiO_2 ratios are noticed in the sediments of the Upper Oxford Clay (0·206) and the Lower Oxford Clay (0·342) respectively, which suggest the highest concentration of total clay minerals in the Lower Oxford Clay; which agrees with the calculated abundances of the clay mineral species shown in Table (4.1B). The variations of the Al_2O_3/SiO_2 ratios are shown in Table (4.1C).

PETTIJOHN (1957) used the Al_2O_3/Na_2O ratio as a measure of maturity index of the sediments. The higher the ratio, the more mature are the sediments. The lowest value of this ratio (16·4) exists in the Upper Oxford Clay and the highest in the sediments of the Kellaways

Formation (23·7), suggesting that the sediments of the Upper Oxford Clay are the less mature. This supports the view that the Upper Oxford Clay sediments are composed of less transported material. The Al_2O_3/combined SiO_2 ratio in Table (4.1C) shows a vertical variation. The lowest ratio (0·34) exists in the Upper Oxford Clay sediments. This ratio in other parts of the sequence is fairly uniform, as is shown in Table (4.1C).

The alumina and silica are the two important components of the clay minerals. SPEARS (1964) used the Al_2O_3/combined SiO_2 ratio to express the composition of the clay minerals present in the sediments studied by him. He did not notice any systematic change in the ratio through the studied sequence, to which he attributed that this ratio was fixed prior to the sediment entering the basin of deposition, and hence during the weathering of the source rock.

The Al_2O_3/combined SiO_2 ratio of bulk chemistry in some cases may give misleading conclusions. Many factors, such as the values of Al_2O_3, combined SiO_2, and the presence of other minerals in the bulk rock may be responsible. The ratio in the present study is calculated by using the values of Al_2O_3 and combined SiO_2. The Al_2O_3 and SiO_2 values are very precise, being determined by Betaprobe. The values of combined SiO_2 are obtained by the difference of total SiO_2 and the abundances of quartz determined by X.R.D., semi-quantitatively. The estimation of quartz by X.R.D. in quartz-rich sediments (e.g. Kellaways sediments of Warlingham Borehole) may not be satisfactory. Therefore the amount of combined SiO_2 thus obtained, which mainly represents the composition of clay minerals, may not be true. If such values of Al_2O_3 and combined SiO_2 are used, the ratios will be misleading. Sediments studied by SPEARS (1964) did not contain high amounts of quartz or carbonate minerals. Therefore the Al_2O_3/combined SiO_2 ratios he used may be realistic to express the composition of the clay minerals.

The sediments of the Oxford Clay and Kellaways Formations, particularly from the Warlingham area, contain comparatively higher amounts of quartz and carbonate minerals, which have caused the dilution effects on the chemical elements present in these sediments. The values of SiO_2, Al_2O_3 and quartz obtained in the bulk analysis may not be suitable for the calculation of Al_2O_3/combined SiO_2 ratio. In view of these problems, it seems appropriate to study the Al_2O_3/SiO_2 ratio of the clay fraction chemistry; free from the undesirable effects of other minerals. This ratio is considered a better and a valid indicator of the composition of clay minerals. The lowest value of this ratio (0·38) is exhibited by the sediments of the Upper Oxford Clay. Other parts of the Oxford Clay and Kellaways Formation show similar trend of the ratio, being higher values in each case. The values of the ratio are shown in Table (4.1C). The average value of the ratio in Kellaways and Lower/Upper Oxford Clay sediments is 0·44, higher than the value in the Upper Oxford Clay. This difference of the ratio suggests that the major component of clay minerals present in the Upper Oxford Clay is probably derived from a different source.

The lowest content of Al_2O_3 in the montmorillonite-rich sediments of the Upper Oxford Clay suggests that, during the formation of montmorillonitic mixed layer clay minerals, the availability of 'Al' from other sources such as transported colloidal material was probably lowest.

The higher Al_2O_3 content of Kellaways and Lower Oxford Clay sediments shown in Table (4.1A) suggests that these sediments contain greater amounts of detrital clay minerals, which is true, as can be seen from Table (4.1B). The higher concentration of 'Al' may also suggest that the chemical weathering in the source rock area was more intensive during that time. It also indicates that these sediments contain greater percentages of fresh detrital clays (formed simultaneously by weathering on the source land; which is also indicated by the higher amounts of illite,mixed-layer clay minerals).

The correlation coefficient in Appendix (4.1C) shows a very strong positive correlation of Al_2O_3 at the 0·01% level of significance with components, depth, SiO_2, TiO_2, MgO, K_2O, Na_2O, V, Cr, Ni, Ba, Rb, Ce, Th, Cu, Nb, $C_{org.}$ and H_2O. The Al_2O_3 also shows a strong positive correlation (at an 0·1% confidence level) with total Fe_2O_3, La,and a weak positive correlation (at a 1·0% confidence level) with Zr ($r = +0·39$), Mo ($r = +0·33$). It shows a strong negative correlation (at an 0·01% confidence level) with non-detrital components, including calcite, smectite CaO and also with Mn.

All these correlations suggest that in these sediments 'Al' is strongly associated with the lattice-held fraction, i.e. clay minerals. The strong positive correlation of Al_2O_3 with total clays is illustrated by Figure (4.1c). The strong positive correlation with K_2O (r = +0·98), TiO_2 (r = +0·99), Rb (r = +0·96), V (r = +0·93) and Cr (r = +0·87) also confirms this statement. Its strong negative correlation with non-detrital components, e.g. CaO, Mn, calcite, etc. further confirms this result. The acetic acid and hydroxylamine hydrochloride leaching (CHESTER et al., 1967) results also show that 96% of the total 'Al' is located in the lattice-held fraction of these sediments. The lattice-held fraction is composed dominantly of clay minerals. WEAVER and POLLARD (1973) suggested that 'Al' is located in crystal lattices of the clay minerals (in tetrahedral and octahedral positions). The Figure (4.1c) confirms that most of the 'Al' occurs in total clays.

The abundance of Al_2O_3 in these sediments shows good agreement with the abundances of Al_2O_3 reported by other workers, in shale and sediments, which are shown in Table (4.3).

d) Iron

The abundance of total iron (Fe_2O_3) in the Winterborne Kingston Borehole sediments varies from 3·63% - 7·91%. The average contents of Fe_2O_3 of 63 samples, on an absolute basis, is 5·28% and on a carbonate free basis 7·59%. In the studied samples Fe_2O_3 occurs in sulphide minerals, particularly in pyrite (FeS_2); it also occurs in the lattices of the clay minerals, as free Fe_2O_3 in the form of oxides/hydroxides (amorphous Fe_2O_3) coated on the surfaces of the clay minerals and other detrital components. Some iron is also associated with organic carbon (r = +0·38). WEAVER and POLLARD (1973) have mentioned that iron occurs in the octahedral position of illite, smectite and chlorite. It seems appropriate to split up the total Fe_2O_3 into the iron associated with pyrite as Fe_2O, and the iron associated with clays and other phases. The iron which is not associated with pyrite may be termed residual or non-pyrite Fe_2O_3.

The distribution of the total Fe_2O_3 in the different parts of the sequence is variable, as is shown in Table (4.1A). The Lower Oxford Clay shows the highest concentration (5·72%), while the Upper Oxford Clay contains the lowest (4·70%) amount of Fe_2O_3. The Lower Oxford Clay also shows the highest contents of pyrite (FeS_2), which may be the reason for the higher concentration of Fe_2O_3. The abundances of pyrite are shown in Table (4.1B).

The Winterborne Kingston Borehole sediments contain higher amounts of pyrite as compared to the Warlingham Borehole sediments, and therefore show greater concentrations of Fe_2O_3. The enrichment of Fe_2O_3 in sediments may be due to changes in weathering conditions in the source area; more intense chemical weathering is related to the enrichment of Fe_2O_3 content in sediments. The abundance of Fe_2O_3 in sediments may also be controlled either by different suites of clay minerals or the presence of free iron-oxide/hydroxide, coating the grains of detrital components and clay minerals.

HIRST (1962), SPEARS (1964) and CALVERT (1978) used the Fe_2O_3/Al_2O_3 ratio as an indicator of association of iron with clay minerals. The highest Fe_2O_3/Al_2O_3 ratio (0·62) exists in the sediments of the Upper Oxford Clay. This ratio shows a decreasing trend in the sequence along the depth, as is shown in Table (4.1C). The lowest ratio (0·37) is exhibited by the sediments of the Lower Oxford Clay. This trend of the ratio suggests that the strongest association of Fe_2O_3 with clay exists in the Upper Oxford Clay sediments, and the weakest in the Lower Oxford Clay sediments, which show the highest contents of pyrite, as is shown in Table (4.1B).

The Mn/Fe ratio in the geochemical studies of sedimentary rocks has been studied by many workers, including GOLDSCHMIDT (1937), WEDEPOHL (1967), NICHOLLS & LORING (1962), SPEARS (1964) and SULAIMAN (1972). This ratio has been used as an indicator of the depositional environments in terms of prevailing Eh and pH conditions. SULAIMAN (1972) found the lowest value of Mn/Fe ratio (0·012) in the near-shore sediments rich in kaolinite contents, and the highest value of this ratio (0.019) in the off-shore sediments.

SULAIMAN (op.cit.) suggested that the leaching process is responsible for the low ratio. Leaching processes could take place at the time of deposition where the 'Eh' is reducing and the 'pH' is acidic. Under these conditions Mn and Fe will be easily removed (Mn^{+2} and Fe^{+2} are the mobile valancies in the two elements). The following factors may influence the Mn/Fe ratio.

1) A low Mn/Fe ratio may indicate selective leaching of manganese during reduction in Eh and pH. The Mn/Fe lowest ratio (0·009) is exhibited by the sediments of the Kellaways and Lower Oxford Clay, which have already shown the existence of the leaching process, by the study of Al_2O_3/Na_2O ratio, and enrichment of these sediments in the contents of titanium and kaolinite. The variations of Mn/Fe and Al_2O_3/Na_2O ratios and abundances of minerals are shown in Tables (4.1C) and (4.1B).

2) Manganese may be enriched in sediments in relation to iron, due to the higher contents of carbonates. In calcite the replacement of Ca^{+2} by Mn^{+2} takes place more easily than the substitution of Ca^{+2} by Fe^{+2}, due to smaller difference in the ionic size between Mn^{+2} (0·91Å), Ca^{+2} (1·08Å) and Fe^{+2} (0·86Å), as suggested by RANKAMA and SAHAMA (1950).

MARSTON (1967) suggested that the total iron contents of sediments doubles when carbonate minerals appear and the Mn content increases by a much greater factor; thus the Mn/Fe ratio for the carbonate rich rocks of the Upper Oxford Clay is highest (0·016) as compared to the sediments of the Lower Oxford Clay or Kellaways (0·009). The comparison of the Mn/Fe ratio is given in Table (4.1C). The sample WBK09 contains the highest Mn (647 p.p.m.) and CaO (30·05%), and belongs to the Upper Oxford Clay sediment.

The Mn shows a very strong positive correlation with calcite (r = +0·81) and smectite (r = +0·68), which suggests that the replacement of Ca^{+2} by Mn^{+2} has taken place in calcite and smectite.

The correlation matrix in the Appendix (4.1C) of the total population of samples showed a very strong positive correlation (at an 0·01% level) of FeO with S, P_2O_5, Cu, Mo, Pb, Ni, Zn, C_{org}, kaolinite and pyrite, indicating its very strong association with the sulphide phase present in the sediments. The sulphide phase exists in reducing conditions; organic carbon and kaolinite in these sediments facilitated the development of anoxic conditions and pyrite (FeS_2) was produced, which is present in each and every sample.

The residual Fe_2O_3 showed a very strong positive correlation (at an 0·01% level) with Mg, V, Zr, and a medium strong positive correlation (at 1-5% level) with Si, Ti, Al, K, Cr, Rb and total clays. This indicates that the residual Fe_2O_3 in the total population of the sediments is associated with clay minerals. Among the clay mineral species, chlorite showed the strongest positive correlation ($r = +0{\cdot}28$) with residual Fe_2O_3.

According to WEAVER and POLLARD (1973) it was thought that the Fe_2O_3 in chlorites was the result of secondary oxidation of FeO. FOSTER (see WEAVER and POLLARD, 1973; p.88) found that in many chlorites much of the Fe^{+3} was necessary to maintain a charge balance. The conversion of OH^- to O^{2-} is necessary for the conversion of Fe^{+2} to Fe^{+3}. FOSTER (op.cit.) found no relation between Fe_2O_3 and O content in excess of 10·0 ions per half cell, and concluded that Fe_2O_3 is a normal constituent of many chlorites. The very strong positive correlation of residual Fe_2O_3 with Mg-V may be due to its strong correlation with chlorite.

The correlation matrix of the Upper Oxford Clay samples showed a very strong positive correlation (at an 0·01% level) of residual Fe_2O_3 with depth, Ti, Al Mg, K, V, Ni, Ba, Rb, H_2O, Si, Cr, Ce, Nb, C_{org} and also with kaolinite, chlorite and total clays. The correlations with calcite and smectite are strongly negative (at an 0·01% level). These correlations indicate that the residual Fe_2O_3 in the Upper Oxford Clay sediments is strongly associated with total clays ($r = +0{\cdot}66$). The strongest positive correlation with kaolinite ($r = +0{\cdot}76$) suggests that some of the residual iron is present as a coating of amorphous iron oxides/hydroxides on the surface of kaolinite grains in these sediments.

The correlation of total Fe_2O_3 in the total population with Al ($r = +0{\cdot}42$), Ti ($r = +0{\cdot}41$), Mg ($r = +0{\cdot}36$), K ($r = +0{\cdot}38$), Cr (r = +0·25), Rb (r = +0·29) and total clays (r = +0·43), as shown in the Appendix (4.1C), suggest that clays, on the whole, do not have a stronger association with Fe_2O_3. On the other hand, the very strong positive correlation of total Fe_2O_3 with depth, Ni, Cu, FeO, H_2O and pyrite suggest that the distribution of iron is dominantly controlled by sulphides. Pyrite is present throughout the sequence which supports this thesis.

The Fe^{+3}/Fe^{+2} ratio shown in Table (4.1C) gives an indication of the redox potential. The highest Fe^{+3}/Fe^{+2} ratio (2·041) has been noticed in the sediments of the Upper Oxford Clay and the lowest ratio (1·058) in the Lower Oxford Clay. This variation of Fe^{+3}/Fe^{+2} ratio suggests that sediments of the Lower Oxford Clay faced the stronger reducing (anoxic) conditions; these sediments show the enrichment of the contents of pyrite and organic carbon, which confirms the above view. The Upper Oxford Clay sediments either experienced some oxidation or the addition of iron oxides as an independent detrital phase took place at the time of the deposition.

The clay fraction chemistry also provides similar results. The Fe^{+3}/Fe^{+2} ratio of the Upper Oxford Clay samples is highest (0·29) as compared to other parts in which the ratio is constant but lower (0·24) than the value of the Upper Oxford clay samples.

This study confirms that in the sediments of the Upper Oxford Clay either the clay minerals have the stronger association with Fe_2O_3 in their lattices or the iron is present as amorphous Fe_2O_3 in the form of oxides/hydroxides, coating the surfaces of the detrital clay minerals. The very strong positive correlation (at an 0·01% level) of detrital clay minerals (kaolinite, illite and chlorite) with Fe_2O_3 in the Upper Oxford Clay sediments supports the idea of the presence of oxides/hydroxides of iron in these sediments.

The contents of total Fe_2O_3 have been plotted against the concentrations of total clay in Figure (4.2a) and with pyrite in Figure (4.2b). From these Figures it is evident that a stronger correlation of Fe_2O_3 exists with pyrite as compared to total clays. The distribution of total Fe_2O_3 in phases like pyrite, total clays,

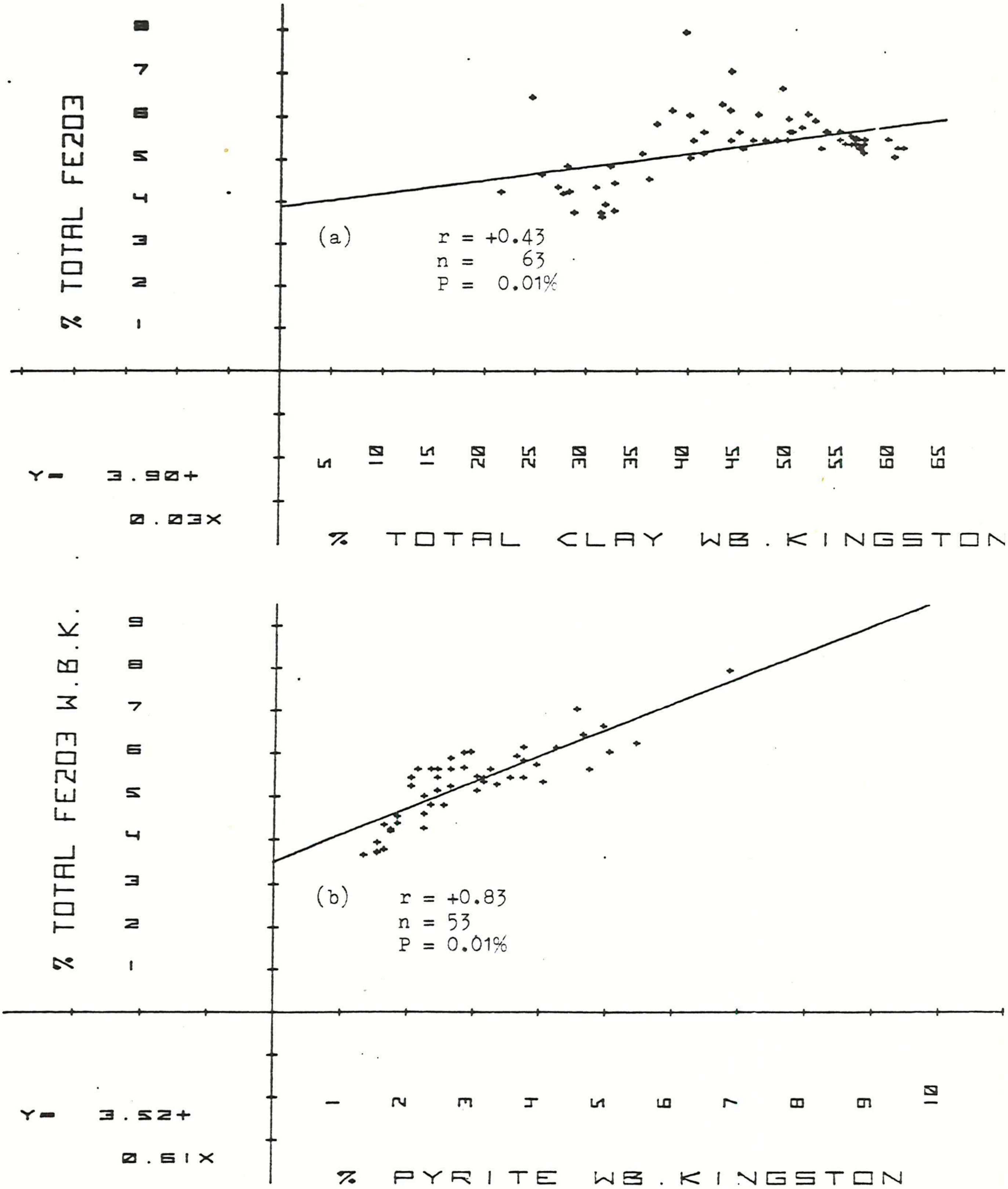

% TOTAL FE2O3
1
2
3
4
5
6
7
8
(a)
r = +0.43
n = 63
P = 0.01%
Y= 3.90+
0.03X
5
10
15
20
25
30
35
40
45
50
55
60
65
% TOTAL CLAY WB.KINGSTON
% TOTAL FE2O3 W.B.K.
1
2
3
4
5
6
7
8
9
(b)
r = +0.83
n = 53
P = 0.01%
Y= 3.52+
0.61X
1
2
3
4
5
6
7
8
9
10
% PYRITE WB.KINGSTON

FIG.(4.2)

organic carbon and free oxides of Fe^{+3} can be roughly calculated as mentioned below:

1) Average contents of Fe_2O_3(total) in bulk rock = 5·28%
2) " " " FeO " " " = 1·90%
3) " " " true Fe_2O_3 " " " = 3·16%
4) " " " total Fe_2O_3 in clay fraction = 5·14%

The plots of Fe_2O_3% - pyrite% in Figure (4.2b) and Fe_2O_3% - total clays % in Figure (4.2a) show the regression equations mentioned below:

$$(\%\ Fe_2O_3)\ Y = 3{\cdot}52 + 0{\cdot}61\ X\ (\%\ \text{pyrite}) \quad - - - - - \quad (1)$$

$$(\%\ Fe_2O_3)\ Y = 3{\cdot}90 + 0{\cdot}03\ X\ (\%\ \text{total clays}) \quad - - - \quad (2)$$

The regression equation No.(1) shows an intercept of 3·52, indicating that 3·52% Fe_2O_3 of the total Fe_2O_3 contents is not associated with pyrite. Therefore pyrite associated Fe_2O_3 may be obtained by subtracting this value from the total amount of total Fe_2O_3 (5·28%). Therefore the pyrite associated Fe_2O_3 will be = 1·76% $\equiv$ 1·58% FeO.

From regression equation No.(2) in a similar manner the fraction of Fe_2O_3 associated with total clays can be obtained. The value of intercept is 3·90, which actually is the amount of Fe_2O_3 not associated with total clays. Therefore the amount of Fe_2O_3 associated with total clays will be = 1·38% (5·28 - 3·90 = 1·38%).

The calculated amounts of Fe_2O_3 in pyrite and total clays give a total of 3·14% (1·76 + 1·38 = 3·14%). The bulk rock contains an average of 5·28% of the total Fe_2O_3 of which 3·14% is found to be associated with pyrite and total clay phases of the sediments. The remaining 2·14% (i.e. 5·28 - 3·14 = 2·14%) of Fe_2O_3 should be associated with other phases, such as amorphous Fe^{+3} oxides/hydroxides associated with clays and Fe^{+2} associated with organic carbon.

The amounts of Fe^{+3} associated as free oxides with clays and Fe^{+2} associated as ferrous iron with organic carbon may be calculated as follows:

1) Average contents of total clays = 44·2%
2) " " " " Fe_2O_3 in clay fraction = 5·14%

$\therefore$ The contents of Fe_2O_3 in
44·2% total clays will be $= \frac{5 \cdot 14}{100} \times 44 \cdot 2 = 2 \cdot 27\%$ Fe_2O_3.

The calculated Fe_2O_3 associated with total clays by the regression equation No.(2) is 1·38%. But the calculated amount of Fe_2O_3 in 44·2% total clays is 2·27%. Therefore the remaining amount of Fe_2O_3, i.e. 0·89% (2·27 - 1·38 = 0·89%) may be associated with clays as oxides/hydroxides of Fe^{+3}.

The amount of Fe^{+2} associated with pyrite is known from regression equation No.(1). Therefore the amount of Fe^{+2} associated with organic carbon can be calculated as shown below:

1) The average contents of FeO = 1·90%
2) " " " " " in pyrite = 1·58%

The additional FeO, i.e. 0·32% (1·90 - 1·58 = 0·32%) may be associated with organic carbon.

The distribution of total Fe_2O_3 in various phases of the sediments may be summarized as under:

1) Fe_2O_3 associated with pyrite contents = 1·76%
2) " " " total clay contents = 1·38%
3) " " " " " as Fe^{+3} = 0·89%
4) " " " organic carbon as Fe^{+2} = 0·36%
Total = 4·39%

These distributions of Fe_2O_3 show good agreement with the correlation coefficient in these phases. The correlation coefficients of Fe_2O_3 with pyrite ($r = +0 \cdot 82$), total clays ($r = +0 \cdot 43$) and organic carbon ($r = +0 \cdot 38$).

The total value of 4·39% of Fe_2O_3 should agree with the original determined total Fe as Fe_2O_3 value in the bulk rock analysis (5·28%) The error (0·89%; < 16%) is not regarded as excessive in view of the many inherent analytical and statistical errors in the procedure. In particular, it should be remembered that the total clay determination can only be regarded as semi-quantitative. The abundances of Fe_2O_3 are compared with the reported abundances of Fe_2O_3 in sediments by other workers, in Table (4.3).

e) Magnesium

The MgO distribution in the Winterborne Kingston sediments shows a range of 0·70% to 1·48%. The average contents of MgO of 63 samples on an absolute basis is 1·12% and on a carbonate free basis is 1·59%. The distribution of MgO in different parts of the Oxford Clay is given in Table (4.1A); it shows its highest concentration (1·27%) in the Middle Oxford Clay and the lowest (0·97%) in the Upper division. The Upper Oxford Clay contains the lowest amounts of illite (42·6%) and chlorite (1·63%), but the concentration of smectite is highest (19·24%). Table (4.1B) shows the abundances of minerals. By the distribution trends of clay minerals and MgO in the various divisions of the Oxford Clay, it appears that it is controlled by the clay minerals, e.g. illite and chlorite.

The MgO/Al_2O_3 ratios given in Table (4.1C) may indicate the composition or the abundance of clay minerals (SPEARS, 1964). The Mg/Al higher ratio indicates the presence of montmorillonite. The highest ratio (0·147) in these sediments exists in the Upper Oxford Clay, which also has the highest concentration of smectite (montmorillonite/illite). The lowest ratio (0·099) is seen in the sediments of the Kellaways Formation, which contain the lowest amount of smectite (the montmorillonite component in the mixed-layer mineral is lowest). The highest value of MgO/Al_2O_3 ratio of the Upper Oxford Clay sediments indicates not only the enrichment of smectite and domination of montmorillonitic component in it, but also suggests a very strong relationship with smectite. The variations of the MgO/Al_2O_3 ratios and mineral abundances are given in Tables (4.1C) and (4.1B). Montmorillonite in its inter-layer position may accept Mg^{+2} to compensate for the excess of the charge on the octahedral layers. DEER et al. (1962), HIRST (1962) have noticed up to 3% MgO contents in the chemical analysis of montmorillonite. Mg^{+2} also replaces Al^{+3} in the octahedral layers of illite (DEER et al., 1962). This is illustrated in Tables (4.1A and 4.1B), which show the distribution of MgO, illite, smectite and chlorite in the Kellaways sediments. Although the MgO/Al_2O_3 ratio in these sediments is poorest, the 'MgO' contents are not lowest, which suggests that Mg^{+2} in these sediments is associated with illite and chlorite.

The correlation coefficient matrix given in the Appendix (4.1C) shows a very strong positive correlation (at an 0·01% level) of MgO with depth, Si, Ti, Al, K, V, Cr, Ni, Ba, Rb, H_2O, illite (r = +0·74), kaolinite (r = +0·66), chlorite (r = +0·64) and total clays (r = +0·83), suggesting that in these sediments the entire amount of MgO is present in the clay minerals. The MgO shows a very strong negative correlation (at an 0·01% level) with Ca, P, Mn and calcite, indicating that the carbonate phase of these sediments does not contain any amount of MgO.

The stronger positive correlation of MgO with illite (r = +0·74) in comparison with other clay minerals suggests that in illite the Mg^{+2} has replaced Al^{+3} in the octahedral layers, as described by DEER et al. (1962). The clay minerals' chemical data of 12 samples shows a very strong positive correlation of MgO with smectite (r = +0·72), indicating that in the inter-layer position of smectite the Mg^{+2} was accepted for the excess of the charge on the octahedral layers.

The MgO showed a very strong positive correlation with illite (r = +0·74) and total clays (r = +0·82). The illite component is highest (28·10%) in the total clays, as is shown in Table (4.1B). The plots of MgO% against the contents of total clays and MgO concentrations against chlorite % are shown in Figure (4.3a & b), and show a very good correlation of MgO with these components. This correlation suggests that a significant amount of total MgO resides in chlorite and illite in these sediments. The chlorite associated amount of MgO may be calculated from the regression equation for MgO-chlorite, which is mentioned below:

$$(\%\ \text{MgO})\ Y = +0{\cdot}92 + 0{\cdot}06\ X\ (\%\ \text{chlorite}).$$

From this regression, it is clear that 0·92% of MgO (the value of the intercept) is the amount of MgO which is not associated with chlorite and resides in other clay minerals. The amount of MgO associated with chlorite may be obtained by subtracting the non-associated amount of MgO, 0·92% (i.e. the value of the intercept) from the average total amount of MgO, 1·59%. Therefore the chlorite associated MgO will be 0·67% (1·59 - 0·92 = 0·67% MgO). The remaining amount of MgO, i.e. 0·92%, is associated with other clay mineral

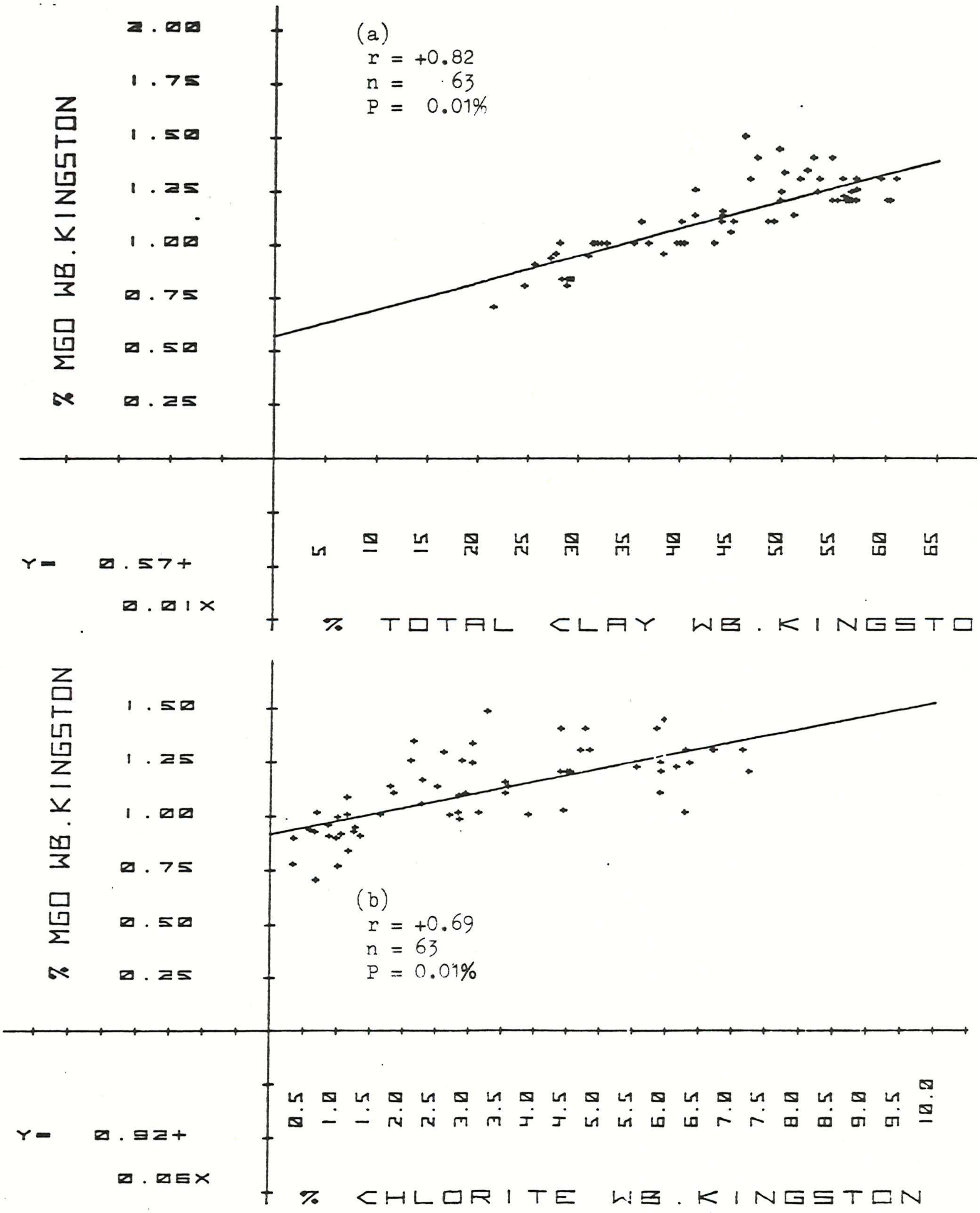

(a)
r = +0.82
n = 63
P = 0.01%
% MGO WB.KINGSTON
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
5
10
15
20
25
30
35
40
45
50
55
60
65
Y= 0.57+
0.01X
% TOTAL CLAY WB.KINGSTO
(b)
r = +0.69
n = 63
P = 0.01%
% MGO WB.KINGSTON
1.50
1.25
1.00
0.75
0.50
0.25
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
Y= 0.92+
0.06X
% CHLORITE WB.KINGSTON

FIG.(4.3)

species, including illite, smectite, etc.

This distribution of MgO is in accordance with the levels of correlations of MgO with clay mineral species already described. The abundance of MgO in these sediments is compared in Table (4.3) with the MgO abundances in sediments reported by other workers.

f) Calcium and Carbon Dioxide

The CaO contents of the Winterborne Kingston Borehole sediments vary from 10•23 to 30•05%. The average contents of 63 samples is 17•54%, which is higher when compared to the contents of the Warlingham Borehole sediments (15•12%). Comparison of the abundance of CaO in the Oxford Clay and other sediments is given in Table (4.3). The Winterborne Kingston Borehole sediments contain an average of 27•19% of total carbonates, which is not much higher than the total carbonate content (26•60%) of the Warlingham Borehole sediments. The big difference in the bulk mineralogy is the abundance of clay mineral species. The Winterborne Kingston Borehole sediments contain abundant amounts of smectite (montmorillonite-illite) as compared to the Warlingham Borehole sediments, which contain mixed-layer minerals having the lowest amount of montmorillonite (illite-montmorillonite). This variation of clay mineral species probably contributes to the higher CaO contents in these sediments. Another factor responsible may be the probable presence of minor amounts of sedimentary phosphates.

The sediments of the Oxford Clay and Kellaways Formations contain very high amounts of CaO (17•54%) as compared to the CaO contents of sedimentary rocks reported by other workers, and shown in Table (4.3). According to GOLDSCHMIDT (1954) the CaO content of hydrolysate sediments does not exceed 1%, apart from those sediments containing admixed calcium carbonate and dolomite. Sediments at present under investigation contain abundant amounts of calcite and dolomite, as is shown in Table (3.2). According to GOLDBERG and ARRHENIUS (1958) a small amount of Ca^{+2} is also located in clay minerals (usually in exchangeable positions), and also in feldspar and pyroxenes. The clay fraction chemistry of 12 samples from these sediments showed an average of 0•91% CaO. The leaching study of these sediments by acid-reducing agents, as described by CHESTER and HUGHES

(1967) also showed 0·365% of CaO, as an average content of the residue (lattice-held fraction), which is dominantly composed of total clays and other resistates. Results of both studies are in accordance with the proposed location of Ca^{+2} in clay minerals, as suggested by GOLDBERG and ARRHENIUS (op.cit.).

The Winterborne Kingston sediments showed abundant concentration of smectite (montmorillonite-illite). Its clay fraction chemistry also showed higher contents (0·91%) of CaO as compared to the clay fraction samples of the Warlingham Borehole sediments, which are poor in montmorillonite. During the leaching study, it was noticed that sample WBK05, from the Winterborne Kingston Borehole sediments, showed the highest amount of CaO (0·49%) in the residue; this sample also contains the highest amount of smectite (70%), having the richest (90%) montmorillonite component. These observations clearly indicate that Ca^{+2} is part of the population of exchangeable cations of montmorillonite in the Winterborne Kingston Borehole sediments.

The correlation coefficients matrix in the Appendix (4.1C) shows a very strong positive correlation of CaO (at an 0·01% level) with CO_2, Mn, calcite and smectite. It also showed a strong positive correlation (at an 0·1% level) with P_2O_5, Sr and quartz. These correlations strongly suggest that the main host of Ca^{+2} in these sediments is calcite. A very strong negative correlation of CaO (at an 0·01% level) with Si, Ti, Al, K, Mg, Na, V, Cr, Ni, Ba, Cu, Zr, Rb and H_2O, suggests its strong antipathetic relationship with these components; which are usually found in clays. The strong antipathetic relation of CaO with clays in these sediments is evident from its very strong negative correlation coefficient with total clays ($r = -0{\cdot}97$), which is confirmed by Figure (4.4a).

The very strong positive correlation of CaO with Mn ($r = +0{\cdot}80$) suggests that perhaps Mn^{+2} was co-precipitated with carbonate as $MnCO_3$ or Mn^{+2} has replaced Ca^{+2} in carbonate, as suggested by RANKAMA and SAHMA (1950). According to KRAUSKOPF (1979), Mn^{+2} like Fe^{+2} is readily oxidized on exposure to air, and Mn^{+2} is seldom abundant in surface waters. These sediments do not show the presence of mineral $MnCO_3$; therefore the association of Mn^{+2}

with CaO may be due to replacement of Ca^{+2} by Mn^{+2}. The positive correlation of CaO with Sr (r = +0·41) suggests that probably Sr^{+2} substitutes for Ca^{+2} in calcite, being of very similar ionic radii, Sr^{+2} (1·12Å)and Ca^{+2} (0·99Å). According to KRAUSKOPF (1979), Sr^{+2} is always present in carbonates because $CaCO_3$ - $SrCO_3$ are both near saturation in sea-water. Another reason for the association of Sr^{+2} may be the probable biogenous origin of calcite. According to CHESTER (1965) Sr^{+2} itself is of biogenous origin, coming from calcareous marine organisms. According to TUREKIAN (1964) foraminiferal tests contain an average of about 1200 ppm of Sr^{+2} and coccoliths in their tests contain between 1000 and 1750 ppm of Sr^{+2}. In the Oxford Clay sediments abundant coccoliths are reported by ROOD et al. (1971) and foraminifera by many workers, including GÜMBEL (1862), SCHWAGER (1865), DEECKE (1886), WHITAKER (1886), CRICK (1887), OVEY (1938), BARNARD (1952 and 1953) and CORDEY (1963).

The strong positive correlation of CaO with P_2O_5(r = +0·42) suggests that either there has been substitution of CO_3 by a few per cent of the PO_4 group in calcite (KRAUSKOPF , 1979) or these sediments contain a carbonate-apatite or hydroxy apatite $Ca_5(OH)_3OH$ in minor amounts. Sedimentary apatite of various compositions is generally not distinguishable by ordinary means; its crystal structure is only revealed by X-rays (KRAUSKOPF, 1979). As KRAUSKOPF(op.cit.) stated, when a solution of Ca^{+2} is added to a solution of phosphate or vice versa, the immediate precipitate developed is $Ca_3(PO_4)_2$ or $CaHPO_4$, depending on the pH of the sedimentary environments. According to the same author, the principal phosphate ion in acidic solutions is $H_2PO_4^-$ and in alkaline solutions $H\ PO_4^{2-}$. The Eh-pH conditions of the environments of the Oxford Clay were fluctuating, as suggested by the presence of authigenic and biogenous minerals. It is therefore possible that phosphate ions of either type, as described by KRAUSKOPF (1979), were easily available in the sedimentary environments and may be responsible for this relationship. According to the same author, substitution in apatite structure is possible, e.g. Cl for F and OH, CO_3 for PO_4 and cations like Sr^{+2}, Y^{+3}, Mn^{+2} for Ca^{+2}. The association of P_2O_5, Mn^{+2}, Sr^{+2} and Ca^{+2}, as shown by the correlation coefficient matrix in the Appendix (4.1C), in the present study might also suggest not only the presence of sedimentary apatite but also the possible substitution of these cations in it. Major substitution of these cations is believed to have taken place in calcite as already described.

The Upper Oxford Clay sediments, as shown in Tables (4.1A) and (4.1B), showed the highest contents of CaO (22·51%) and calcite (39·35%) as compared to other parts of the studied sequences. According to KRAUSKOPF (1979), precipitation of $CaCO_3$ is favoured where the water is warm and CO_2 is being lost through evaporation or photosynthesis, as on the shallow banks off Florida and the Bahamas. BERNER (1971) also suggested widespread precipitation of $CaCO_3$ in areas of shallow water such as continental shelves. By the application of these suggestions and taking into consideration the abundances of calcite in the sequence of the Oxford Clay and Kellaways Formations, it may be postulated that the deposition of Upper Oxford Clay took place under relatively shallow water conditions, which has already been suggested from the highest contents of quartz (23·67%).in these sediments.

The Winterborne Kingston Borehole sediments show exceptionally high abundance of CaO, when compared with the CaO contents of the shale and other sediments reported by other workers, and are shown in Table (4.3).

g) Sodium

The sodium contents of the Winterborne Kingston Borehole sediments vary from 0·26 to 0·80%. The average contents of 63 samples, on an absolute basis is 0·55% and on a carbonate-free basis is 0·78%. Twelve clay fraction ($< 2\mu$) samples show an average of 0·67% of Na_2O. The Winterborne Kingston sediments showed higher contents of Na_2O (0·55%) as compared to the Warlingham Borehole sediments (0·34%), but much lower than the reported contents of shale, as reported in Table (4.3). The distribution of Na_2O in different parts of the sequence, like potassium, shows an increase in its contents with depth in the Borehole, as is shown in Table (4.1A). The lowest amount of Na_2O (0·46%)occurs in the Upper Oxford Clay and the highest amount (0·60%) is shown by the Kellaways sediments. The reason for the lower contents of Na_2O in the Upper Oxford Clay may be the presence of a significant amount of smectite (montmorillonite-illite) and lower concentration of illite. The Kellaways sediments contain the highest amount of illite (36·02%) and the lowest amount of smectite (3·01%); having the lowest montmorillonitic layers in it. The distribution of minerals in the studied sequence is given in Table (4.1B). According to WEAVER and POLLARD (1973), montmorillonite contains smaller amounts of Na^+ in the inter-layer position in comparison with other cations such as Ca^{+2} - Mg^{+2}.

The Na^+/K^+ ratio has been studied in these sediments and are given in Table (4.1C). The highest ratio (0·26) exists in the Upper Oxford Clay, suggesting the highest rate of sedimentation for this part of the succession, as suggested by NICHOLLS and LORING (1960). This ratio showed a lower value in the remaining parts of the succession; the average value being 0·23, indicating a slow rate of deposition for these sediments. The sediments of the Upper Oxford Clay show the highest concentration of quartz (23·7%) and sandy-silty component, supporting the higher rates of deposition of these sediments. The Na^+/K^+ ratio has been used by SPEARS (1964) as an indicator of ion-exchange. The lowest average value of the ratio of Na^+/K^+ (0·23) for the sediments, excluding the Upper Oxford Clay sediments, suggests that due to the slow rate of deposition of these sediments, some of the Na^{+2} is exchanged by K^+ from the sea-water through ion-exchange, as suggested by SPEARS (1964).

The leaching study of the sediments by acid-reducing agents (CHESTER & HUGHES, 1967) shows that only 32% of the total Na_2O content is present in the lattice-held or lithogenous fraction of the sediments. It indicates that a significant amount of Na_2O is located in the exchangeable positions of clay minerals (affected by acid-reducing agents). Some of the Na^+ may be associated with the secondary salts precipitated from the interstitial waters. These samples are the borehole samples, so some Na^+ may also be contributed by the salts used in drilling muds. But most of the lattice-held fraction contains sodium in the inter-layers of clay minerals, particularly illite. Some $Na^+$is also associated with minor amounts of feldspar (plagioclase).

The correlation coefficient matrix in the Appendix (4.1C)

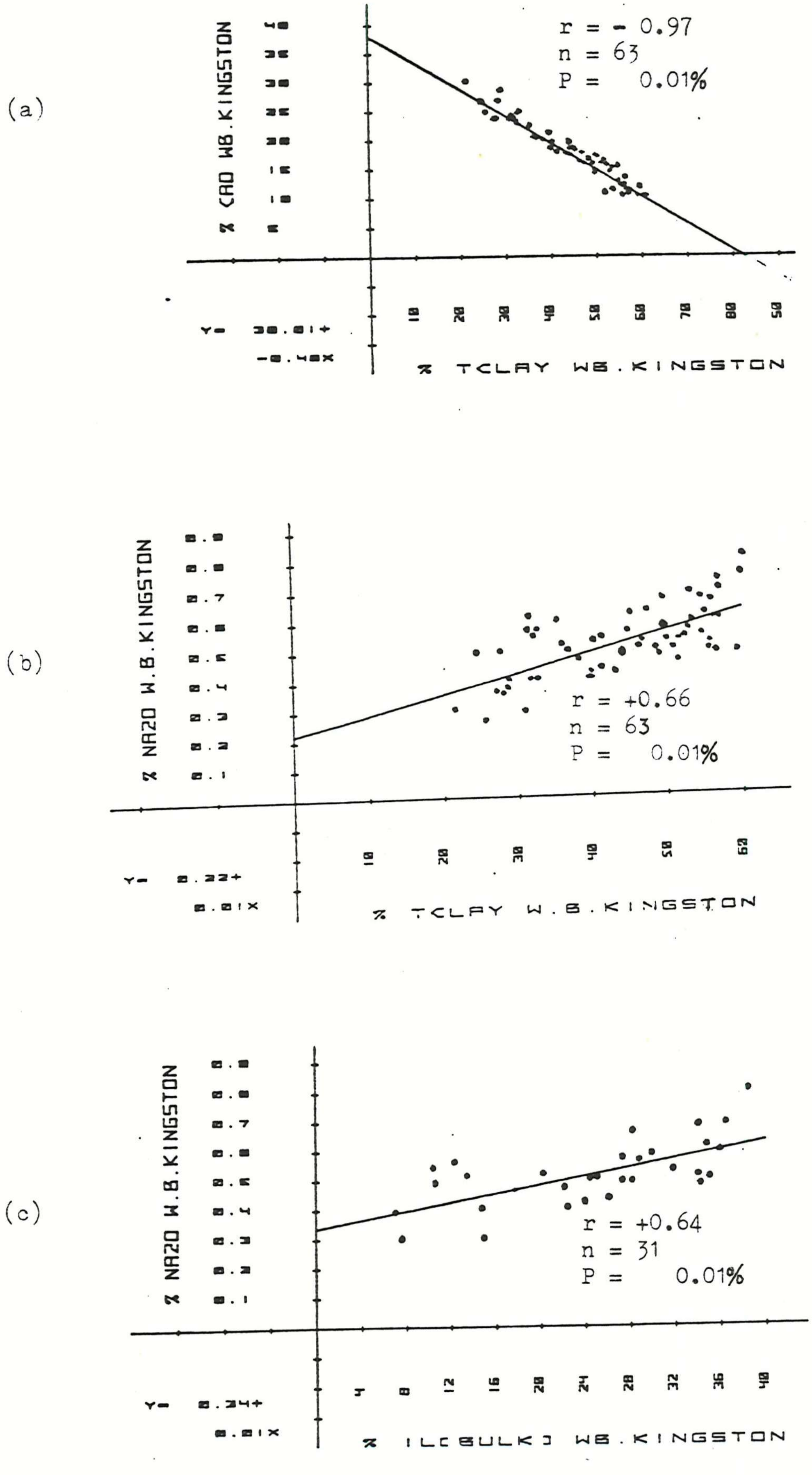
(a)
% CAO WB.KINGSTON
5
10
15
20
25
30
35
40
r = - 0.97
n = 63
P = 0.01%
Y= 30.01+
-0.40X
10
20
30
40
50
60
70
80
90
% TCLAY WB.KINGSTON
(b)
% NA2O W.B.KINGSTON
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
r = +0.66
n = 63
P = 0.01%
Y= 0.22+
0.01X
10
20
30
40
50
60
% TCLAY W.B.KINGSTON
(c)
% NA2O W.B.KINGSTON
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
r = +0.64
n = 31
P = 0.01%
Y= 0.34+
0.01X
4
8
12
16
20
24
28
32
36
40
% ILC(BULK) WB.KINGSTON

FIG.(4.4)

shows very strong positive correlations of Na_2O (at an 0·01% level) with depth, Si, Ti, Al, Mg, K, V, Cr, Ba, Ce, Rb, Nb, H_2O, illite and total clays. The sodium also shows a very strong negative correlation (0·01% level) with Ca, Mn, calcite and smectite. It has shown similar trends of correlations, as exhibited by K_2O, which strongly suggest that sodium in these sediments is strongly associated with clays, particularly in the inter-layers of illite (r = +0·50).

The concentrations of sodium and the amounts of total clays are plotted in Figure (4.4b), which shows a very strong positive correlation of Na_2O with total clays (r = +0·66). Another plot of Na_2O against the contents of illite in the bulk rock is shown in Figure (4.4c), which shows a strong positive correlation (r = +0·64) of Na_2O with illite, indicating that sodium generally is associated with clays, particularly with illite, as has been expressed already. The plot in Figure (4.4b) shows an intercept of +0·22, which means that 0·22% Na_2O of the total sodium contents in the rock is not associated with clays. It may occur in other phases, most likely in minor amounts of feldspar present in the sediments. The presence of feldspar in these sediments has been indicated by the weak X.R.D. peaks of feldspar in some of the samples. Sodium, like potassium, also showed strong positive correlations (at an 0·01% level) with components like Si, Zr, Nb, quartz and kaolinite, shown in the Appendix (4.1C). All being detrital, this suggests the presence of feldspar, probably plagioclase. The abundance of Na_2O is compared with the reported abundances of Na_2O by other workers, in Table (4.3).

h) Potassium

The contents of potassium in the Winterborne Kingston Borehole sediments vary from 1·04 to 2·69%. The average contents of 63 samples on an absolute basis and on a carbonate-free basis are 2·00% and 2·84% respectively. The average of 12 samples of clay fraction ($< 2\mu$) is 3·50%. The Winterborne Kingston Borehole samples have shown depletion in the contents of K_2O (2·00%) when compared with the Warlingham Borehole sediments (2·43%) and other sediments reported in Table (4.3). Generally, the depletion or enrichment of K_2O in sediments is associated with the contents of the total clays present in the sediments. The contents of total clays in the Winterborne Kingston Borehole samples is higher (56·3%) than the Warlingham Borehole sediments (46·31%), so the depletion of K_2O in these sediments may not be associated with the concentration of total clays. The clay mineral species and their contents may be the reason for depletion. Montmorillonite usually contains smaller amounts of K_2O and Na_2O in the inter-layer positions as compared to other cations such as Ca^{+2} and Mg^{+2} (WEAVER and POLLARD, 1973). The same authors have reported 7·02% of K_2O as an average content of 24 samples of illite. The illite contents in the bulk rock of the Winterborne Kingston Borehole sediments is lower (28·10%) as compared to the Warlingham Borehole sediments (30·20%).

The association of K^+ and Na^+ with clay minerals is a well-known fact. Many authors, including CHESTER (1965), CHESTER and ASTON (1976) and ELDERFIELD (1976) have concluded that K^+ and Na^+ are associated with clay minerals. ELDERFIELD (op.cit.) proposed that K^+ and Na^+ may be associated with clay minerals either in the inter-layer position or in the exchangeable positions. CHESTER and HUGHES (1967) noticed that the greater part of the K^+ is located in the inter-layer position of clay minerals and cannot be removed by the acid-reducing agents. The leaching study of these sediments by acid-reducing agents, as described by CHESTER and HUGHES (op.cit.),proved that 90% of the total contents of K_2O of these sediments is associated with the lattice-held fraction of the sediments. According to ELDERFIELD (1976), the fixation of cations with low hydration energy (e.g. K^+, NH_4^+, Rb^+ and Cs^+) leads to inter-layer dehydration and layer collapse (SAWHENY, 1972); in this way cations can be fixed in the inter-layer positions. In contrast to this, cations with high hydration energy (e.g. Ca^{+2}, Mg^{+2} and Sr^{+2}) produce hydrated expanded inter-layers and these ions remain exchangeable. The result is an affinity sequence for ion exchange - the Hofmeister series.

$$Cs^+ > K^+ > Na^+ > Li^+$$

$$Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2}$$

The distribution of K_2O and clay mineral species in the different parts of the sequence, as is shown in Tables (4.1A and 4.1B) clearly indicates its strong relationship with the contents of illite and smectite. The Upper Oxford Clay shows the lowest contents of K_2O (1·28%), illite (18·15%) and the highest amount of smectite (19·24%) in the bulk rock, as well as in the clay fraction, as is shown in Tables (4.1A and 4.1B).

BLOXAM and THOMAS (1969) used the Na^+/K^+ ratio as a measure of rate of sedimentation and the nature of crystallinity of illite. According to these authors, the highest ratio indicates the highest rate of sedimentation of the sediments and the degraded nature of illite. The high sedimentation rate of sediments depends on the rapid supply of the detritus,which ultimately depends on the intensity of the chemical weathering and running water in the area of weathering. The highest value (0·26) of the Na/K ratio occurs in the sediments of the Upper Oxford Clay, suggesting the highest rate of deposition of these sediments, and also the presence of degraded illite. The Upper Oxford Clay sediments contain a higher proportion of sand and also the highest contents (23·7%) of quartz; these observations also provide evidence of high sedimentation rate for these sediments. CALVERT (1976) used the K_2O/Al_2O_3 ratio to obtain an idea of the proportions of sand in sediments; the highest ratio indicating abundance of sand component in the sediments. In the sediments under study, the highest value of K_2O/Al_2O_3 ratio (0·204) exists in sediments of the Upper Oxford Clay, suggesting the presence of a higher sand fraction in these sediments, which indicates the rapid rate of sedimentation. The values of K_2O/Al_2O_3 ratios are given in Table (4.1C).

WILLIAMS (1965) used the K/Rb ratio as a measure of paleosalinity and origin of illite. If the ratio is constant, it implies that the origin of illite is the same, i.e. detrital. The K/Rb ratio in these sediments is highest (185·5) in the Upper Oxford Clay; in other parts of the sequence this ratio is lower and fairly constant (av.161). The variation of the K/Rb ratio, which is shown in Table (4.1C), suggests that in the Upper Oxford Clay some illite of different origin is also present.

TABLE (4.1A): Average concentrations of Major Elements and Minor Elements in the Divisions of the Oxford Clay and Kellaways Formations, Winterborne Kingston Borehole

	SiO_2%	TiO_2%	Al_2O_3%	Fe_2O_3%	MgO%	CaO%	Na_2O%	K_2O%	S%	P_2O_5%	Combined SiO_2%	H_2O^+%
Upper Oxford Clay	36·47 (60.13)	0·36 (0.59)	7·53 (12.42)	4·70 (7.75)	0·97 (1·60)	22·51	0·46 (0·76)	1·54 (2·54)	1·23 (2·03)	0·15	12·8 (36·46)	3·57
Middle Oxford Clay	38·40 (53·64)	0·53 (0·74)	11·55 (16·13)	5·94 -	1·27 (1·77)	16·84	0·52 (0·73)	2·17 (3·03)	1·58 -	0·15	19·4 (34·63)	5·07
Lower Oxford Clay	37·57 (49·29)	0·57 (0·75)	12·86 (16·87)	5·72 -	1·14 (1·49)	14·81	0·58 (0·76)	2·19 (2·87)	1·99 -	0·17	19·8 (31·54)	6·08
Kellaways Sediments	46·28 (55·91)	0·64 (0·77)	14·21 (17·16)	5·28 -	1·23 (1·48)	10·90	0·60 (0·72)	2·59 (3·13)	1·45 (1·75)	0·13	25·5 (35·11)	5·93

/contd.over

TABLE (4.1A) contd.

	V	Cr	Mn	Ba	La	Ce	Th	Pb	As	Zn	Cu
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Upper Oxford Clay	81	93	535	153	16	41	7	52	12	386	13
	(134)	(153)		(252)		(68)	(11)	(86)	(20)	(636)	(21)
Middle Oxford Clay	115	122	517	217	28	55	11	45	15	353	19
	(161)	(170)		(303)	(39)	(77)					
Lower Oxford Clay	110	130	383	243	41	42	11	73	10	751	27
	(144)	(170)		(319)	(54)	(55)	(14)				
Kellaways Sediments	119	150	345	306	43	74	14	34	9	257	23
	(144)	(181)		(370)	(52)	(89)					

/contd.over

TABLE (4.1A) contd.

	Ni	Rb	Sr	Y	Zr	Nb	Mo	Fe^{+2}%	Fe^{+3}%	C_{org}%
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.			
Upper Oxford Clay	40	69	350	22	152	11	0			2·79
	(66)	(114)		(36)	(251)	(18)		1·048	2·139	
Middle Oxford Clay	61	108	361	25	161	12	0·30			1·87
		(151)		(35)	(225)	(17)		1·405	2·586	
Lower Oxford Clay	64	116	361	32	139	13	8			4·32
		(152)		(42)	(182)	(17)		1·818	1·923	
Kellaways Sediments	59	135	308	40	182	19	2			1·50
	(71)	(163)		(48)	(220)	(23)		1·272	2·271	

TABLE (4.1B): Average values of the mineral abundance in different parts of the Oxford Clay and Kellaways Formations in the Winterborne Kingston Borehole.

	Quartz %	Calcite %	Pyrite %	Total Clays %	*Illite %	*Kaolinite %	*Chlorite %	*Smectite %	+Illite %	+Kaolinite %	+Chlorite %	+Smectite %
(U.O.C.)	23·67	39·35	2·25	33·26	42·60	8·40	3·84	45·16	14·17	2·79	1·28	15·02
(M.O.C.)	19·01	28·43	2·95	47·73	58·31	17·69	7·38	16·61	27·83	8·44	3·52	7·93
(L.O.C.)	17·75	23·76	3·89	50·28	60·38	21·77	7·77	10·08	30·36	10·94	3·91	5·07
(K.F.)	20·80	17·22	2·72	56·47	63·75	21·08	10·50	5·33	35·99	11·90	5·93	3·00

* Clay mineral abundances in $< 2\mu$ fraction.
\+ " " " " Bulk rock.

TABLE (4.1C): Ratios of elements in the different parts of the sediments of Oxford Clay and Kellaways Formations, Winterborne Kingston Borehole samples.

	$\frac{SiO_2}{Al_2O_3}$	$\frac{Quartz}{Zr}$	$\frac{Quartz}{^1Combd\ SiO_2}$	$\frac{TiO_2}{Al_2O_3}$	$\frac{TiO_2}{Zr}$	$\frac{Al_2O_3}{Na_2O}$	$\frac{Mg}{Al}$	$\frac{Al_2O_3}{SiO_2}$	$\frac{Al_2O_3}{^1Combd\ SiO_2}$	$\frac{Al_2O_3}{TiO}$	$\frac{^2Fe_2O_3}{Al_2O_3}$	$\frac{^3Fe_2O_3}{Al_2O_3}$
(U.O.C.)	4·84	1552·6	1·83	0·048	23·68	16·4	0·147	0·206	0·59 (0·38)	20·92	0·62	0·405
(M.O.C.)	3·32	1180·7	0·98	0·046	32·92	22·2	0·125	0·300	0·59 (0·43)	21·79	0·51	0·320
(L.O.C.)	2·92	1273·4	0·89	0·044	41·00	22·2	0·100	0·342	0·65 (0·45)	22·56	0·44	0·214
(K.F.)	3·26	1141·2	0·81	0·045	36·81	23·7	0·099	0·307	0·56 (0·46)	22·20	0·37	0·228

Note:
1. Combined SiO_2
2. Total iron.
3. Iron oxide.
4. Ratios in parenthesis are in clay fraction ($< 2\mu$)

/contd.over

TABLE (4.1C) contd.

	$\frac{Mn}{Fe}$	$\frac{Na}{K}$	$\frac{K_2O}{Al_2O_3}$	$\frac{K}{Rb}$	$\frac{K}{Ba}$	$\frac{Quartz}{C_{org}}$	$\frac{V}{Al}$	$\frac{V}{Mg}$	$\frac{Cr}{V}$	$\frac{Cr}{Al}$	$\frac{Cr}{Mg}$
(U.O.C.)	0·016	0·26	0·204	185·5	83·66	15·78	0·0020	0·014	1·15	0·0023	0·016
(M.O.C.)	0·012	0·21	0·187	166·7	82·95	10·16	0·0019	0·015	1·06	0·0020	0·016
(L.O.C.)	0·009	0·24	0·170	156·9	74·90	4·11	0·0016	0·016	1·18	0·0019	0·020
(K.F.)	0·009	0·24	0·182	159·2	70·26	7·45	0·0016	0·016	1·26	0·0020	0·020

/contd.over

TABLE (4.1C) contd.

	$\frac{Ba}{K}$	$\frac{Ba}{K + Na}$	$\frac{Fe^{3+}}{Fe^{2+}}$	$\frac{Rb}{K}$	$\frac{Cu}{Al \times 10^3}$	$\frac{Ni}{C_{org} \times 10^3}$	$\frac{Ni}{Al}$	$\frac{Th}{Al \times 10^4}$	$\frac{Th}{K \times 10^4}$	$\frac{Zr}{Th}$	$\frac{Al}{Th}$	$\frac{\Sigma Ce/2}{Y}$	$\frac{\Sigma Ce}{Y}$
(U.O.C.)	0·0119	0·0094	2·041	0·00539	3·26	2·67	$1{\cdot}00 \times 10^2$	1·76	5·48	21·71	569·28	1·295	2·59
(M.O.C.)	0·0120	0·0099	1·841	0·00600	3·11	3·26	$9{\cdot}98 \times 10^3$	1·80	6·11	14·64	555·64	1·660	3·32
(L.O.C.)	0·0133	0·0108	1·058	0·00637	3·97	1·48	$9{\cdot}40 \times 10^3$	1·62	6·05	12·64	618·64	1·297	2·59
(K.F.)	0·0142	0·0118	1·785	0·00628	3·06	2·11	$7{\cdot}84 \times 10^3$	1·86	6·51	13·00	537·14	1·462	2·92

SPEARS (1964), during his studies of the Mansfield marine band sediments, considered the variation in the Na^+/K^+ ratio as the result of the variation of contents of one or the other, or both of them. He noticed a decrease in the contents of Na^+ with the increase of the contents of K^+ in the sediments. He further observed that decrease in Na^+ is equal to the increase in K^+; this phenomenon he suggested as the mechanism of cation exchange, as was also suggested by NICHOLLS and LORING (1960). But in the sediments at present under study, the increase of Na^+ and K^+ contents is directly proportional, which suggests that either the phenomenon of cation exchange has not occurred in these sediments or it took place and the amounts of K^+ and Na^+ exchanged were in equal proportions. The ion exchange in sediments is influenced by many factors, including the time allowed for a solution to act, concentration of ion in solution and the granular size of clay minerals. RÖSLER and LANGE (1972) have described the ion exchange ability of clay minerals. According to these authors, the highest ability is in vermiculite (100-150, m-e/100g), second to it is in montmorillonite (80-150, m-e/100g); illite shows an ability of 10-40, m-e/100g, and the lowest ability has been mentioned for kaolinite (3-15, m-e/100g).

The correlation coefficient matrix in the Appendix (4.1C) shows a very strong positive correlation of K_2O (at an 0·01% level) with depth, Si, Ti, Al, Mg, Na, V, Cr, Ni, Ba, Ce, Th, Cu, Rb, Nb, C_{org}, H_2O, illite, kaolinite, chlorite and total clays. The K_2O also shows a very strong negative correlation (at an 0·01% level) with Ca, Mn, calcite and smectite, components generally authigenic/biogenous in origin. These correlations strongly suggest that K_2O is associated with total clays, composed of detrital clay minerals. Figure (4.5a) shows how strongly K_2O is associated with total clays ($r = +0{\cdot}97$). The correlation of K_2O with the contents of illite in the bulk rock is also very strong ($r = +0{\cdot}96$), suggesting that K_2O is mostly present in illite. The strong association of illite and K_2O is shown in Figure (4.5b).

The distribution of K_2O in different phases of the sediments can be studied with the help of the regression equation (1) of K_2O - total clays in bulk rock. The regression equation is given below.

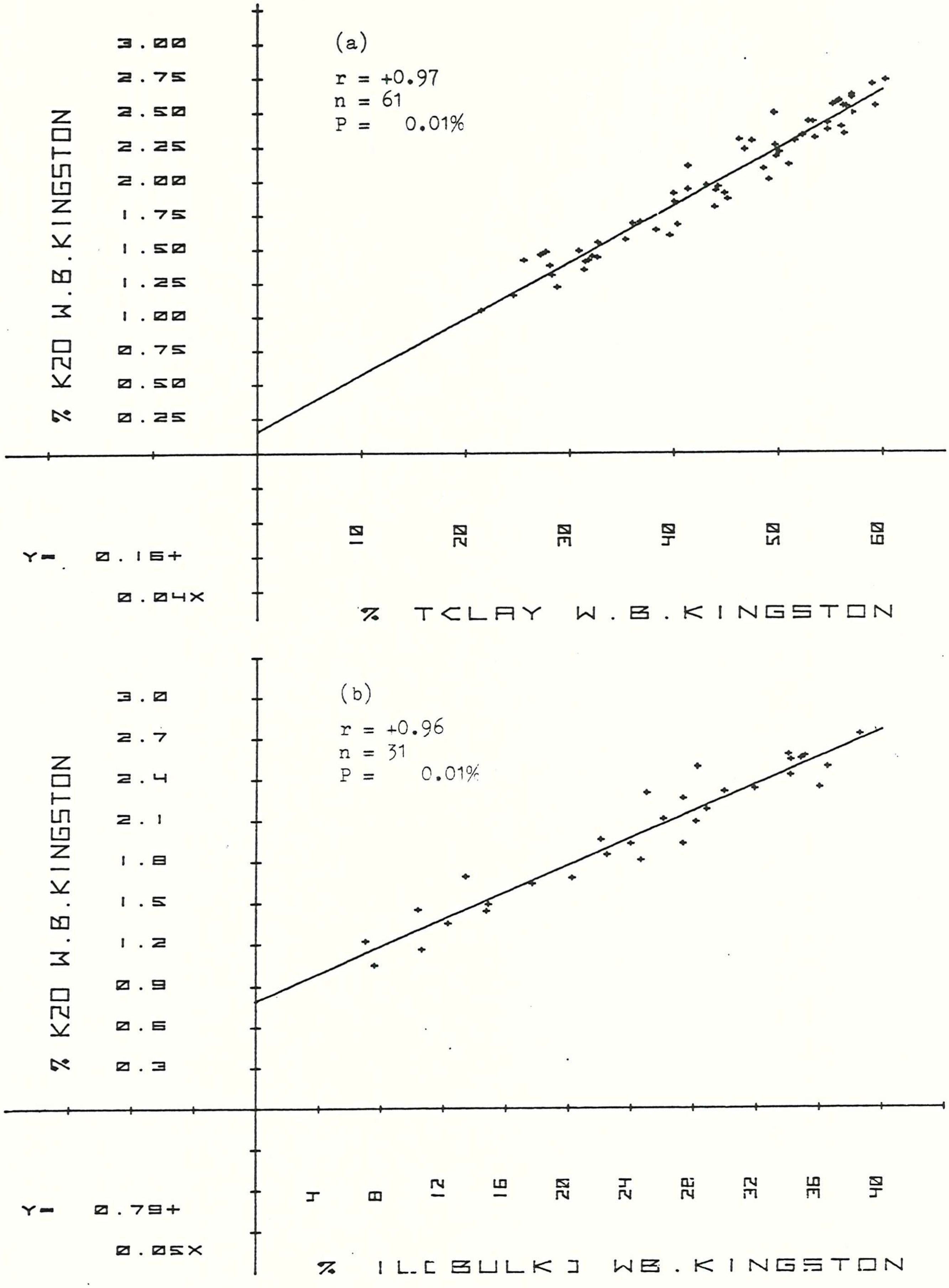

(a)
r = +0.97
n = 61
P = 0.01%
% K2O W.B.KINGSTON
3.00
2.75
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
10
20
30
40
50
60
Y= 0.16+
0.04X
% TCLAY W.B.KINGSTON
(b)
r = +0.96
n = 31
P = 0.01%
% K2O W.B.KINGSTON
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
4
8
12
16
20
24
28
32
36
40
Y= 0.79+
0.05X
% IL.[BULK] WB.KINGSTON

FIG.(4.5)

Regression equation:

$$(\% \ K_2O) \ Y = +0{\cdot}16 + 0{\cdot}04 \ X \ (\% \text{ total clays}) \quad - \ - \ - \ - \quad (1)$$

The regression equation (1) shows the intercept value of +0·16%. It indicates that 0·16% K_2O of the total K_2O contents is not associated with total clays. The proportion of K_2O associated with total clays can be obtained by subtracting the value of the intercept (+0·16%) from the average total contents of K_2O (2·00%).

$\therefore$ The amount of K_2O associated with total clays =
2·00 - 0·16 = 1·84%.

The remaining amount of K_2O (0·16%) may be associated with other phases, e.g. feldspars present in the sediments. CHESTER (1965), CHESTER and ASTON (1976) suggested that extra amounts of K_2O in sediments are associated with sodic feldspar. The sediments of the Oxford Clay (all divisions) show a very strong positive correlation of K_2O at an 0·01% level with the components like Si, Zr, Nb, quartz and kaolinite; all components being detrital, this suggests the presence of feldspars in these sediments. Some of the samples showed weak peaks of feldspars on the X.R.D. diffractograms, and confirm the above conclusions.

A rough estimate of the amount of K_2O associated with illite can be made by the regression equation No.2, which is obtained from Figure (4.5b), and is given below:

Regression equation No.2 $(\%K_2O) \ Y = +0{\cdot}79 + 0.05 \ X \ (\% \text{ illite in bulk rock})$

The total contents of K_2O in the bulk rock = 2·00%
The value of intercept from the regression equation No.2 = +0·79
$\therefore$ The amount of K_2O associated with illite = 2·00 - 0·79 = 1·21%

which is in accordance with the coefficient correlation value of K_2O ($r = +0{\cdot}96$) for illite, indicating that the major part of K_2O in these sediments is present in illite and perhaps on average (1·84-1·21 = 0·63%) is associated with other clay minerals.

i) Sulphur

The sulphur contents of the Winterborne Kingston Borehole sediments vary from 0·71 to 3·66%. The average content of 63 samples on an absolute basis is 1·50% and on a carbonate free basis 2·16%. These sediments show very large concentrations of sulphur when compared with the Warlingham Borehole sediments and other sediments studied by other workers, as is shown in Table (4.3). The Warlingham Borehole sediments contain 0·89% of sulphur on an absolute basis, and 1·24% on a carbonate free basis. KRAUSKOPF (1979) and MINAMI (1935a) reported average sulphur contents of 0·25% and 0·32% in "average shale" and "European Palaeozoic shales" respectively. The very high concentration of sulphur in the Oxford Clay and Kellaways sediments of both the boreholes reflects the existence of strong reducing conditions under which these sediments were deposited. High sulphur concentration also indicates the abundant availability of metabolizable organic matter, sulphate reducing bacteria and dissolved sulphide in the depositional environments.

BERNER (1971) , PRICE (1976), CALVERT (1976), KAPLAN et al. (1963) and SHISHKINA (1964) contributed valuable information regarding the diagenesis and diagenetic behaviour of sulphur in sediments. According to BERNER (1971) marine sediments may be supplied with sulphur by organic compounds; H_2S in organic-rich sediments is supplied by the breakdown of protein and amino acids such as 'methionine', which contains sulphur. Sulphur may also be added by dissolved SO_4^{-2}, depending on its original concentration in the interstitial- and sea-water. BERNER (op.cit.) mentioned that,under aerobic conditions, organic sulphur compounds will be oxidized to sulphate, which is added to the original sulphate, which does not undergo any change. The same author suggests that under anaerobic conditions, sulphate reducing bacteria will reduce SO_4^{-2} to H_2S and HS^-, and additional sulphide may be added by the bacterial degradation of sulphur in organic matter. BERNER (1970b) believes that the rate of sulphate reduction in a sediment is directly proportional to the concentration of metabolizable organic matter. But, according to KAPLAN et al. (1963), the sulphur contents of organic matter averages only 1% of its dry weight,and it is insufficient to contribute significantly to the sulphides found in the sediments. This observation was further confirmed by the sulphur 'isotopes' study of various sulphur-containing minerals by KAPLAN et al. (1963). BERNER (1971) also mentioned that in many marine sediments the concentration of pyritic sulphur (which forms H_2S) is far greater than that which could have been originally supplied as organic sulphur.

From these observations it becomes clear that the sulphur contents of marine sediments are derived mainly from the reduction of dissolved SO_4^{-2} by anaerobic bacteria, although there is a small contribution from organic matter. OSTROUMOV (1953) and VOLKOV (1961) suggested that the presence of much iron sulphide in deep water organic-rich anoxic sediments, such as those of the Black Sea, is perhaps more a reflection of the concentration of H_2S in overlying water than of the organic matter contents of the sediments. SHISHKINA (1964) believes that the high contents of the organic matter and high accumulation rate of the sediments is the main reason for the existence of sulphides in certain Pacific Ocean trenches.

The correlation coefficient matrix in the Appendix (4.1C) shows a very strong positive correlation (at an 0·01% level) of sulphur with Fe_2O_3, P_2O_5, Ni, Pb, Zn, Cu, Mo, Fe^{+2} and pyrite. Sulphur also shows a strong positive correlation, significant at an 0·1% level, with depth, organic carbon and kaolinite. These correlations indicate that sulphur occurs in the sulphide phase, mainly in the form of pyrite (FeS_2); the association of sulphur with metals like Ni, Cu, Zn, Pb and Mo suggests that either sulphides of these metals (DEGENS, 1965) are present in these sediments in minor amounts, or this association is based on the pronounced affinity of these metals for sulphur, being the metals of the chalcophile group (GOLDSCHMIDT, 1954; and BROWNLOW, 1979). The correlation shown by sulphur with P_2O_5($r = +0{\cdot}53$) may be either due to 'organism biophile' group (GOLDSCHMIDT, 1937), as both may be derived from organic organisms, or this relationship may be due to similar ionic potential (MASON, 1952); being the soluble complex-anions, as explained by RÖSLER & LANGE (1972) and GOLDSCHMIDT (1937) in the distribution of chemical elements in sediments, minerals and rocks. The correlation of sulphur with kaolinite ($r = +0{\cdot}49$) may be related, due to the rate of accumulation of sediments; kaolinite being coarse grained settles rapidly and may promote the diagenesis of sulphides (SHISHKINA, 1964) from the available H_2S and Fe^{+2} present in the environments. The strong negative correlation of sulphur with Zr ($r = -0{\cdot}47$) and quartz ($r = -0{\cdot}50$) suggests that sulphur is of diagenetic origin. The diagenetic origin of sulphur is very well illustrated by Figure(4.6a & b), which shows strong positive correlation of sulphur with pyrite and organic carbon.

j) Phosphorus

P_2O_5 contents of the Winterborne Kingston Borehole sediments vary from 0·12 to 0·21%. The average value of 63 bulk rock samples is 0·15% and of 12 clay fraction samples is 1·31%. The lattice-held fraction of 12 samples showed an average value of 0·11%. The P_2O_5 contents of these sediments are very close to the average values of average shales, reported by KRAUSKOPF (1979), RANKAMA and SAHAMA (1950) and TURIKIAN and WEDEPOHL (1961), as shown in Table (4.3). The lower and higher contents of P_2O_5 respectively in clay and lattice-held fractions of these sediments, as compared to the Warlingham Borehole sediments, indicate that P_2O_5 in these sediments occurs in different phases than the Warlingham Borehole sediments. The higher content of the lattice-held fraction suggests its residence in the lattices of minerals such as sedimentary phosphate. The strong positive correlation of P_2O_5 with CaO (r = +0·42) supports this occurrence. The Eh - pH conditions of the environments were frequently changing at the time of deposition of these sediments, and the principal phosphate ions $H_2PO_4^-$ in acidic solutions and HPO_4^{2-} in alkaline solutions (KRAUSKOPF ,1979) were both probably available from time to time. The quantity of phosphates in the sediments was too small for detection by X.R.D in the bulk rock; the silt fraction samples showed peaks for "hydroxy apatite" in the X.R.D. diffractograms. CHOWDHURY (1980) reported the occurrence of apatite and higher contents of phosphorus in the Corallian sediments from the Dorset coast samples. Like organic-rich sulphide bearing sediments of South Africa, as reported by CALVERT (1976), the Winterborne Kingston Borehole sediments also contain higher amounts of organic carbon (2·40%), sulphur (1·50%) and pyrite (2·82%); these sediments are believed to have been deposited under strong reducing (anoxic) conditions. These observations point to the occurrence of sedimentary apatite in minor amounts in these sediments.

The correlation coefficient matrix in the Appendix (4.1C) shows a very strong positive correlation of P_2O_5 significant (at an 0·01% level) with Ca, S, Pb, Mo, Fe^{+2}, pyrite, calcite, CO_2, Zn and Sr. These associations suggest the relationship of P_2O_5 with carbonates and sulphides. The very strong positive correlation of

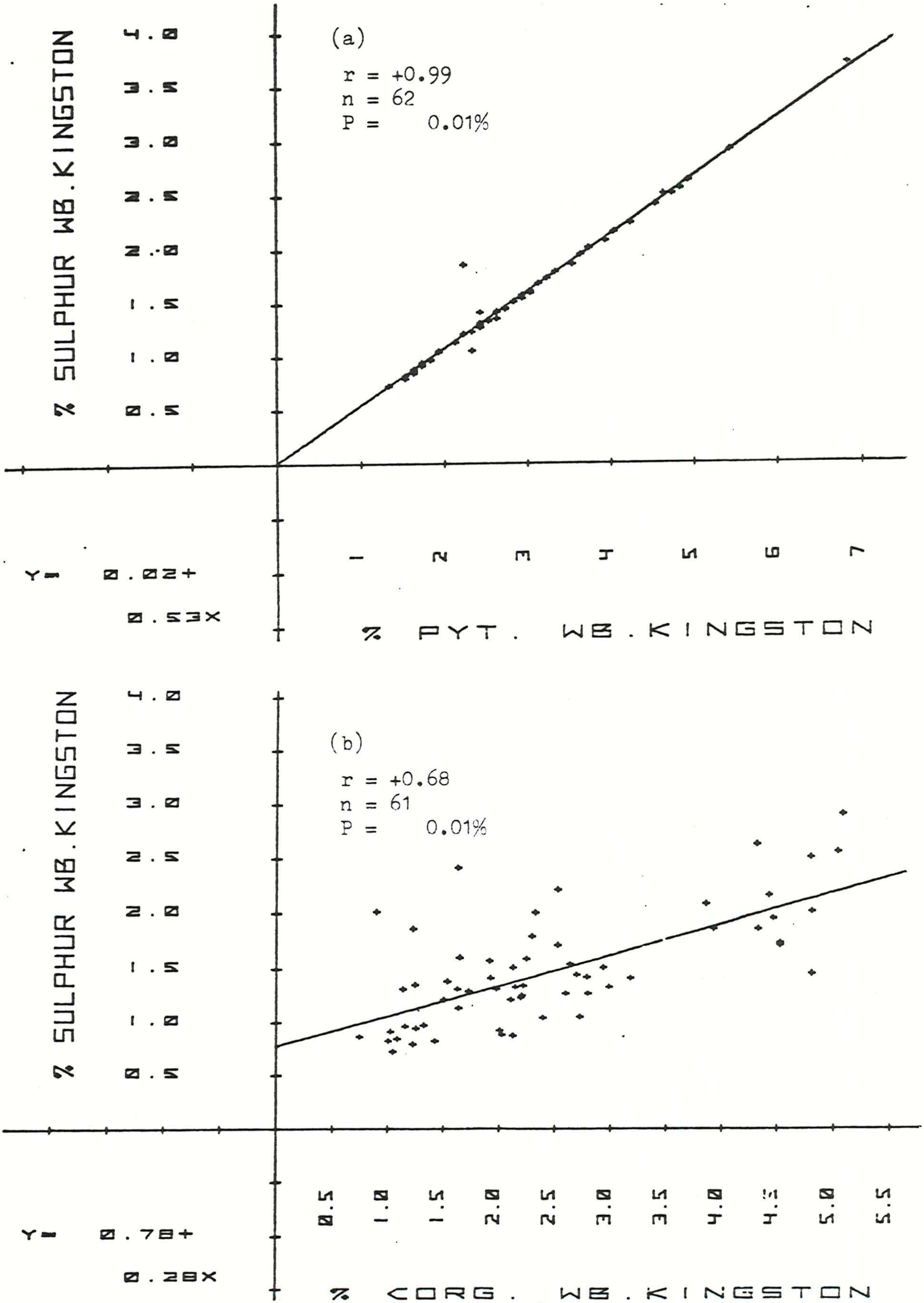

(a)
r = +0.99
n = 62
P = 0.01%
% SULPHUR WB.KINGSTON
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Y= 0.02+
0.53X
1
2
3
4
5
6
7
% PYT. WB.KINGSTON
(b)
r = +0.68
n = 61
P = 0.01%
% SULPHUR WB.KINGSTON
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Y= 0.78+
0.28X
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
% CORG. WB.KINGSTON

FIG.(4.6)

P_2O_5 with Ca (r = +0·42) suggests occurrence of sedimentary phosphate. The association of P_2O_5 with S, Pb, Mo, Fe^{+2}, Zn and pyrite is due to the fact that under anoxic conditions these elements are concentrated in sediments. The positive correlation of P_2O_5, significant at a 5 - 1% level, with organic carbon, Mn and total Fe as Fe_2O_3 is also to be expected. The correlation of P_2O_5 with organic carbon is also well known, as described by WOLF et al. (1967) and CALVERT (1976). The relationship of phosphorus with organic carbon may be due to solutions of phosphate derived from the decomposition of phosphate-bearing organic matter and by the diagenetic replacement of calcareous material. The positive correlation of P_2O_5 with Mn (r = +0·21) and Fe_2O_3 (r = +0·24) may be due to the similar mode of transportation of Mn, Fe and P, as suggested by STRAKHOV (1967). The concentration of a significant amount of phosphorus by adsorption onto ferric oxide coats of mineral grains is well documented (PRICE, 1976; CALVERT, 1976).

The very strong negative correlation of P_2O_5, significant at an 0·01% level, with Si, Mg, K, Ce, Rb, Zr, Nb and residual Fe_2O_3 and a strong negative correlation (at a 5 - 1% level) with depth, Ti, Al, Na, V, Cr, Ba, Th, illite, chlorite, quartz and total clays, suggest that clays of these sediments, in general, do not contain phosphorus.

It may be concluded that phosphorus in these sediments occurs in carbonate minerals (substituted for CO_3); this relationship is illustrated by Figure (4.7a). It is associated with organic carbon and clay minerals (adsorbed on the surfaces) and a minor amount as directly precipitated phosphate. The relationship of P_2O_5 with organic carbon is shown in Figure (4.7b).

k) Organic Carbon

Organic carbon contents in the studied sediments were determined by the amount of carbon dioxide representing organic carbon, which is obtained by the difference between the total CO_2 and carbonate CO_2, determined by an Infra-red gas analyser. The analytical organic carbon contents thus determined are considered to represent the equivalent contents of organic matter of these sediments and therefore are reported as 'organic carbon' in percentage, without employing any conversion factor. A conversion factor (from 1·25 to 1·80) is commonly used by other workers to multiply the organic carbon value to produce "organic matter".

The sediments of the Winterborne Kingston Borehole contain variable concentrations of organic carbon (0·44 - 5·05%). The average value of 63 samples of organic carbon is 2·4%, which is much higher than the average content of the Warlingham Borehole sediments (1·66%) and average values reported by other workers, tabulated in Table (4.3). The Winterborne Kingston Borehole sediments contain average values of organic carbon of 4·32% in the Lower Oxford Clay and 1·50% in the Upper Oxford Clay. The distribution of organic carbon is shown in Table (4.1B).

CHOWDHURY (1980) reported higher contents of organic carbon in the samples of Corallian mud-rocks from Dorset, which are mentioned in Table (4.3). BLOXAM and THOMAS (1969) noticed an increase in the abundance of organic carbon and a decrease in the quartz/organic carbon ratio in off-shore sediments. The present sediments contain the highest (4·32%) and lowest (1·50%) abundances of organic carbon in the Lower and Upper Oxford Clays respectively. The quartz/organic carbon ratios of these sediments are in agreement with the observations of BLOXAM and THOMAS (1969), and are shown in Table (4.1C). The lowest ratio (4.11) exists in the Lower Oxford Clay sediments, distinguishing them as the 'offshore sediments' as compared to the Upper Oxford Clay sediments, which show the highest value (15·78) of the ratio, indicating the 'near-shore' environment of their deposition.

The correlation coefficient matrix in the Appendix (4.1C) shows a very strong positive correlation of organic carbon (at the 0·01% level) with depth, Ti, Al, K, S, V, Cr, Ni, Ba, Cu, Rb, Mo, H_2O, Fe^{+2}, illite, kaolinite, pyrite and total clays. These correlations suggest a very strong relationship of organic carbon with total clays, minerals of the sulphide phase (pyrite) and metallic elements. According to SCHNITZER and SKINNER (1965), DROZDOVA (1968) and ZUNNINO et al. (1972), it is established that organic matter reacts with various metals and produces 'organo-metal complexes' of a reasonably stable nature. BATURIAN et al. (1967) and PRICE and CALVERT (1973a) interpreted the close association of

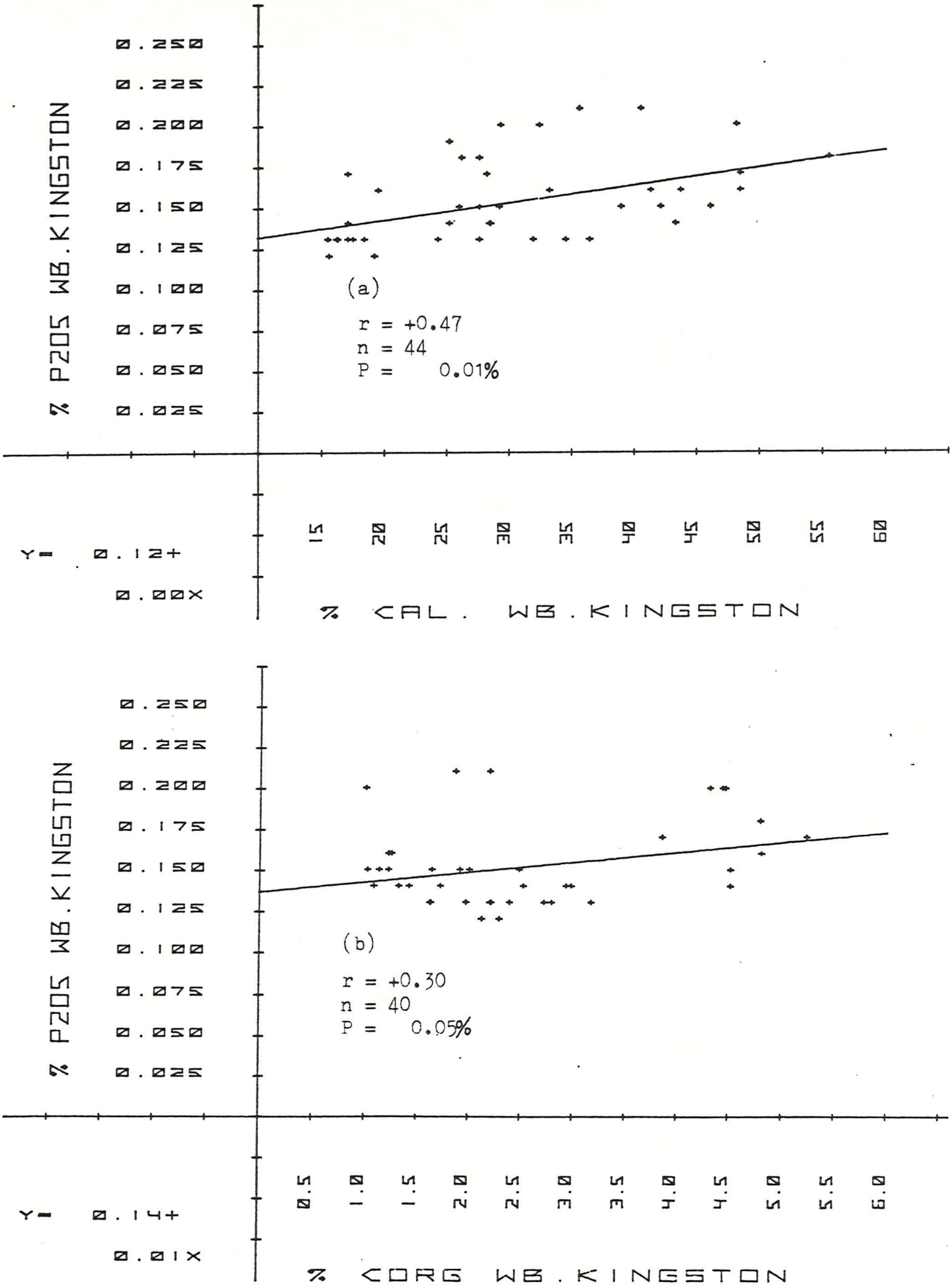
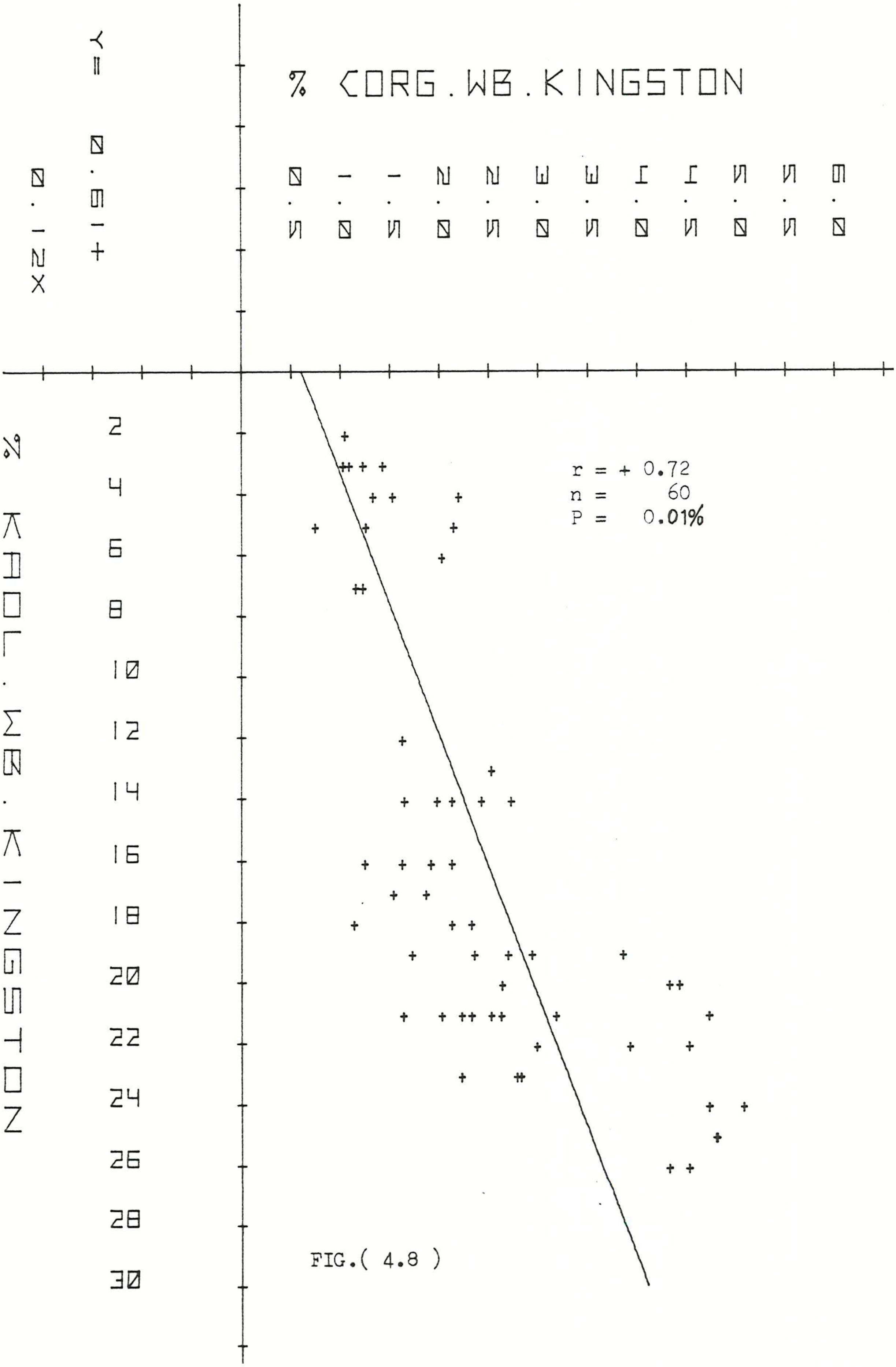

% P2O5 WB.KINGSTON
0.250
0.225
0.200
0.175
0.150
0.125
0.100
0.075
0.050
0.025
(a)
r = +0.47
n = 44
P = 0.01%
Y= 0.12+
0.00X
15
20
25
30
35
40
45
50
55
60
% CAL. WB.KINGSTON
% P2O5 WB.KINGSTON
0.250
0.225
0.200
0.175
0.150
0.125
0.100
0.075
0.050
0.025
(b)
r = +0.30
n = 40
P = 0.05%
Y= 0.14+
0.01X
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
% CORG WB.KINGSTON

FIG.(4.7)

organic carbon with many minor metals, e.g. Cu, Ni, Mo, Zn, Pb and U, especially in the sediments of reducing environments, due to the existence of 'metal-organic' substances. According to SWANSON et al. (1966), the ability of organic substances such as 'humates' to take up metals, e.g. Ag, Co, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn, in appreciable quantity is well known. The Lower Oxford Clay sediments showed enrichment in Cu, Mo, S, Zn, Pb, Ni, Fe^{+2}, pyrite and organic carbon, as is shown in Tables (4.1A and 4.1B). This concentration may be due either to the occurrence of 'organo-metal' complexes, as suggested by PRICE and CALVERT (1973a), or this relationship was already in existence in the sediments prior to entering the basin of deposition. The strongest positive correlation of organic carbon with kaolinite ($r = +0{\cdot}72$), significant at an 0·01% level, as compared to other parts of the Oxford Clay, suggests that the aforesaid relationship of organic carbon and metals was probably already existing and these metals were accompanied by the detrital organic carbon being supplied to the basin of deposition.

The very strong positive correlation of C_{org} with sulphur ($r = +0{\cdot}46$), significant at the 0·01% level, may be due to the organic origin of sulphur. This relationship also suggests the existence of strong reducing conditions and high bacterial activity, soon after the deposition of these sediments. Framboidal aggregates of early diagenetic pyrite, shown in Plate (3.1), in these sediments indicate that sulphate reducing bacteria were active,and reducing conditions existed below the sediment-water interface. The strong correlation of organic carbon with total clays ($r = +0{\cdot}53$) is a very much expected association. Clays are deposited in the deepest part of the basin, where strong reducing conditions exist. Both clay minerals, illite and kaolinite, showed a strong positive correlation (at an 0·01% level) with organic carbon, but kaolinite shows the highest correlation coefficient ($r = +0{\cdot}72$), which is also shown in Figure (4.8), suggesting that a significant proportion of organic carbon is of detrital or terrestrial origin; kaolinite being a typical detrital mineral. It is possible that terrestrial/detrital organic carbon reached the site of deposition accompanied by kaolinite in the detritus. The presence of non-marine/terrestrial organic carbon in marine sediments is a common observation of many workers. CHOWDHURY



r = + 0.72
n = 60
P = 0.01%

FIG.(4.8)

(1980) and SULAIMAN (1972) reported the presence of non-marine/ terrestrial organic carbon in the mud-rocks of Corallian sediments from the Dorset coast and Namurian Argillites of Ireland respectively.

4.2 Geochemistry of the Major Elements of the Warlingham Borehole Sediments

a) Silicon

The contents of silicon of the Warlingham Borehole sediments varies from 17·11 to 84·83%. The average contents of silicon on an absolute and on a carbonate free basis are 43·89% and 61·82% respectively. The silicon showed slightly higher contents when compared with the abundances of silica in sediments reported by other workers, which are shown in Table (4.3). The distribution of silica in the different parts of the stratigraphic sequence is recorded in Table (4.2A). The highest concentration (69·56%) of silica is in the sediments of Kellaways Formation. The highest concentration (62·89%) of silica, in the divisions of the Oxford Clay, is present in the sediments of the Upper Oxford Clay. The abundances of free silica (quartz) in these sediments are variable, from 10 to 78%. The highest concentration (40·70%) of quartz occurs in the sediments of Kellaways Formation, as is shown in Table (4.2B). But in the Oxford Clay divisions, as in the Winterborne Kingston Borehole, the higher concentration (20·41%) of quartz is in the Upper Oxford Clay sediments, as is shown in Table (4.2B). The Si/Al ratio in the divisions of the Oxford Clay ranges from 2·96 to 3·66 in the Lower and Upper Oxford Clay sediments respectively. The highest Si/Al ratio (5·19) exists in the sediments of Kellaways Formation; it may be due to very high abundances of quartz in these sediments. A comparison of Si/Al ratios is shown in Table (4.2C). The low Si/Al ratio of the Oxford Clay sediments (2·96 - 3·66) is below the value (4·2) of the Si/Al ratio suggested by COUTURE (op.cit.), as an indicator of biogenous/diagenetic silica, and suggests that these sediments do not contain any amount of biogenous/ diagenetic silica. The strong negative correlation of SiO_2 with calcite, dolomite, mixed-layered minerals, CaO, MgO, Mn, CO_2 and Sr, all significant at an 0·01% level of significance, also supports the absence of non-detrital silica in these sediments. The correlation coefficient (r) matrix is given in the Appendix (4.2C). The highest value (54·43%) of the abundance of total clays can be seen in the sediments of the

Lower Oxford Clay, as has been observed in the sediments of the Winterborne Kingston Borehole.

The highest value (1·93) for the free silica/combined silica ratio exists in the sediments of Kellaways Formation, as is shown in Table (4.2C), indicating a comparatively high rate of sedimentation for these sediments. The free silica/combined silica ratio shows its highest value (1·09) in the sediments of the Upper Oxford Clay, indicating a relatively high rate of sedimentation. This repeats the pattern observed in the study of the Winterborne Kingston Borehole sediments. The highest value (1275·6) of the free silica/Zr ratio exists in the sediments of the Upper Oxford Clay. The next highest value of this ratio is present in the sediments of Kellaways Formation. A comparison of different ratios is given in Table (4.2C). The Upper Oxford Clay sediments of the Winterborne Kingston Borehole also showed the highest value of the free silica/Zr ratio, as is shown in Table (2.1C). These observations suggest the highest rate of sedimentation during the time of deposition of the Upper Oxford Clay sediments in both the areas.

The highest concentration (40·70%) of quartz in the sediments of Kellaways Formation, according to RONOV (<u>op.cit</u>.), suggests that these sediments were laid down near the shore and the deepest basin conditions existed at the time when the sediments of the Lower Oxford Clay were being deposited; as quartz shows its lowest concentration (18·06%) in these sediments. This observation agrees with its counterpart at the Winterborne Kingston Borehole.

The correlation coefficient matrix in the Appendix (4.2C) shows a very strong positive correlation of SiO_2 with depth, Ti, Na, Ba, Zr, kaolinite and quartz, all significant at an 0·01% level of significance. It also shows a strong negative correlation (at an 0·01% confidence level) with Nb, Y and Th. It also showed a medium strong positive correlation (at a 1·0% confidence level) with Al and combined SiO_2. It has shown a weak positive correlation with total clays ($r = +0{\cdot}27$) and Rb ($r = +0{\cdot}25$). It also shows a very strong negative correlation (at an 0·01% level) with calcite, dolomite, Mn, Mg, Ca, CO_2 and mixed-layered clay minerals. The very strong positive correlation of silica with quartz ($r = +0{\cdot}77$), kaolinite ($r = +0{\cdot}69$) and Zr ($r = +0{\cdot}89$)

TABLE (4.2A): Average values of major, minor elements and other components in the sediments of Oxford Clay and Kellaways Formations from Warlingham Borehole samples.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	S	P_2O_5
(U.O.C.)	39·09 (62·70)	0·61 (0·98)	10·68 (17·13)	3·62 (5·81)	2·92 *(3·27)	19·71	0·30 (0·48)	2·36 (3·75)	0·55 (0·88)	0·076 -
(M.O.C.)	41.81 (60·21)	0.71 (1·02)	13·00 (18·72)	3·91 (5·63)	2·47 *(2·59)	15·98	0·34 (0·49)	2·50 (3·60)	0·95 (1·37)	0·09 (0·13)
(L.O.C.)	44·69 (57·02)	0·76 (0·97)	15·08 (19·24)	3·43 (4·38)	2·36 *(2·45)	10·88	0·38 (0·48)	2·55 (3·25)	1·04 (1·33)	0·155 (0.20)
(K.F.)	61·82 (69·67)	0·69 (0·78)	11·93 (13·44)	3·80 (4·28)	1·03 *(1·04)	6·05	0·42 (0·47)	2·30 (2·59)	1·62 (1·82)	0·17 -

/contd.over

TABLE (4.2A) contd.

	C_{org}	H_2O^+	Fe^{2+}	Fe^{3+}	Combined SiO_2	V	Cr	Mn	Ba	La	Ga
(U.O.C.)	0·59	2·59	0·48	2·00	18·68	107	105	203	209	39	17
						(172)	(168)	-	(335)	(63)	(27)
(M.O.C.)	1·13	3·51	0·82	1·81	23·18	101	94	160	269	45	17
						(146)	(135)	-	(388)	(65)	(24)
(L.O.C.)	3·93	5·19	0·90	1·28	26·63	101	132	111	281	55	18
						(129)	(168)	-	(358)	-	(23)
(K.F.)	2·84	3·58	1·41	1·10	21·10	85	116	84	407	47	14
						(96)	(131)	-	-	(53)	(16)

/contd.over

TABLE (4.2A) contd.

	Ce	Th	Pb	As	Zn	Cu	Ni	Rb	Sr	Y	Zr	Nb	Mo
(U.O.C.)	66	9	19	20	84	17	46	120	254	28	160	18	0·19
	(106)	(15)	(30)	-	(135)	(28)	(74)	(193)		(45)	(257)	(29)	
(M.O.C.)	76	10	18	9	70	17	36	136	283	35	172	17	0·42
	(110)	(14)	(26)	(13)	(101)	(24)	(52)	(196)		(50)	(248)	(24)	(0·60)
(L.O.C.)	75	13	18	6	52	24	47	158	281	43	180	16	4
	(96)	(17)	(23)	(8)	(66)	(31)	(60)	(202)		(55)	(230)	(20)	(5)
(K.F.)	77	11	17	11	40	18	37	117	171	42	347	25	6
	(87)	(12)	(19)	-	-	-	-	(132)		-	(391)	(28)	-

Note:
1. Major elements as oxides in %.
2. Minor elements in p.p.m.
3. Values in parenthesis are carbonate free.
4. Values in parenthesis with asterisk mark are only dolomite free.

TABLE (4.2B): Average values of mineral abundances in different parts of the Oxford Clay and Kellaways Formations, in Warlingham Borehole sediments.

	Quartz	Calcite	Dolomite	Pyrite	Total Clays	* Illite	* Kaolinite	* Chlorite	* M/Layer	+ Illite	+ Kaolinite	+ Chlorite	+ M/Layer
	%	%	%	%	%	%	%	%	%	%	%	%	%
(U.O.C.)	20·41	26·86	10·82	1·04	40·29	66·50	7·69	4·72	21·00	26·80	3·10	1·90	8·46
(M.O.C.)	18·63	25·95	4·70	1·78	47·81	66·26	12·26	6·68	14·74	31·68	5·86	3.19	7·04
(L.O.C.)	18·06	17·96	3·67	1·94	54·43	65·41	14·47	5·94	14·12	35·60	7·87	3·23	7·68
(K.F.)	40·70	9·83	1·45	3·03	42·70	62·00	23·70	3·90	10·40	26·78	10·12	1·66	4·78

Note: * Clay mineral abundances as calculated in $<2\mu$ fraction.
+ " " " " " " bulk rock samples.

TABLE (4.2C): Ratios of elements in the different parts of the sediments of Oxford Clay and Kellaways Formations, Warlingham Borehole samples.

	$\frac{SiO_2}{Al_2O_3}$	$\frac{Quartz}{Zr}$	$\frac{TiO_2}{Al_2O_3}$	$\frac{TiO_2}{Zr}$	$\frac{Al_2O_3}{Na_2O}$	$\frac{Mg}{Al}$	$\frac{Al_2O_3}{SiO_2}$	$\frac{Al_2O_3}{{}^{1}Combd\ SiO_2}$	$\frac{Al_2O_3}{TiO_2}$	$\frac{{}^{2}Fe_2O_3}{Al_2O_3}$	$\frac{Mn}{Fe}$	$\frac{Quartz}{C_{org}}$	$\frac{Quartz}{{}^{1}Combd\ SiO_2}$
(U.O.C.)	3·66	1275·6	0·057	38·12	35·6	0·31	0·273	0·57 *(0·48)	17·43	0·34	0·008	35·81	1·09
(M.O.C.)	3·22	1083·2	0·055	41·28	38·2	0·22	0·311	0·56 *(0·51)	18·31	0·30	0·006	16·49	0·80
(L.O.C.)	2·96	1004·4	0·050	42·22	39·7	0·18	0·337	0·57 *(0·54)	19·84	0·23	0·005	4·59	0·68
(K.F.)	5·19	1171·2	0·058	19·88	28·4	0·098	0·197	0·56 *(0·52)	17·29	0·32	0·003	17·85	1·93

	V/Al	$\frac{V}{Mg}$	$\frac{Cr}{V}$	$\frac{Fe^{3+}}{Fe^{2+}}$	$\frac{Na}{K}$	$\frac{K_2O}{Al_2O_3}$	$\frac{K}{Rb}$	$\frac{K}{Ba}$	$\frac{Cr}{Al}$	$\frac{Cr}{Mg}$	Ba/K	Ba/K+Na	Rb/K
(U.O.C.)	0·0020	0·006	0·98	4·160	0·113	0·220	163·33	93·78	0·0018	0·006	0·0107	0·0096	0·0061
(M.O.C.)	0·0015	0·007	0·93	2·085	0·122	0·190	151·65	76·95	0·0014	0·006	0·0130	0·0116	0·0066
(L.O.C.)	0·0013	0·007	1·31	1·462	0·133	0·169	133·56	75·33	0·0016	0·009	0·0132	0·0117	0·0075
(K.F.)	0·0014	0·014	1·365	0·78	0·163	0·193	163·25	46·93	0·0018	0·019	0·0213	0·0183	0·0061

/contd.over

TABLE (4.2C) contd.

	$Cu/Al \times 10^3$	$\frac{Ni}{C_{org}} \times 10^3$	$\frac{Ni}{Al} \times 10^3$	$Ga/Al_2O_3 \times 10^{-4}$	$Th/Al \times 10^4$	$Th/K \times 10^4$	Zr/Th	Al/Th	$\frac{\sum Ce/2}{Y}$	$\frac{\sum Ce}{Y}$
(U.O.C.)	3·00	8·07	8·14	1·59	1·59	4·59	17·78	628·00	1·875	3·75
(M.O.C.)	2·50	3·18	5·23	1·31	1·45	4·81	17·20	688·00	1·728	3·46
(L.O.C.)	3·00	1·19	5·89	1·19	1·63	6·14	13·85	613·84	1·512	3·02
(K.F.)	2·85	1·62	5·86	1·17	1·74	5·76	31·54	573·91	1·476	2·95

suggest that silica occurs in these sediments as detrital quartz and also as combined silica in clay minerals.

b) Titanium

The contents of TiO_2 in the sediments of the Oxford Clay and Kellaways Formations from the Warlingham Borehole showed a range from 0·17 to 0·90%. The average contents of TiO_2 of 78 samples on an absolute and a carbonate free basis are 0·68% and 0·96% respectively. The abundance of TiO_2 of these sediments shows good agreement with the TiO_2 abundances of the sediments reported by other workers, and are tabulated in Table (4.3). The distribution of TiO_2 in the divisions of the Oxford Clay and Kellaways sediments is also shown in Table (4.2A), where it shows its highest concentration (0·76%) in the sediments of the Lower Oxford Clay.

The highest value of TiO_2/Al_2O_3 ratio (0·058) exists in the sediments of the Kellaways Formation. The TiO_2/Al_2O_3 ratio for the sediments of the Oxford Clay Formation shows a gradual increase, being 0·05 in the sediments of the Lower Oxford Clay and 0·057 in the sediments of the Upper Oxford Clay. The variation of TiO_2/Al_2O_3 ratios are shown in Table (4.2C); which suggests that the coarsest grained sediments compose the Kellaways Formation and the sediments of the Oxford Clay Formation gradually change from mud-rocks to silty sediments, from the Lower Oxford Clay to the Upper Oxford Clay. The distribution of quartz in these sediments, shown in Table (4.2B), also confirms the above thesis. From Table (4.2B) it is clear that the highest concentration (40·70%) of quartz is in the sediments of the Kellaways Formation, which supports the grain size study of these sediments. The distribution of quartz and organic carbon, as shown in Table (4.2B), shows an antipathetic relationship of these components in the sediments of the Oxford Clay Formation. The Upper Oxford Clay shows the highest and lowest contents of quartz (20·4%) and organic carbon (0·56%) respectively. On the other hand, the Lower Oxford Clay sediments show the lowest and highest concentrations of quartz (18%) and organic carbon (3·90%) respectively. These observations support the views expressed above regarding the grain size of the sediments.

The TiO_2/Al_2O_3 ratio, according to MIGDISOV (1960), is a

TABLE (4.3): Comparison of the abundance of elements of sediments of the Oxford Clay and Kellaways Formations from the (W.K.B.) and (W.B.), with the values in sedimentary rocks, reported by other workers.

Major Elements as Oxides %	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	50·91	59·10	58·39	59·70	46·85	38·97	55·90	52·03	43·89	61·82	46·85	58·40
TiO_2	0·45	0·90	0·77	0·70	1·10	0·49	0·69	0·84	0·68	0·96	0·88	0·77
Al_2O_3	17·38	19·30	15·10	13·40	20·78	10·73	15·26	22·64	12·36	17·40	23·61	15·10
Fe_2O_3	6·72	7·10	6·75	8·30	7·40	5·28	7·59	5·63	3·67	5·32	5·32	6·73
CaO	3·50	2·10	3·09	9·80	1·96	17·54	-	0·91	15·12	-	0·54	3·12
MgO	2·32	1·70	2·49	2·32	1·69	1·12	1·59	1·88	2·44	3·15	2·12	2·32
Na_2O	1·21	0·60	1·29	0·40	0·44	0·55	0·78	0·68	0·34	0·44	1·01	1·31
K_2O	3·01	4·30	3·20	2·63	2·75	2·00	2·84	3·45	2·43	3·14	4·10	3·25
P_2O_5	0·17	0·13	0·16	0·10	0·62	0·15		1·31	0·11	0·15	1·54	0·17
S	0·25	-	0·24	n.d.	2·70	2·16		0·35	0·89	1·24	n.d.	-
C_{org}	0·10	-	-	1·72	2·57	2·40		1·60			n.d.	-
Minor Elements (p.p.m.)												
V	130	131	130	121	160	101	143	196	102	155	202	120
Cr	100	n.d.	90	86	129	118	166	192	110	157	191	-
Mn	850	767	850	382	250	467	691	196	157	244	174	620
Ni	80	61	68	48	66	53	75	70	42	60	73	24
Ba	600	533	580	283	485	214	298	421	265	368	458	460
Ce	70	82	59	76	n.r.	50	70	98	72	104	73	-
La	40	52	92	38	n.r.	29	40	65	45	65	40	-
Th	12	13	12	n.d.	n.r.	10	14	16	10	15	13	-

/contd.over

TABLE (4.3) contd.

Minor Elements (p.p.m.)	1	2	3	4	5	6	7	8	9	10	11	12
Pb	20	30	20	36	21	51	76	84	18	26	25	20
As	10	23	13	22	n.r.	12	17	7	13	20	6	-
Zn	90	95	95	118	94	430	623	253	68	95	88	-
Cu	50	22	45	37	41	19	27	26	19	26	27	-
Rb	140	176	140	125	n.r.	99	138	224	132	186	261	-
Sr	400	307	300	n.d.	250	347	-	151	256	-	105	170
Y	35	33	26	31	n.r.	28	40	32	35	49	27	-
Zr	180	245	160	214	175	157	225	154	191	264	158	-
Nb	15	15	11	22	n.r.	13	18	20	18	26	18	-
Mo	2	n.d.	2·6	8	3·7	*7·5		4·5	$^{+}$10		1	-
Ga	25	21	19	16	22	n.d.	n.d.	n.d.	17	24	n.d.	-

/contd.over

Explanation of Table (4.3)

1. Average elements abundance in shales (KRAUSKOPF, 1979)
2. " " " " Red bed mudstones (COSGROVE, 1973)
3. " " " " shales (TURIKIAN & WEDEPOHL, 1961)
4. " " " " Corallian mud-rocks (CHOWDHURY, 1980)
5. " " " " Whitbian shales (GAD et al. 1969)
6. " " " " 63 samples of the Oxford Clay and Kellaways Formations (W.K.B.) absolute values
7. " " " " " " " " " " " " " " carbonate free values
8. " " " " 12 " " " " " " " " in Clay fraction ($<2\mu$) from (W.K.B.)
9. " " " " 78 " " " " " " " " (W.B.) absolute values
10. " " " " " " " " " " " " " " carbonate free values
11. " " " " 12 " " " " " " " " " Clay fraction ($<2\mu$) values
12. " " " " shales reported by RANKAMA and SAHAMA (1950).

* Average value of 18 samples

\+ " " " 14 "

n.d. = not detected

n.r. = not reported.

measure of climate. The TiO_2/Al_2O_3 ratios of the Warlingham Borehole sediments showed similar trends to those exhibited by the Winterborne Kingston Borehole sediments. Values of TiO_2/Al_2O_3 ratios for the sediments of both the boreholes are given in Tables (4.1A and 4.2A) respectively. The concentrations of TiO_2(0·76%) and Al_2O_3 (15·08%), being highest in the sediments of the Lower Oxford Clay, suggest a humid type of climate for that period. The concentration of kaolinite also indicates a humid nature of climate. The sediments of the Lower Oxford Clay show the highest concentration of kaolinite (14·50%), which also supports the views about the climate. The distribution of kaolinite is shown in Table (4.2B).

The TiO_2/Zr ratio showed its lowest value (19·88) in the sediments of the Kellaways Formation and a constant trend in the three divisions of the Oxford Clay Formation, as is shown in Table (4.2C). The sediments of the Oxford Clay Formation show a much higher value of the TiO_2/Zr ratio as compared to the sediments of the Kellaways Formation. This variation of the TiO_2/Zr ratio in the sediments suggests two different sources of these sediments. This ratio in the Warlingham Borehole samples shows an opposite trend when compared with the trends in the Winterborne Kingston Borehole sediments. The antipathetic trend of this ratio in the sediments of the two boreholes indicates that at the time of deposition different sources were available to the two localities throughout the sequence.

The concentrations of TiO_2, Al_2O_3 and total clays in the three divisions of the Oxford Clay Formation follow an increasing trend, as is shown in Tables (4.2A and 4.2B). All these components show an increasing trend from the Upper to the Lower Oxford Clay, indicating a strong relationship between these components. By examination of the correlation coefficient matrix for each division of the Oxford Clay sediments, it becomes clear that TiO_2 shows a very strong positive correlation with Al_2O_3 ($r = +0{\cdot}92$) and total clays ($r = +0{\cdot}87$), significant at the 0·01% level in both cases. From this observation, it becomes clear that these components are very strongly associated in the total population of the Oxford Clay sediments. A strong correlation of TiO_2 with Al_2O_3 ($r = +0{\cdot}76$) and total clays ($r = +0{\cdot}76$) also exists in the total population of the Kellaways sediments. The correlation coefficient of TiO_2 with kaolinite ($r = +0{\cdot}61$), highly significant at an 0•01% level, occurs in the sediments of the Oxford Clay population, but in the Kellaways sediments the TiO_2 shows a negative correlation coefficient with kaolinite (r = -0•08). This indicates that TiO_2 occurs independently or in clay mineral species other than kaolinite in the sediments of the Kellaways Formation. On the contrary, TiO_2 showed a very strong association with kaolinite and total clays in the sediments of the Oxford Clay Formation. The relationship of TiO_2 with kaolinite in the sediments of the two boreholes is shown in Table (4.3A), in which abundances of TiO_2 and kaolinite of some of the samples, representing the complete sequence of the two boreholes, are tabulated.

In the total population of the Oxford Clay and Kellaways sediments, TiO_2 shows a very strong positive correlation, shown in the Appendix (4.2C), with depth, Si, Al, Na, K, Rb, Ba, V, Th, Y, H_2O, total clays and chlorite; all correlations significant at an 0•01% confidence level. It also shows a strong positive correlation, significant at an 0•1% level, with Ce (r = +0•40), kaolinite (r = +0•38) and a weak positive correlation, significant at 1-5% confidence levels, with Zr (r = +0•33), La (r = +0•37), Cr(r = +0•33), and total Fe_2O_3 (r = +0•22), Cu (r = +0•24), Pb (r = +0•23), Ni (r = +0•26), Ga (r = +0•28), Nb (r = +0•23) and organic carbon (r = +0•25). TiO_2 shows a very strong negative correlation, significant at an 0•01% confidence level, with Mg, Ca, CO_2, calcite, dolomite and mixed-layered minerals.

The correlation coefficient of TiO_2 with total clays (r = +0•82), Al_2O_3 (r = +0•89) and K_2O (r = +0•67), on the whole suggests its very strong association with clays in the sediments of the Warlingham Borehole. The strong relationship of TiO_2 with total clays, for the Winterborne Kingston Borehole sediments, is illustrated in Figure (4.1b); a similar association is present in the sediments of the Warlingham Borehole.

The abundance of TiO_2 in these sediments showed a good agreement with TiO_2 abundances in the sediments reported by other workers, and are tabulated in Table (4.3).

TABLE (4.3A): Distribution of TiO_2 and Kaolinite in some of the Representative Samples of the Oxford Clay and Kellaways Formations of the two Boreholes

	WINTERBORNE KINGSTON BOREHOLE SEDIMENTS			WARLINGHAM BOREHOLE SEDIMENTS		
	Sample No.	% TiO_2	% Kaolinite	Sample No.	% TiO_2	% Kaolinite
UPPER OXFORD CLAY	WBK-01	0.32	3	BR-115	0.51	0
	WBK-05	0.26	3	BR-129	0.25	0
	WBK-07	0.34	5	BR-199	0.72	2
	WBK-15	0.45	14	BR-236	0.57	12
	WBK-22	0.48	14	BR-278	0.49	10
	WBK-26	0.52	21	BR-543	0.78	10
				BR-706	0.78	11
MIDDLE OXFORD CLAY	WBK-28	0.58	18	BR-820	0.42	13
	WBK-30	0.50	14	BR-855	0.67	12
	WBK-33	0.43	17	BR-920	0.79	12
	WBK-36	0.56	21	BR-1008	0.55	10
	WBK-38	0.59	17	BR-1157	0.79	11
				BR-1339	0.75	11

/contd.over

TABLE(4.3A) contd.

	WINTERBORNE KINGSTON BOREHOLE SEDIMENTS			WARLINGHAM BOREHOLE SEDIMENTS		
	Sample No.	% TiO_2	% Kaolinite	Sample No.	% TiO_2	% Kaolinite
LOWER OXFORD CLAY	WBK-43	0.57	18	BR-1424	0.70	12
	WBK-50	0.64	22	BR-1513	0.77	16
	WBK-51	0.66	26	BR-1636	0.80	13
	WBK-53	0.65	21	BR-1683	0.81	14
				BR-1713	0.82	14
				BR-1750	0.78	16
KELLAWAYS FORMATION	WBK-54	0.65	19	BR-1755	0.67	14
	WBK-56	0.66	19	BR-1771	0.88	15
	WBK-59	0.63	21	BR-1811	0.39	33
	WBK-63	0.67	23	BR-1831	0.71	26
	WBK-65	0.65	22	BR-1852	0.65	34
				BR-1877	0.81	31
				BR-1890	0.90	30

c) Aluminium

The contents of Al_2O_3 in the Warlingham Borehole sediments vary from 2·95 to 20·81%. The average contents of 78 samples on an absolute and a carbonate free basis are 12·36% and 17·4% respectively. The distribution of Al_2O_3 in the sequence is variable and the lowest (10.7%) and highest (15·08%) contents of Al_2O_3 are present in the Upper and Lower Oxford Clay sediments respectively. The Kellaways sediments showed the lowest concentration (11·93%) of Al_2O_3 when they are compared with the average contents (12·93%) of total population of the Oxford Clay sediments. The distribution of Al_2O_3 appears to be controlled by the contents of total clays and species of the clay minerals. The distributions of Al_2O_3 and minerals in the sediments of the Oxford Clay and Kellaways Formations are given in Tables (4.2A and 4.2B). The lowest concentration (10·7%) of Al_2O_3 in the sediments of the Upper Oxford Clay is related to the species and abundances of the clay minerals. The Upper Oxford Clay contains the lowest amount of illite (26·80%) and total clays (40·3%). But the mixed-layer clay mineral, having a montmorillonitic component in it, is highest (8·5%). The mixed-layer clay minerals, having a montmorillonitic component, contain less amount of 'Al' in comparison with illite and kaolinite.

The distribution of Al_2O_3 and total clays in the different divisions of the Oxford Clay and Kellaways Formations shows a very good agreement, as is shown in Tables (4.2A & 4.2B). The Lower Oxford Clay showed the highest contents (54·43%) of the total clays, which justifies the highest concentration (15·08%) of Al_2O_3 in these sediments.

The Al_2O_3/SiO_2 ratio also indicates the abundance of total clay present in the sediments. The highest value (0·34) of the Al_2O_3/SiO_2 ratio exists in the sediments of the Lower Oxford Clay, which also showed the highest abundance (54·43%) of the total clays. The lowest value (0·19) of the Al_2O_3/SiO_2 ratio occurs in the sediments of the Kellaways Formation, suggesting depletion of total clays; which is true, and is shown in Table (4.2B).

PETTIJOHN (1957) used the Al_2O_3/Na_2O ratio as a measure of maturity of the sediments. This ratio shows its lowest value (28·4) in the sediments of the Kellaways Formation, indicating less maturity for these sediments; it also suggests that these sediments have suffered less cycles of transportation and sedimentation, as compared to the sediments of the Oxford Clay Formation. The highest value of the Al_2O_3/Na_2O ratio (39·7) exists in the sediments of the Lower Oxford Clay. Amongst the three divisions of the Oxford Clay, the lowest value (35·5) of the Al_2O_3/Na_2O ratio is present in the sediments of the Upper Oxford Clay, suggesting less maturity of these sediments as compared to the sediments of the Lower and Middle Oxford Clay.

The Al_2O_3/combined SiO_2 ratio for the bulk rock samples shows consistency throughout the whole sequence, as is shown in Table (4.2C). This consistency of ratio suggests that the composition of clay minerals in the different parts of the sequence is uniform. But the Al_2O_3/SiO_2 ratio of the clay fraction chemistry shows variation, which is more realistic and is shown in Table (4.2C). The lowest value of this ratio (0·48) is shown by the sediments of the Upper Oxford Clay, when they are compared with the sediments of other divisions of the Oxford Clay, which showed a higher value (av. 0·52). The Al_2O_3/SiO_2 ratio of clay fraction of the Warlingham Borehole sediments shows similar trends as exhibited by the clay fraction samples of the Winterborne Kingston Borehole sediments. All the values of ratios are shown in Tables (4.1C and 4.2C). Although the variation of this ratio in the Warlingham Borehole sediments is not so large as it is in the Winterborne Kingston Borehole sediments, it still shows variation, and suggests similar conclusions regarding the composition of clay minerals, as has been described for the sediments of the Winterborne Kingston Borehole. The lowest contents of Al_2O_3(10·68%) of the Upper Oxford Clay, as well as of the Kellaways (11·93%) sediments, suggest a less intensive chemical weathering in the source areas, when the deposition of these sediments was in progress.

The correlation coefficient matrix in the Appendix (4.2C) shows a very strong positive correlation of Al_2O_3(at an 0·01% confidence level) with depth, TiO_2, K_2O, Na_2O, Th, Rb, Y, Ce, H_2O

and total clays. A strong positive correlation (at an 0·1% confidence level) is also displayed by Al_2O_3 with components including organic carbon, SiO_2, Fe_2O_3(total iron), Cr and La. Al_2O_3 shows a very strong negative correlation (at an 0·01% confidence level) with CaO, CO_2, dolomite, calcite and mixed-layer clay minerals.

The correlations mentioned above strongly suggest that Al_2O_3 in these sediments is mainly associated with the lattice-held fraction, i.e. total clays. The results of the acetic acid and hydroxylamine hydrochloride leaching (CHESTER & HUGHES, 1967) also showed 98% amount of Al_2O_3 associated with the lattice-held fraction. The strong association of Al_2O_3 with total clays (lithogenous fraction) is also indicated by very strong positive correlation of Al_2O_3 with the lithophile elements, particularly Rb (r = +0·95), Ti (r = +0·88), K (r = +0·72) and H_2O (r = +0·73). The strong relationship of Al_2O_3 with total clays is very well illustrated in Figure (4.9a), which shows an intercept of +1·15, indicating that 1·15% Al_2O_3 is not associated with the total clays. The amount of Al_2O_3 associated with total clays may be obtained by subtracting 1·15% from the average value (12·36%) of Al_2O_3; and it will thus be 11·21%. This amount represents 90·7 $\equiv$ 91% of the total Al_2O_3, which is not very far from the 98% value given by the leaching study results. The remaining amount of Al_2O_3 may be associated with the minor amount of feldspars present in these sediments. The very strong negative correlations of Al_2O_3 with CaO (r = -0·73), dolomite (r = -0·54), calcite (r = -0·50) and mixed-layer clay minerals (r = -0·50), all correlations being highly significant at an 0·01% confidence level, strongly confirm the above conclusions. The abundance of Al_2O_3 in these sediments is compared in the Table (4.3), which also shows the abundances of Al_2O_3 in sediments reported by other workers.

d) Iron

The contents of total Fe_2O_3 in the Warlingham Borehole sediments vary from 1·02 to 9·29%. The average contents of 78 samples on an absolute and a calcite-free basis are 3·67% and 5·32% respectively. The distribution of Fe_2O_3 in the different parts of the studied

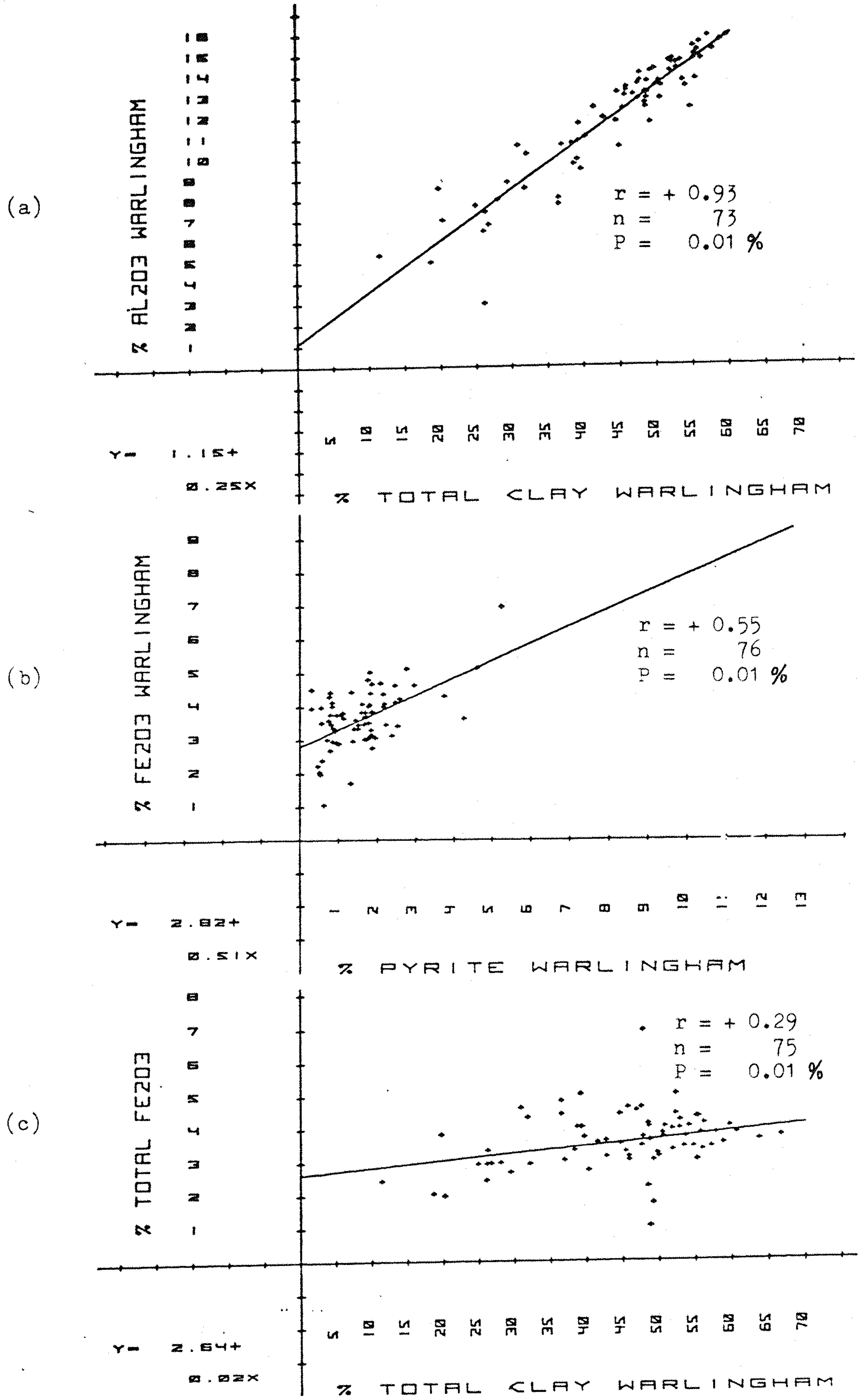

(a)
% AL2O3 WARLINGHAM
r = + 0.93
n = 73
P = 0.01 %
Y= 1.15+
0.25X
5 10 15 20 25 30 35 40 45 50 55 60 65 70
% TOTAL CLAY WARLINGHAM
(b)
% FE2O3 WARLINGHAM
1 2 3 4 5 6 7 8 9
r = + 0.55
n = 76
P = 0.01 %
Y= 2.82+
0.51X
1 2 3 4 5 6 7 8 9 10 11 12 13
% PYRITE WARLINGHAM
(c)
% TOTAL FE2O3
1 2 3 4 5 6 7 8
r = + 0.29
n = 75
P = 0.01 %
Y= 2.64+
0.02X
5 10 15 20 25 30 35 40 45 50 55 60 65 70
% TOTAL CLAY WARLINGHAM

FIG.(4.9)

sequence is shown in Table (4.2A). It showed the highest concentration (5·81%, calcite free basis) in the sediments of the Upper Oxford Clay and its lowest concentration (4·28%) in the sediments of the Kellaways Formation. Like the Winterborne Kingston Borehole sediments, the Warlingham Borehole sediments also contain Fe_2O_3 in the sulphide phase (pyrite), lattices of the clay minerals, and also in the form of free Fe_2O_3, as oxides/hydroxides of Fe-Mn, adsorbed on the surfaces of the detrital components and clay minerals. It is also associated with organic carbon.

The total Fe2O3 has been sub-divided into FeO, associated with sulphides (pyrite), and the residual iron as Fe_2O_3, associated with clays and other detrital components, present either in their lattice structure or adsorbed as amorphous iron-oxide on detrital components, and also with organic carbon. The highest concentration (2·85%) of the residual Fe_2O_3 occurs in sediments of the Upper Oxford Clay and the lowest contents (1·57%) in the sediments of the Kellaways Formation. Sediments of the Kellaways Formation showed the presence of the highest concentrations of FeO (1·41%) and pyrite (3·03%).

The highest value (0·34) of the Fe_2O_3/Al_2O ratio occurs in the sediments of the Upper Oxford Clay. This ratio shows a decreasing trend with depth, as is shown in Table (4.2C), indicating that the clays of the Upper Oxford Clay are associated more strongly with Fe_2O_3. The lowest value (0·23) of the Fe_2O_3/Al_2O_3 ratio exists in the sediments of the Lower Oxford Clay, which also show the highest contents of pyrite. The clay fraction samples showed a similar trend of the Fe_2O_3/Al_2O_3 ratios. The highest value of the ratio (0·26) exists in the samples from the Upper Oxford Clay, and the lowest value of the ratio (0·17) in the sediments of the Lower Oxford Clay.

The Mn/Fe ratio, an indicator of the depositional environments (SPEARS, 1964), shows in Table (4.2C) similar trends to those exhibited by the sediments of the Winterborne Kingston Borehole, which already are described in this chapter (see 4.1d). The calcite showed a very strong positive correlation, significant at an 0·01% confidence level, with Mn^{+2}, indicating that replacement of Ca^{+2} by Mn^{+2} was preferred rather than the substitution of Ca^{+2} by Fe^{+2}, as described by RANKAMA and SAHAMA (1950).

The correlation coefficient matrix of the total population of samples is given in the Appendix (4.2C), which shows that total Fe_2O_3 is very strongly correlated positively (at an 0·01% level) with S, Mo, Fe^{+2}, V and pyrite. Its strong relationship with pyrite is illustrated in Figure (4.9b). It also shows a strong positive correlation (at an 0·1% level) with Cr, K, Al, H_2O, illite, mixed-layer clay minerals, indicating its association with clays. A strong relationship of Fe_2O_3 and total clays is shown in Figure (4.9c).

The residual iron (Fe_2O_3) in the total population of samples showed a very strong positive correlation (at an 0·01% level) with Mg, V and Mn, indicating its association with clays in their lattices and also the presence of Fe-Mn, oxides/hydroxides coating the surfaces of the clay minerals. The residual iron (Fe_2O_3) showed its strongest positive correlation with kaolinite ($r = +0{\cdot}38$), which supports the idea of the presence of Fe-Mn, oxides/hydroxides coating the fine grains of kaolinite. The residual iron (Fe_2O_3) shows its strongest negative correlation (at an 0·01% level) with depth ($r = -0{\cdot}42$), which indicates that the residual iron (Fe_2O_3) is present, mainly in the sediments of the Upper Oxford Clay.

The very strong positive correlation of FeO (at an 0·01% level) with S, Mo, organic carbon, H_2O^+ and pyrite, indicates a very strong relationship of FeO with the minerals of sulphide phase, particularly pyrite, which originates under the reducing (anoxic) conditions. The strong positive correlations (at an 0·01% level) of FeO with Mo ($r = +0.77$) and organic carbon ($r = +0.49$) strongly support these views. The Fe^{+3}/Fe^{+2} ratios highest value (4·16) exists in the sediments of the Upper Oxford Clay, indicating the presence of oxic conditions in these sediments, which supports the idea of the presence of iron as free iron oxides/hydroxides in these sediments. The Fe^{+3}/Fe^{+2} ratio showed a decreasing trend with depth in the borehole, as is shown in Table (4.2C), suggesting that more residual iron (Fe_2O_3) is associated with clays and less with pyrite in the sediments of the Upper Oxford Clay.

The distribution of total iron (Fe_2O_3) in different phases, e.g. pyrite, total clays, organic carbon and free oxides/hydroxides, can be calculated by following the same method as applied for the sediments of the Winterborne Kingston Borehole. For these calculations, the required data is as follows:

1) Average contents of total Fe_2O_3 in bulk rock = 3·67% *
2) " " " FeO = 1·13%
3) " " " residual Fe_2O_3 = 2·40%
4) " " " Fe_2O_3 in clay fraction samples = 5·23%
5) " " " total clays = 45·50%
6) " " " " Fe_2O_3 in 45·5% clays = 2·38%

Following is the break-up of the distribution of 3·67% of total Fe_2O_3 in the above-mentioned phases.

i) Fe_2O_3 associated with clays = 1·03%
ii) " " " pyrite = 0·85%
iii) " " " clays as Fe^{+3} = 1·35%
iv) " " " organic carbon as Fe^{+2} = 0·41%
TOTAL = 3.64% *

(* In view of the relatively low agreement in the similar calculation for the Winterborne Kingston Borehole samples, it is worth mentioning that the discrepancy above (0·03%; $<$ 1%) is insignificant.)

The abundance of Fe_2O_3 in these sediments is compared in Table (4.3) with the abundances of Fe_2O_3 in sediments reported by other workers.

e) Magnesium

The contents of MgO in the Warlingham Borehole sediments vary from 0 to 7·04%. The average contents of 78 samples on an absolute and on a calcite free basis are 2·44% and 3·15% respectively. GOLDSCHMIDT (1954) reported that marine shales contain from 1·5 to 2·5% MgO. The samples of the Warlingham Borehole sediments show higher contents of MgO than its contents in the Winterborne Kingston Borehole sediments, due to the presence of dolomite, which is absent in the sediments of the Winterborne Kingston Borehole. The abundances of MgO in sediments of the Oxford Clay and the Kellaways Formations, of the two boreholes, are shown in Table (4.3).

The distribution of MgO in the studied sequence shows its highest concentration (2·92%) in the sediments of the Upper Oxford

Clay which also contain the highest amounts of dolomite (10·82%) and mixed-layer (illite-montmorillonite) clay minerals (21%). The mixed-layer (illite-montmorillonite) clay minerals contribute the highest fraction (8·5%)of the total clays.

The highest value (0.31) of the MgO/Al_2O_3 ratio occurs in the sediments of the Upper Oxford Clay and the lowest (0·098) in the sediments of the Kellaways Formation, indicating that Mg^{+2}-containing clays are abundant in the sediments of the Upper Oxford Clay. The mixed-layer (illite-montmorillonite) clay mineral shows the highest concentration in the Upper Oxford Clay. Its abundance decreases in the borehole with depth, as is shown in Table (4.2B). Mixed-layer (illite-montmorillonite) clay mineral and chlorite, which are the possible sites for the residence of Mg^{+2}, showed their lowest abundance in the sediments of the Kellaways Formation. There is a decrease of the montmorillonitic component in the mixed-layer (illite-montmorillonite) minerals with the increase of the depth in the borehole.

The correlation coefficient matrix in the Appendix (4.2C) shows a very strong positive correlation (at the 0·01% confidence level) of MgO with dolomite, mixed-layer (illite-montmorillonite) clay minerals, CO_2, Mn and V, suggesting its strong association with dolomite and mixed-layer (illite-montmorillonite) clay minerals. Figure (4.10a) shows a very strong positive correlation of MgO with dolomite ($r = +0·73$), highly significant at the 0·01% level. The MgO shows a strong negative correlation (at an 0·01% level) with depth, Si, Zr, kaolinite and quartz, suggesting a non-detrital origin of MgO. According to KAHLE (1965), montmorillonite could exchange Ca^{+2} for Mg^{+2} or it may lose Mg^{+2} on burial or alteration to illite, and thus enhance the pore-water concentration of Mg^{+2} during burial. The exchange of Ca^{+2} for Mg^{+2} may be reversible ($Ca^{+2} \rightleftharpoons Mg^{+2}$). DREVER (1971) suggested that clays, generally smectite (montmorillonite rich mixed-layer), in anoxic sediments take up magnesium. He stated that 1 gm. of smectite can incorporate 0·01 gm. of Mg^{+2} in its lattices. In the presence of free hydrogen sulphide (or $H\bar{S}$), iron (Fe^{+2}) is extracted from clay minerals to form sulphides (pyrite), and Mg^{+2} from the surrounding sea-water or interstitial waters enters the clay mineral structure to fill the vacant sites. The similar ionic radii of Fe^{+2} (0·86Å) and Mg^{+2} (0·80Å) facilitates this replacement.

The Oxford Clay sediments contain pyrite throughout the succession. It is therefore possible that the present mixed-layer mineral (illite-montmorillonite) of the Warlingham Borehole sediments was very much like the smectite (montmorillonite-illite) of the Winterborne Kingston Borehole sediments. At the time of deposition, or immediately after the burial, the mixed-layer minerals concentrated Mg^{+2} according to the mechanism described above. Later the Mg^{+2} was released by Fe^{+2} substitution to form dolomite. The smectite (montmorillonite-illite), as a consequence of the release of Mg^{+2}, was converted to the present form (illite-montmorillonite). The mixed-layer mineral of the Warlingham Borehole sediments shows the poorest contents of the montmorillonite component in it, as compared to its counterpart in the Winterborne Kingston Borehole sediments.

From the correlation coefficient matrix given in the Appendix (4.2C) and the Figure (4.10a), it is evident that Mg^{+2} in the Warlingham Borehole sediments resides dominantly in dolomite ($r = +0{\cdot}73$). It also resides in mixed-layer clay minerals ($r = +0{\cdot}54$). Its association with mixed-layer clay minerals is illustrated in Figure (4.10b). A weak positive correlation of MgO with illite ($r = +0{\cdot}18$) suggests that some of the Mg^{+2} has been replaced by Al^{+2} in the octahedral layer of illite, as suggested by DEER _et al_. (1962).

The regression equation for MgO-dolomite, as shown in Figure (4.10a) may be used for interpreting the location of MgO in dolomite and other mineral phases, as follows:

Regression Equation:

$$(\%\ \text{MgO})\quad Y = 1{\cdot}96 + 0{\cdot}08\ X\ (\%\ \text{Dolomite}).$$

This equation gives an intercept of a value of +1·96, indicating that 1·96% MgO of the total MgO contents is not associated with dolomite. The dolomite associated MgO may be obtained by subtracting the value of 1·96 from the total contents of MgO, as mentioned below:

Total contents of MgO = 3·15%

MgO not associated with dolomite = 1·96% (value of intercept)

$\therefore$ MgO associated with dolomite = 3·15 - 1·96 = 1·19%

The dolomite associated MgO = 1·19% $\equiv$ 0·72% Mg^{+2}

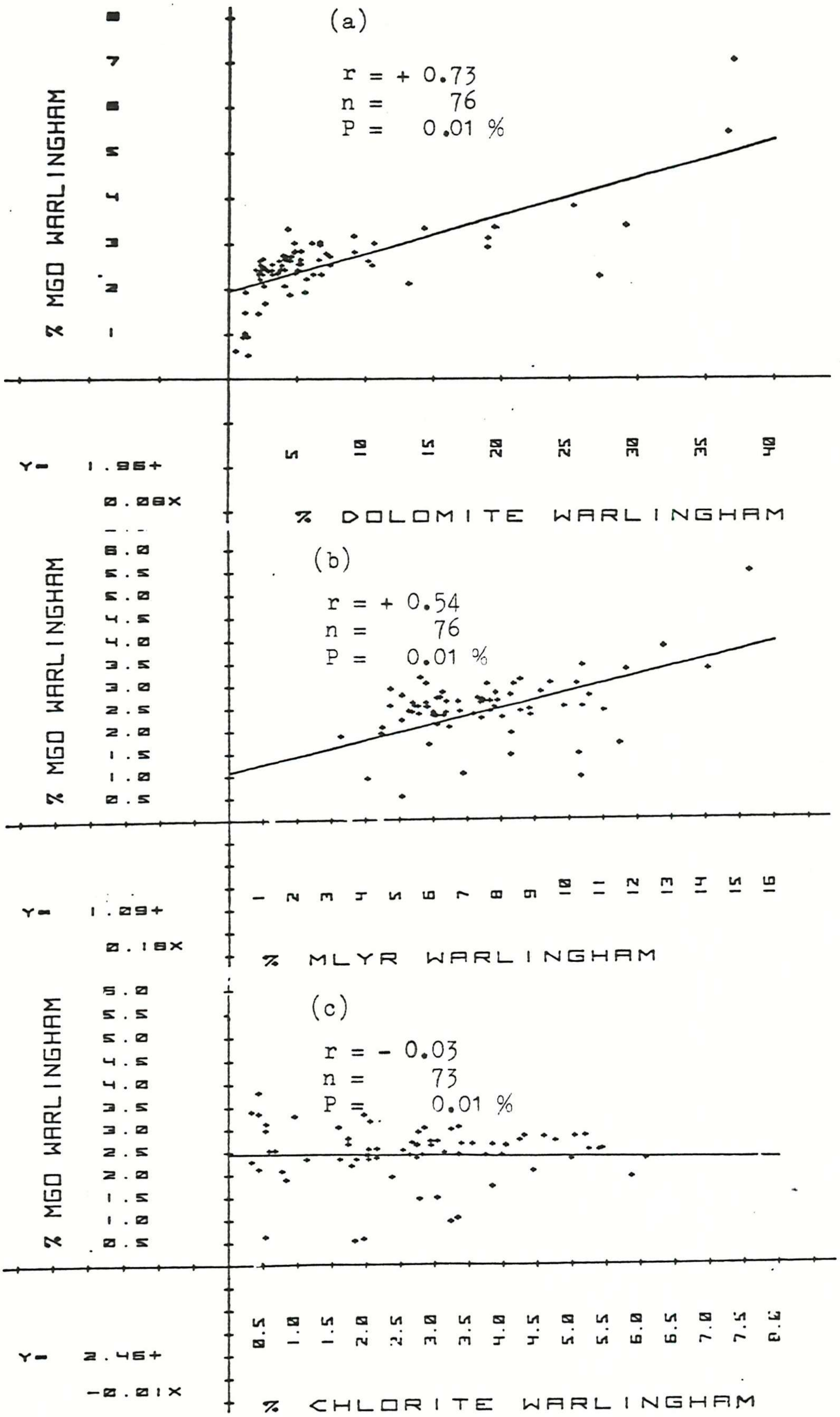

(a)
r = + 0.73
n = 76
P = 0.01 %
% MGO WARLINGHAM
1 2 3 4 5 6 7 8
Y= 1.96+
0.08X
5 10 15 20 25 30 35 40
% DOLOMITE WARLINGHAM
(b)
r = + 0.54
n = 76
P = 0.01 %
% MGO WARLINGHAM
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
Y= 1.09+
0.18X
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
% MLYR WARLINGHAM
(c)
r = - 0.03
n = 73
P = 0.01 %
% MGO WARLINGHAM
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
Y= 2.46+
-0.01X
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
% CHLORITE WARLINGHAM

FIG.(4.10)

The amount of Mg^{+2} required for the formation of dolomite present in the sediments can be calculated if the amount of dolomite is already known. The dolomite of the Warlingham Borehole sediments is a ferroan dolomite. BELLAMY (1980) found similar ferroan dolomite in the Kimmeridgian sediments from the Dorset area. BELLAMY (op.cit.) calculated the necessary amount of Mg^{+2} for the formation of dolomite in the Kimmeridgian sediments (for details see BELLAMY, 1980). According to BELLAMY (op.cit.) 100 gms. Mg^{+2} will produce 1015 gms. of ferroan dolomite. This information is used and an attempt has been made to estimate the amount of Mg^{+2} required for the formation of ferroan dolomite contents of the Warlingham Borehole sediments. The details are as follows:

1015 gms dolomite are produced by 100 gms. of Mg^{+2}

1 gm. " will be " " $\frac{100}{1015}$ = $0{\cdot}0985$ gm.Mg^{+2}

$\therefore$ 6.57 gms. of dolomite of the Warlingham Borehole sediments would need an amount of Mg^{+2} = $6{\cdot}57 \times 0{\cdot}0985$

= $0{\cdot}65\%$ Mg^{+2}.

If the dolomite figure is rounded to the nearest number, i.e. 7%, then the Mg^{+2} required = $7{\cdot}0 \times 0{\cdot}0985$

= $0{\cdot}689\% \equiv 0{\cdot}70\%$ Mg^{+2}

Now: i) Mg^{+2} calculated from the MgO-dolomite regression equation = $0{\cdot}72\%$

ii) Mg^{+2} " " " amount of dolomite = $0{\cdot}70\%$

The two results show an excellent agreement.

The remaining amount of MgO is present in the clay minerals. Mixed-layer clay minerals (illite-montmorillonite) showed the highest positive correlation ($r = +0{\cdot}54$) in the total population of clay minerals in bulk rock. The very strong association of MgO and mixed-layer clay minerals (illite-montmorillonite) is exhibited by the Figure (4.10b). Chlorite present in these sediments showed a weak negative correlation ($r = -0{\cdot}03$), which is shown in Figure (4.10c).

f) Calcium and Carbon Dioxide

The CaO contents of the Warlingham Borehole sediments range between 0•23 and 39•40%. The average value of the CaO contents of 78 samples is 15•12%, slightly lower than the average contents (17•54%) of the Winterborne Kingston Borehole sediments. The reason for the lower contents may be associated with the variation in clay mineral species. These sediments contain mixed-layer (illite-montmorillonite) clay minerals which contain a lower amount of montmorillonitic layers in their structure. As previously described in the study of the Winterborne Kingston Borehole sediments, montmorillonite contains Ca^{+2} in the exchangeable position. These sediments, being deficient in montmorillonite and the contents of total carbonate (26•60%) as compared with the Winterborne Kingston Borehole sediments, they show slightly lower contents of CaO, as is shown in Table (4.3). The clay fraction (average value of 12 samples) showed 0•54% CaO, and the leaching study by acid-reducing agents (CHESTER and HUGHES, 1967) showed an average value of 0•26% CaO (for 11 samples). The leaching study further clarified that most of the CaO resides in the carbonate minerals, e.g. calcite and dolomite. The highest contents of CaO, 0•62%, was found in the residue of sample BR-134, after leaching with the acid-reducing agent. This sample also contains the highest amount (27%) of dolomite in the total population of samples, which received the leaching treatment by the acid-reducing agents. It seems that dolomite during the leaching treatment was not fully attacked by the acidlreducing agents. The lowest value of 0•08% of CaO is shown by sample BR-1771 in the leached residue; this sample contains the highest amount (76%) of total clays, indicating that the total clays of these sediments do not contain much amount of Ca^{+2} in their lattices.

The correlation coefficient matrix, as is given in the Appendix (4.2C), shows the correlation of CaO with other components. Some of the correlations in this matrix are different from those already observed in the Winterborne Kingston Borehole sediments. The most significant difference of correlations in these sediments is exhibited by P_2O_5 ($r = -0{\cdot}26$); a negative correlation, suggesting that phosphorus in these sediments is not associated with carbonates. The very strong positive correlation of CaO (at the 0•01% level) with CO_2, Mn, calcite, total carbonates, dolomite and mixed-layer clay minerals indicates that the main hosts of Ca^{+2} in these sediments are the carbonate minerals, i.e. calcite and dolomite. These two minerals are present in each and every sample.

The very strong positive correlation of CaO with total carbonates (dolomite + calcite) is shown in Figure (4.11a). Some Ca^{+2} is also associated with the mixed-layer (illite-montmorillonite) clay minerals in their exchangeable positions, as has been described earlier in the study of the Winterborne Kingston Borehole sediments. Its association with Mn ($r = +0{\cdot}56$) and Sr ($r = +0{\cdot}37$) seems to be due to its replacement by Mn^{+2} and Sr^{+2}, which is very common in carbonates. The replacement of Ca^{+2} by Mn^{+2} and Sr^{+2} has already been studied and described in the study of the Winterborne Kingston Borehole sediments.

The very strong negative correlations (at the 0•01% level) of CaO with depth, Si, Ti, Al, Na, K, Ba, Th, Rb, Y, Zr, H_2O and kaolinite suggest its negative relationship with clays. A very strong negative correlation of CaO with total clays ($r = -0{\cdot}91$) is illustrated in Figure (4.11b). On the basis of these observations, it may be concluded that the sediments of the Warlingham Borehole contain CaO mainly in the carbonate minerals, e.g. calcite and dolomite. A small amount of CaO is also associated with the mixed-layer (illite-montmorillonite) clay minerals in their lattices.

The stratigraphic distribution of carbonates in Table (4.2B) shows their highest (37•7%)and lowest (11•3%) concentrations in the sediments of the Upper Oxford Clay and Kellaways Formation respectively. The sediments of the Kellaways Formation also contain the highest amounts (40•7%) of quartz and kaolinite (23•7%); the concentration of kaolinite in sediments suggests the action of leaching processes. It is therefore possible that leaching processes were active in the environments at the time of deposition of these sediments and, due to that, the 'Eh-pH' conditions were less suitable for the precipitation of carbonates; and through that, lesser amounts of carbonates were precipitated in these sediments, deposited relatively under shallow water conditions. The highest concentration of carbonates in the sediments of the Upper Oxford Clay suggest that either relatively stronger alkaline conditions existed in the environments at the time of deposition of these sediments, or the rate of loss of CO_2 was

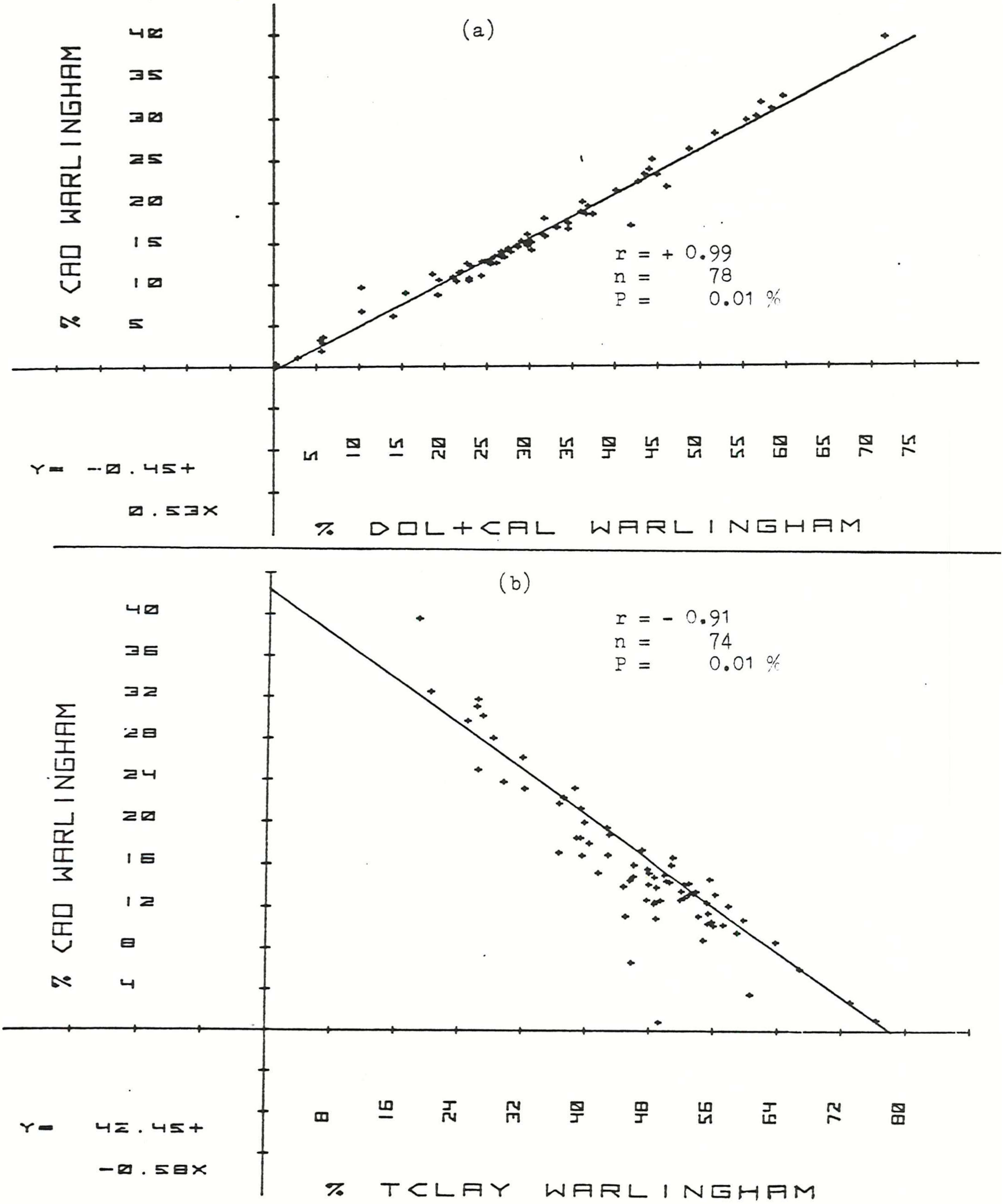

(a)
% CAO WARLINGHAM
40
35
30
25
20
15
10
5
r = + 0.99
n = 78
P = 0.01 %
Y= -0.45+
0.53X
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
% DOL+CAL WARLINGHAM
(b)
% CAO WARLINGHAM
40
36
32
28
24
20
16
12
8
4
r = - 0.91
n = 74
P = 0.01 %
Y= 42.45+
-0.58X
8
16
24
32
40
48
56
64
72
80
% TCLAY WARLINGHAM

FIG.(4.11)

higher. A higher rate of loss of CO_2 in sedimentary environments is generally related to the higher rates of evaporation or photosynthesis.

g) Sodium

The contents of Na_2O of the Warlingham Borehole sediments vary from 0·05 to 0·50%. The average contents of 78 samples on an absolute and carbonate free basis are 0·34% and 0·44% respectively. The average contents of 12 samples of the clay fraction is 1·01%. The sediments of the Warlingham Borehole showed the lowest (0·34%) abundance of Na_2O as compared to the Winterborne Kingston Borehole sediments (0·55%) and other sediments in which its abundance is reported by other workers, which are shown in Table (4.3). The stratigraphic distribution of Na_2O shows its lowest (0·30%) amount in the sediments of the Upper Oxford Clay and highest concentration (0·42%) in the sediments of the Kellaways Formation, as is shown in Table (4.2A). The depletion of Na_2O in the Upper Oxford Clay may be due to the presence of a significantly high amount (8·5%) of the mixed-layer (illite-montmorillonite) and the lowest concentration of illite (26·80%) in the bulk rock. Already it has been described in the study of the Winterborne Kingston Borehole how montmorillonite or mixed-layer containing montmorillonitic component contains smaller amounts of Na^+ in the inter-layer positions. The Upper Oxford Clay shows the highest concentration of the mixed-layer (illite-montmorillonite) clay minerals. The sediments of the Kellaways Formation showed the highest concentrations of Na_2O (0·42), illite (26·9%) and a depletion in the abundance of mixed-layer (illite-montmorillonite) clay minerals (4·8%). The enrichment of Na_2O in the sediments of Kellaways Formation may be related to the abundance of illite. The rate of deposition of sediments of the Kellaways Formation was relatively highest; due to the high rate of sedimentation, Na^{+2} incorporated in the clay minerals of these sediments remained intact, or the exchange rate was probably less, as stated by NICHOLLS and LORING (1960) and SPEARS (1964). The lowest value (0·113) of Na^+/K^+ ratio is shown by the sediments of the Upper Oxford Clay. The sediments of the Oxford Clay Formation, on the whole, showed an average value (0·112) of the Na^+/K^+ ratio, which suggests that, due to the slow rate of deposition of these sediments, some of the Na^+ might have been exchanged by K^+ from the sea-water, through ion-exchange, as stated by SPEARS (op.cit.). The stratigraphic variation of the Na^+/K^+ ratio is shown in Table (4.2C).

The leaching study of these sediments (CHESTER and HUGHES, 1967) shows that only 33% Na_2O of the total Na_2O contents of these sediments is present in the lattice-held fraction of the sediments. That lattice-held fraction is composed of detrital clay minerals, e.g. quartz, feldspar, etc. This study suggests that a significant amount of Na_2O is present in the exchangeable positions of the clay minerals (affected by the acid-reducing agent). Some Na^+ may be present in secondary salts precipitated from the interstitial solutions. Because these samples are borehole samples, some sodium may be contributed by the salts used in drilling muds. The amount of Na^+ present in these salts is liable to be leached out by the attack of acid-reducing agents. Most of the sodium of the lattice-held fraction may be associated mainly in the inter-layers of illite and some in the feldspars.

The correlation coefficient matrix shown in the Appendix (4.2C) indicates a very strong positive correlation of Na_2O (at the 0·01% level) with Si, Ti, Al, K, Ba, Th, Rb, Zr and total clays, and also illite contents in the bulk rock. It has also shown a medium strong positive correlation (at the 1-5% level) with depth, Cr, Ce, La, Y, Nb, H_2O, kaolinite, chlorite and quartz. It also shows a very strong negative correlation (at the 0·01% level) with Ca,CO_2 and calcite, and a strong negative correlation (at the 1-5% level) with Mg, Mn, Sr, mixed-layer clay minerals and dolomite. These correlations strongly suggest that Na_2O in these sediments is mainly associated with total clays, particularly in the inter-layer positions of illite($r = +0·36$) contents present in the bulk rock. This relationship is also illustrated in Figure (4.12b). The positive correlations of Na_2O, as shown in the correlation coefficient matrix in the Appendix (4.2C), with quartz, Zr, Nb, Si and kaolinite tend to suggest that some of the Na_2O in these sediments is also associated with feldspars, probably sodic feldspar, present in minor amounts in these sediments. The presence of feldspars in minor amounts in these sediments has been detected in some of the X.R.D. diffractograms.

A very strong association of Na_2O with total clays is illustrated in Figure (4.12a) by its very strong positive correlation with total clays ($r = +0·75$), highly significant at the 0·01% confidence level. From the regression equation, which shows an intercept of a value of +0.06, it is evident that most of the Na_2O in these sediments is related to total clays. The amount of Na_2O associated with total clays will be 0·28% (i.e. 0·34 - 0·06% = 0·28%). The remaining amount , 0·06% of Na_2O, may be present in phases other than clays.

h) Potassium

The potassium content of the Warlingham Borehole sediments varies from 0·09 to 3·68%. The average contents of 78 samples on an absolute basis is 2·43% and on a carbonate free basis is 3·14%. The potassium contents of the clay fraction is 4·10% (average of 12 samples). The K_2O contents of the Warlingham Borehole sediments in the bulk rock and in the clay fractions is higher than its abundance in the Winterborne Kingston Borehole sediments. The average abundance of K_2O in these sediments is compared with the reported average contents of K_2O in sediments by other workers in Table (4.3). The slightly higher concentration of K_2O in the Warlingham Borehole sediments may be due to higher contents of illite and the lowest amounts of montmorillonite present in the total clays. Montmorillonite usually contains smaller amounts of K_2O and Na_2O in the inter-layer positions as compared to Ca^{+2} and Mg^{+2} (WEAVER and POLLARD, 1973). The association of K^+ and Na^+ with clay minerals has been described earlier in detail, in the study of the Winterborne Kingston Borehole sediments. The leaching study of these sediments by acid-reducing agents (CHESTER and HUGHES, 1967) showed that 90% K_2O of the total K_2O contents resides in the lithogenous fraction of these sediments, which is mainly composed of clay minerals.

The distribution of K_2O and clay minerals species in different parts of the sequence is shown in Tables (4.2A and 4.2B), which clearly indicates that K_2O is strongly associated with the contents of illite in the bulk rock. The Na^+/K^+ ratio shows its highest value (0·163) in the sediments of the Kellaways Formation; according to BLOXAM and THOMAS (1969), it indicates the highest rate of sedimentation and the presence of degraded illite in these sediments. The sediments of the Kellaways Formation contain a higher proportion of sandy-silty material and also the highest concentration of quartz (40·70). The K_2O/Al_2O_3 ratio of these sediments also shows a higher trend, suggesting higher sand fraction in the sediments. The K/Rb ratio also shows variation. The highest value (163·33) of this ratio exists in the sediments

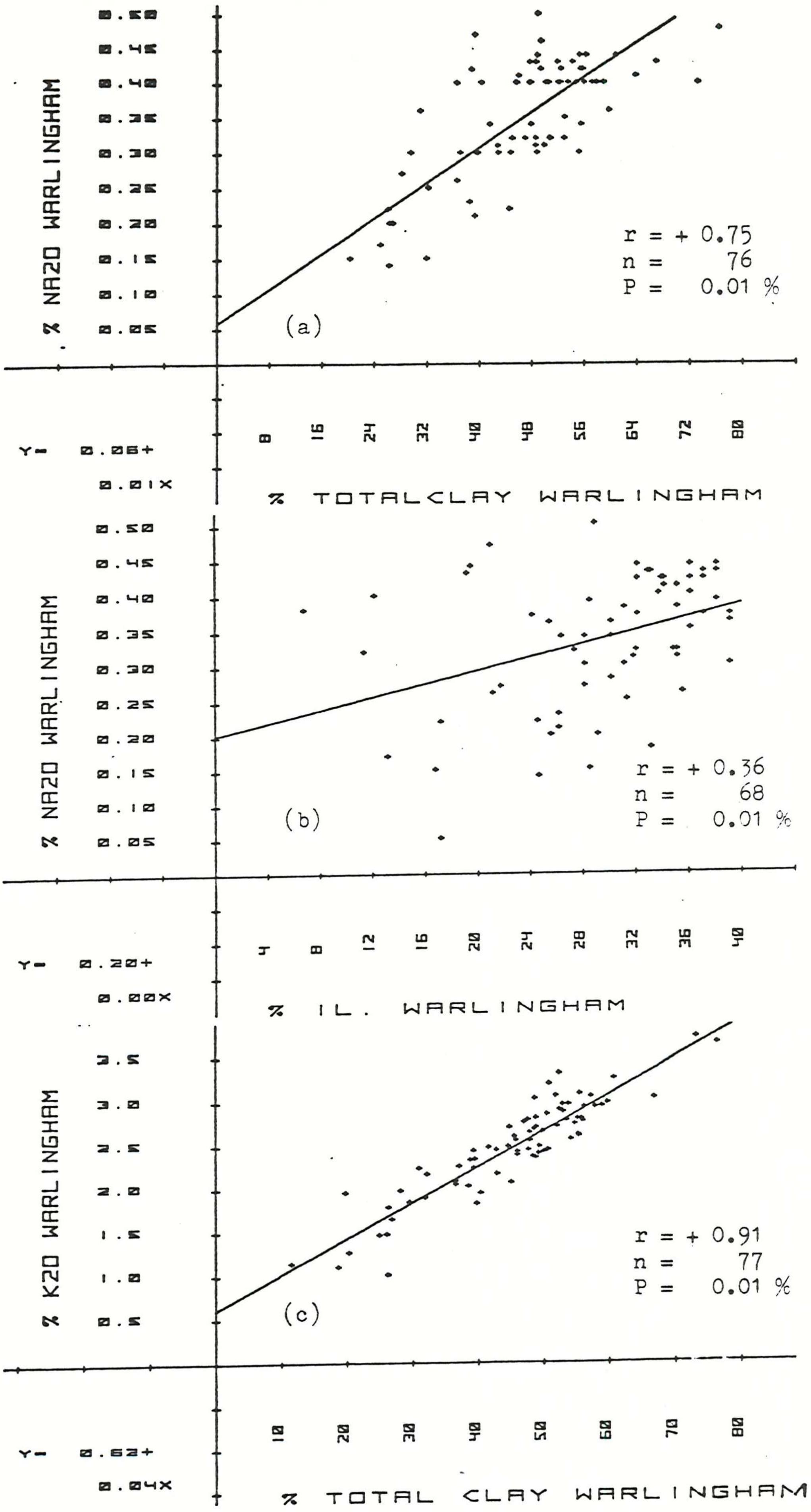

% NA2O WARLINGHAM
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
(a)
r = + 0.75
n = 76
P = 0.01 %
8
16
24
32
40
48
56
64
72
80
Y= 0.06+
0.01X
% TOTALCLAY WARLINGHAM
% NA2O WARLINGHAM
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
(b)
r = + 0.36
n = 68
P = 0.01 %
4
8
12
16
20
24
28
32
36
40
Y= 0.20+
0.00X
% IL. WARLINGHAM
% K2O WARLINGHAM
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(c)
r = + 0.91
n = 77
P = 0.01 %
10
20
30
40
50
60
70
80
Y= 0.62+
0.04X
% TOTAL CLAY WARLINGHAM

FIG.(4.12)

of the Upper Oxford Clay and Kellaways Formation, suggesting that the illite of these sediments differs from the illite present in sediments of other parts of the sequence. The Na^+/K^+ ratio, according to SPEARS (1964), gives an indication of the ion exchange in the sediments. The Na^+/K^+ ratio in the sediments of the Oxford Clay is consistent, and its average value is 0·122, which is much lower than the value (0·163) exhibited by the sediments of the Kellaways Formation. The sediments of the Kellaways Formation show an inversely proportional trend of the contents of Na^+ and K^{+2}. This variation of Na^+ and K^+ in these sediments may be due either to ion exchange or to the presence of feldspars; it may be related to the depletions of illite and total clays. The contents of illite and total clays do not show a great difference as compared to the Upper Oxford Clay, as is shown in Table (4.2B). Thus only two possibilities are left: either ion exchange took place, or sediments of the Kellaways Formation contain feldspar in them. The K^+/Ba^+ ratio, according to WILLIAMS (1965), indicates the paleosalinity and also origin of illite. This ratio is not constant in the divisions of the Oxford Clay. The highest value of K^+/Ba^+ (93·78) occurs in the sediments of the Upper Oxford Clay and the lowest value (46·93) of the ratio in the Kellaways Formation, suggesting the presence of a different type of illite in these sediments.

The correlation coefficient matrix in the Appendix (4.2C) shows a very strong positive correlation (at an 0·01% level) of K_2O with Ti, Al, V, Th, Na, Rb, H_2O and total clays. It also shows a medium strong positive correlation (at the 1-5% level) with total Fe_2O_3, Cr, Ba, La, Ce, Ni, Y, Nb, organic carbon, illite and chlorite. It shows a very strong negative correlation with Ca and calcite. These correlations strongly suggest that K_2O, in these sediments, is mainly associated with total clays, having a stronger relationship with illite.

Figure (4.12c) shows the strong association of K_2O with total clays ($r = +0{\cdot}91$). The distribution of K_2O in total clays and other mineral phases may be calculated in a way similar to that done for the Winterborne Kingston sediments. The regression equation of K_2O - total clays gives an intercept of a value of +0·62, suggesting that 0·62% of the total K_2O in these sediments is not associated with total clays. The amount of K_2O associated with total clays can be obtained as under:

The total contents of K_2O in bulk rock = 2·43%

The value of intercept =+0·62%

∴ The amount of K_2O associated with total clays = 2·43 - 0·62 = 1·81%

The contents of K_2O associated with total clays shows a good agreement with the contents of K_2O associated with the total clays of the Winterborne Kingston Borehole sediments. The Warlingham Borehole sediments show a slightly lower value (1·81%) of K_2O as compared to the Winterborne Kingston Borehole sediments (1·84%). The Winterborne Kingston Borehole sediments contain a higher amount of total clays (56·26%)as compared to the Warlingham Borehole sediments (46·31%). The difference in the contents of total clays explains the variation of K_2O in the sediments of the two boreholes.

The remaining amount of K_2O (0·62%) may be associated with feldspars. The correlations of K_2O with Zr, Nb, quartz, Si, particularly in the Upper and Middle Oxford Clay sediments, suggest the occurrence of feldspars. The remaining amount of K_2O (0·62%) is higher and suggests a higher amount of feldspar in these sediments as compared to the sediments of the Winterborne Kingston Borehole. The amount of K_2O associated with illite may be calculated from the known abundance of illite in these sediments. According to WEAVER and POLLARD (1973), a hundred per cent pure illite contains about 7·02% of K_2O. From this knowledge and the known amount of illite in these sediments, the amount of K_2O associated with illite is calculated as follows:

The average amount of illite = 30·22%

100 per cent pure illite contains K_2O = 7·02%

∴ 30·22% illite will contain K_2O = $\frac{7 \cdot 02}{100} \times 30 \cdot 22 = 2 \cdot 12\%$

i) Sulphur

The Warlingham Borehole sediments show a variation of sulphur contents from 0·24 to 6·79%. The average concentration of sulphur on an absolute basis is 0·89% and on a carbonate free basis is 1·24%. Only one sample, BR-1762, showed a particularly high amount of sulphur (6·79%) and pyrite (12·70%). The Warlingham Borehole sediments show depletion in the contents of sulphur when compared with those of the

Winterborne Kingston Borehole sediments, but a much higher concentration when compared with its reported abundance in sediments by other workers as is shown in Table (4.3). Sulphur deficiency of these sediments is also reflected by the lower concentrations of organic carbon and pyrite, as shown in Tables (3.1 and 3.2). It appears that these sediments were deposited under less reducing conditions with perhaps a lower supply of dissolved SO_4^{-2} and metabolizable organic matter. The role of anaerobic bacteria for the reduction of dissolved sulphate, metabolizable organic matter and the diagenesis of sulphur in sediments, have already been described earlier in detail in the study of the Winterborne Kingston Borehole sediments. The sulphur contents of the Warlingham Borehole sediments showed correlations different from those shown by the Winterborne Kingston Borehole sediments; which are tabulated in the Appendix (4.2C) and described as follows:

The sulphur contents of these sediments show a very strong positive correlation (at an 0·01% level) with Fe_2O_3, Mo, Fe^{+2} and pyrite, suggesting that sulphur in these sediments is mainly associated with iron sulphide, i.e. pyrite (FeS_2). The very high correlation coefficient values of sulphur with pyrite ($r = +0{\cdot}99$) and Fe^{+2} ($r = +0{\cdot}99$) confirm this relationship. The very strong positive correlation of sulphur with Mo ($r = +0{\cdot}77$) may suggest the occurrence of sulphide of molybdenum, probably molybdenite (MoS_2), in minor amounts in these sediments.

The strong positive correlation of sulphur with P_2O_5($r = +0{\cdot}48$) and organic carbon ($r = +0{\cdot}44$) suggests a similar nature of relationship as has been observed and described earlier, during the study of the Winterborne Kingston Borehole sediments. The metals of the chalcophile group (BROWNLOW, 1979), of both the borehole sediments, showed a varied type of relationship and behaviour with sulphur. The Winterborne Kingston Borehole sediments showed a very strong positive correlation of sulphur (at an 0·01% level) with chalcophile metals, including Pb, Cu, Zn, Mo, Ni, suggesting the occurrence of sulphides in these metals in minor amounts. But this association is very poor in the case of the Warlingham Borehole sediments; only a few metals, e.g. Cr ($r = +0{\cdot}36$), Cu, ($r = +0{\cdot}19$) and Ni ($r = +0{\cdot}11$) showed a very weak positive correlation with sulphur. The poor correlation of these metals with sulphur in the Warlingham Borehole sediments suggests that these metals were less concentrated in the environments of the deposition of these sediments.

The sediments of the Kellaways Formation showed the highest concentration of sulphur (1·82%) and pyrite (3·03%) as compared to the three divisions of the Oxford Clay Formation, shown in Tables (4.2A and 4.2B). According to SHISHKINA (1964), the higher rate of accumulation of sediments and their higher organic matter content facilitate the diagenesis of sulphides. The sediments of the Kellaways Formation contain the highest concentrations of quartz, kaolinite and Zr, as is shown in Tables (4.2B and 4.2A); enrichment of these detrital components in these sediments provides significant evidence of a rapid rate of sedimentation. The enrichment of sulphur and pyrite may also be the result of abundantly available dissolved SO_4^{-2} in sea-water, interstitial water, and metabolizable organisms, and the presence of very active anaerobic bacteria, which carried out the reduction of sulphur. PRICE (1976) mentioned that the occurrence of iron sulphide, e.g. pyrite (FeS_2) etc. in marine sediments seems to be dependent on (i) the supply of reactive iron, and (ii) an abundance of metabolizable organic matter. The latter factor is of significant importance; it is required for the growth of sulphate reducing bacteria, which produces H_2S by the reduction of sulphate in sea-water and interstitial water.

It may be concluded that sulphur in the Warlingham Borehole sediments is mainly associated with pyrite (FeS_2), and some amount is also associated with organic carbon. Besides pyrite, the presence of sulphide of molybdenum, in minor amounts, is also expected in these sediments.

j) Phosphorus

The Warlingham Borehole sediments contain a variable amount of P_2O_5 which varies from 0·02 to 0·39%. The average values of 78 samples on an absolute and carbonate free basis are 0·11% and 0·15% respectively. The average contents of 12 samples of the clay and lattice-held fractions of these sediments are 1·54% and 0·04% respectively. The higher contents of P_2O_5 (1·54%) in the clay fraction and the lower contents of P_2O_5 (0 04%) in the lattice-held fraction suggest that in these sediments

P_2O_5 is strongly associated with clays, and a very small amount is present in the lattices of minerals. WEAVER and WAMPLER (1972) mentioned adsorbed phosphorus on the surfaces of the clay minerals. The association of phosphorus and clay minerals may be due to ferric-oxide coatings on the clay minerals, which is a well known fact and explained by PRICE (1976). A detailed study of the phosphorus and its associations have been described earlier in the study of the Winterborne Kingston Borehole sediments.

The Warlingham Borehole sediments showed different correlations of P_2O_5 as compared to the sediments of the Winterborne Kingston Borehole. The correlations are shown in the Appendix (4.2C) and are described as follows.

The P_2O_5 shows a very strong positive correlation, significant at the 0·01% level, with depth, S, Ce, Y, Mo, organic carbon, H_2O^+, pyrite, Fe^{+2} and a medium strong positive correlation, significant at the 5-1% level, with Al_2O_3, Fe_2O_3, Cr, Ba, La, Th, Cu, Rb and total clays. These correlations suggest a strong association of phosphorus with clays. The association of P_2O_5 with sulphur, Mo,Fe^{+2}, pyrite and organic carbon may be due to the fact that concentration of phosphorus and the mentioned components takes place under the anoxic conditions. The strongest positive correlation displayed by P_2O_5 with organic carbon ($r = +0{\cdot}55$) in these sediments suggests that P_2O_5 is mainly associated with organic carbon. WOLF et al. (1967) and CALVERT (1976) have mentioned the association of organic carbon and phosphorus. The strong relationship of P_2O_5 with organic carbon in sediments of the Warlingham Borehole is very well illustrated in Figure (4.13a).

The strong negative correlations of P_2O_5, significant at the 5-1% levels, with Mg, Ca, V, Mn, CO_2, dolomite and calcite suggest that carbonate minerals, e.g. calcite and dolomite, present in these sediments,do not contain any amount of phosphorus. It further suggests that these sediments do not contain directly precipitated phosphate, as is expected in sediments of the Winterborne Kingston Borehole.

According to DOFF (1969), high phosphorus values may be shown by the near-shore anoxic sediments. The same author further suggested that the higher concentration of phosphorus may be partly contributed by the organic matter. The sediments of the Kellaways Formation show higher abundances of the organic carbon (2·23%) and phosphorus (0·17%), indicating that these sediments belong to the near-shore anoxic type of sediments.

The regression equation in Figure (4.13a) shows an intercept of a value of +0·04, suggesting that this amount (0·04%) of P_2O_5 is not associated with organic carbon; it may be associated with another phase. The organic carbon associated amount of P_2O_5 may be obtained by subtracting the value of the intercept (0·04%) from the total amount (0·15%) of P_2O_5; it will thus be 0·11% P_2O_5. The amount of P_2O_5 (0·04%) not associated with organic carbon may be associated with clays; however, the correlation coefficient of P_2O_5 with total clays is very poor ($r = +0{\cdot}21$).

It may be concluded that sediments of the Warlingham Borehole contain phosphorus associated with organic carbon, and it is also adsorbed on clay minerals/ferric oxide coatings on the clay minerals.

k) Organic Carbon

The Warlingham Borehole sediments, as has been mentioned earlier, contain lower amounts of organic carbon as compared to the Winterborne Kingston Borehole sediments. The reason may be either the less strong reducing conditions at the time of deposition, or a lesser supply of organic matter to the sediments. The organic carbon contents in these sediments vary from 0·01 to 11·35%. Sample BR-1721 from the Lower Oxford Clay sediments showed the highest contents of organic carbon (11·35%). The average contents of organic carbon of 78 samples is 1·66%. The Lower Oxford Clay sediments contain the highest (3·93%) and the Upper Oxford Clay the lowest contents of organic carbon (0·57%); which are shown in Table (4.2A). The quartz/organic carbon ratio, as shown in Table (4.2C), follows a similar trend to that observed in the case of the Winterborne Kingston Borehole sediments. The Upper Oxford Clay sediments showed the highest value (35·8),and the Lower Oxford Clay the lowest value (4·59) of the quartz/organic carbon ratio, suggesting that the Lower Oxford Clay sediments are 'off-shore' type and the Upper Oxford Clay sediments are 'near-shore' type. The study of the sediments of both boreholes suggests that, at the time of deposition of the Lower Oxford Clay sediments, both sites of the deposition were

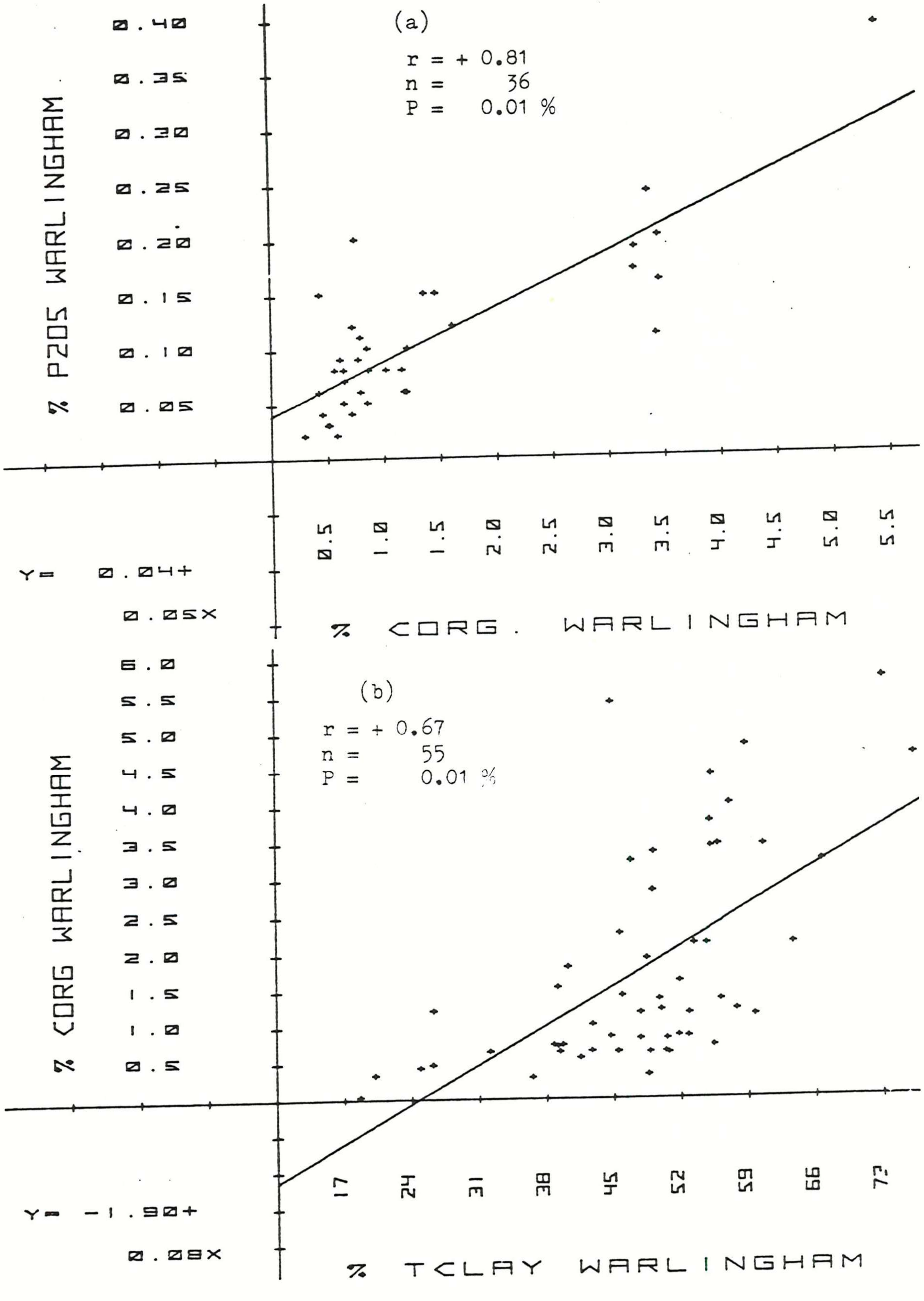
(a)
r = + 0.81
n = 36
P = 0.01 %
% P2O5 WARLINGHAM
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
% CORG. WARLINGHAM
Y= 0.04+ 0.05X
(b)
r = + 0.67
n = 55
P = 0.01 %
% CORG WARLINGHAM
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
17
24
31
38
45
52
59
66
73
% TCLAY WARLINGHAM
Y= -1.90+ 0.08X

FIG.(4.13)

'off-shore' and the deposition of the Upper Oxford Clay sediments took place near the 'shore-lines'.

The correlation coefficient matrix in the Appendix (4.2C) shows similar trends of correlations to those exhibited by the sediments of the Winterborne Kingston Borehole, but not very strong. These sediments showed a very strong positive correlation of organic carbon (at an 0·01% level) with depth, Al, S, P, Rb, Y, Mo, H_2O, Fe^{+2}, pyrite and total clays. Organic carbon in these sediments also showed medium positive correlations (at an 0·1-5% level) with Ti, Na, K, Cr, Ba, La, Ce, Th, Cu, Ni and kaolinite. These correlations suggest a strong association of organic carbon with total clays, as is shown in Figure (4.13b). The weak positive correlations of organic carbon with kaolinite, Ti, Na, K, Cr, etc. also suggest that these sediments contain a very small amount of detrital/terrestrial organic carbon, as compared to the Winterborne Kingston Borehole sediment, and thus that most of the organic carbon is of marine origin. The very strong negative correlation of organic carbon (at an 0·01% level) with Ca, CO_2, Mn and residual iron oxides (Fe_2O_3) also suggests that organic carbon in these sediments exists as a separate phase, having no relationship with the authigenically precipitated carbonate minerals. This view is confirmed by the strong negative correlation of organic carbon with calcite ($r = -0{\cdot}41$) and dolomite ($r = -0{\cdot}23$).

The relationship of organic carbon with various metals in these sediments is not identical with the organic carbon rich sediments of the Lower Oxford Clay of Winterborne Kingston Borehole. The Lower Oxford Clay sediments of the Warlingham Borehole show the highest concentration (3·93%) of organic carbon with the highest contents of Cu (30 p.p.m.) and Cr (169 p.p.m.) only, which are shown in Table (4.2A), suggesting the probable existence of 'organo-metal complexes' of only these two metals, as suggested by BATURIAN et al. (1967), CALVERT and PRICE (1973a). The concentrations of sulphur (1·82%) Fe^{+2} (1·59%) and molybdenum (7 p.p.m.) in the sediments of Kellaways Formation, which also contain the second most abundant concentration (2·28%) of organic carbon suggest that sulphate reducing bacteria was vigorously active in these sediments. These bacteria created a stronger reducing condition below the sediment-water interface and resulted in the concentration of the aforesaid components. The high rate of deposition is related to the stronger reducing conditions. The sediments of Kellaways Formation provide the evidence of a high rate of deposition, being rich in quartz (40·7%), kaolinite (23·70%) and Zr (391 p.p.m.) contents, as shown in Tables (4.2B & 4.2A).

The concentrations of organic carbon and metals, e.g. Cu, Mo, Cr, Ni, Fe^{+2}, Pb, V, Zn and sulphur in the different parts of the Oxford Clay show different trends, as can be seen in Table (4.2A). These concentrations may be due to the varying nature of organic matter. According to TOURTELOT (1964) and HIRST(1962), the varying nature of the organic matter causes a profound effect on the concentration of trace elements in carbon-rich argillaceous sediments, i.e. whether the organic matter itself was of terrestrial or marine origin, and its residence time in the marine environments.

The sediments of the Warlingham Borehole showed the concentration of higher abundance of organic carbon. A comparison of the abundances of organic carbon in these sediments with the reported abundances by other workers is given in Table (4.3).

4.3 Geochemistry of the Minor Elements of the Winterborne Kingston and Warlingham Borehole Sediments

Introduction

The minor elements studied in 63 samples of Winterborne Kingston Borehole and 78 samples of Warlingham Borehole sediments were analysed in the bulk rock by X-ray Fluorescence Spectrometer, as described in Chapter Two. They include V, Cr, Ni, Cu, Mo, Ba, Rb, Mn, Sr, Pb, Zn, Ga, As, Ce, Th, La, Zr, Nb, Y, I and U. Their distributions, correlations and geochemical behaviour are described in the following section. At the beginning of each element description, the factual analytical data is given so that easy comparative study of the element, at a glance, in the sediments of both boreholes can be done. The abbreviations used in this section are as follows:

(W.K.B.)	Winterborne Kingston Borehole
(W.B.)	Warlingham Borehole
(U.O.C.)	Upper Oxford Clay

(M.O.C.)	Middle Oxford Clay
(L.O.C.)	Lower Oxford Clay
(K.F.)	Kellaways Formation.

a) Vanadium

Table (4.3a)

		(W.K.B.)	(W.B.)
Bulk	Range	56 - 12$\overset{*}{9}$ p.p.m.	34 - $\overset{+}{2}$00 p.p.m.
	Average	101 p.p.m.	102 p.p.m.
Carbonate free: Average		143 p.p.m.	155 p.p.m.
Clay fraction : Average		196 p.p.m.	202 p.p.m.
Highest in Bulk rock		119 p.p.m.(K.F.)	85 p.p.m.(K.F.)
Lowest " " "		81 p.p.m.(U.O.C.)	107 p.p.m.(U.O.C.)

* Sample WBK-29 showed the highest concentration of vanadium.
\+ Sample BR-115 " " " " " "

The average abundances of vanadium in the (W.K.B.) and (W.B.) sediments showed a good agreement with the average abundance of vanadium in shales and sedimentary rocks reported by other workers, and shown in Table (4.3). It is clear from Table (4.3a) that the average contents of the vanadium of the two borehole sediments do not show a large variation, and the highest abundance of vanadium is shown by the clay fraction ($> 2\mu$) of the (W.B.) sediments. The distribution, association and geochemical behaviour of vanadium in sediments and sulphide minerals etc. has been studied by many workers. LANDERGREN (1974) stated that vanadium may be adsorbed onto clay minerals, and it can be incorporated in the structure of the clay minerals or in iron-oxide coatings on the clay minerals. On weathering of the source rock, vanadium is transported as vanadate ion (VO_4^{-3}), either in solution or in association with iron-oxides. Under the reducing conditions the vanadate ion (VO_4^{-3}) reduces to V^{+3} and is concentrated by absorption in organic matter and iron-hydroxides. NICHOLLS and LORING (1962) reported the highest amounts of acid soluble vanadium in a sample containing the highest organic carbon. KRAUSKOPF (1956) mentioned that hydrated Fe_2O_3 is an effective adsorbent for vanadium. Association of vanadium with clay minerals may be either due to absorption or substitution in the lattice structure. HIRST (1962) found a strong association of vanadium with clays in the sediments of the Gulf of Paria, and concluded its presence in the lattices of montmorillonite.

WEDEPOHL (1960) suggested that most vanadium is of terrestrial origin. CHESTER (1965) and CALVERT (1976) assigned a detrital origin to vanadium due to its very strong association with 'Al' and other 'lithophile' elements. CHESTER (1965) and CALVERT (1976) noted its association with clay minerals (especially montmorillonite), mainly in their lattices. CHESTER and HUGHES (1969) and CHESTER and MESSIHA-HANNA (1970), during their geochemical studies of the partitioning of elements, confirmed the above conclusions. The enrichment of vanadium in the clay fractions of both the borehole samples, as observed by the present author, and also similar enrichment reported by CHOWDHURY (1980) in the clay fraction of the Corallian sediments, supports the above view.

WEDEPOHL (1964) found a strong correlation of vanadium with organic carbon. LE-RICHE (1959) suggested that vanadium adsorbed by organic matter could migrate to the silicate lattices. HIRST (1968) reported higher vanadium contents associated with carbon in the slowly deposited fine-grained black mud-stones, as compared to the carbon present in the silty micaceous mud-stones. He concluded that the nature of organic matter in the silty mud-stone is of terrestrial origin, and the rate of sedimentation was the main factor in the distribution of vanadium in the two environments. TOURTELOT (1964) found that marine off-shore shales are enriched in the vanadium contents in comparison with the non-marine clay-stones. LANDERGREN (1974) stated that vanadium enrichment in sediments is influenced by the reducing character of the environments, and not by primary vanadium contents of the original sediments. According to LANDERGREN (op.cit.), in reducing environments, V^{4+} reduces to V^{2+} which forms insoluble hydroxides. SPENCER et al. (1968) mentioned the existence of an 'oxide factor', consisting of the association and high loadings of Fe, Mn, V and Co. CALVERT (1976) noticed a strong correlation of vanadium with Zr and Fe_2O_3 ; he explained that these elements are associated with the dispersed phase of 'oxides'.

The correlation coefficient matrix of the Winterborne Kingston Borehole sediments in Appendix (4.1C) shows a very strong positive correlation of vanadium, at the 0.01% level, with depth and lithophile elements, e.g. Al, Ti, Mg, K, Si, Na, Cr, Ni, Ba, Ce, Nb, Th and Zr; it also showed a very strong positive correlation, significant at the 0·01% level, with illite, kaolinite, chlorite and total clays, suggesting that vanadium in these sediments is mainly associated with clays. The Upper and the Middle Oxford Clay sediments of the (W.K.B.) show the highest values for the V/Al ratios, as shown in Table (4.1C). The average value of the V/Al ratios of these sediments is 0·00195 which suggests the preferred association of vanadium with smectite (montmorillonite-illite), as observed by HIRST (1962). The highest values of the V/Al ratios in the Upper Oxford Clay sediments of both the borehole samples, as shown in Tables (4.1C and 4.2C) confirm the preferred association of vanadium for smectite and the mixed-layer clay minerals respectively. The association of vanadium with clays in these sediments seems to be mainly in the lattice structure of the clay minerals, as suggested by CHESTER (1965), CALVERT (1976) and HIRST (1962). The strong relationship of vanadium with clays is illustrated in Figure (4.14). The average amount of vanadium associated with clays may be determined by the regression equation in Figure (4.14). This regression equation gives an intercept of+24·14 ppm, indicating that this amount of vanadium is not associated with clays. The average amount of vanadium associated with clays will be 77 p.p.m., i.e. 101 p.p.m. - 24·14 p.p.m. = 76·86 p.p.m. ≅ 77 p.p.m.; this value corresponds to 76% of the total vanadium contents. The origin of vanadium seems to be detrital (terrestrial), as it showed very strong positive correlations with typical detrital elements, e.g. Si, Ti, Al, Zr, Nb, etc. WEDEPOHL (1960), CHESTER (1965) and CALVERT (1976) mentioned a detrital (terrestrial) origin of vanadium.

The strong positive correlations of vanadium with Fe^{+3}, Fe_2O_3 (total iron) and Zr, all being significant at the 0·1% level, suggests that some amount of vanadium in these sediments is present as a dispersed phase of 'oxides', as notices by CALVERT (1976). The results of factor analysis of chemical data of these sediments in Chapter Five show the existence of an 'oxide factor', having positive loadings of Mn, Fe^{+3}, Ni, V and As. The strong positive correlation of vanadium with C_{org} suggests that some of the vanadium is associated, by absorption, with organic carbon. The strong positive correlation of vanadium with Fe_2O_3 (total iron), Cu, Ni and Cr, and its weak positive correlation with S, Mo, As and pyrite suggests that a minor amount of vanadium is associated with sulphides and pyrite present in these sediments. A similar association is reported by MOHR (1959a), CARSTENS (1943) and AUGER (1941). BIRD and CALCOT (1914) precipitated a sulphide from the vanadate solutions in the presence of sulphide ions and organic matter; both of these parameters were available abundantly all the time, during the sedimentation of these sediments.

The Middle Oxford Clay sediments show the highest concentration (161 p.p.m.) of vanadium and Fe_2O_3(total iron) on a carbonate free basis. This enrichment may be due either to the strong association of vanadium with montmorillonite due to its substitution in the lattices of montmorillonite, as observed by HIRST (1962), or it may be due to higher contents of iron, as stated by CATT etal. (1971) or adsorbed by iron-oxides. The geochemical correlations of the clay fraction samples showed a very strong positive correlation of vanadium with smectite ($r = +0{\cdot}52$), significant at the 0·01% level, which is shown in Appendix (7.1D) and in Chapter **Seven**

Vanadium in the (W.B.) sediments showed weaker and different correlations to those shown by the (W.K.B.) sediments. The correlation coefficient matrix in Appendix (4.2C) shows a strong positive correlation of vanadium (at 0·01 - 0·1% levels) with Ti, Al, Fe_2O_3(total iron), Mg, K, Na, Cr, Th, Rb and Nb, suggesting its association with the alumino-silicate phases of these sediments. The very strong positive correlation of vanadium with total clays ($r = +0{\cdot}54$), significant at an 0·01% level, supports the view expressed above. The positive correlation of vanadium with total Fe_2O_3($r = +0{\cdot}46$), Fe^{+3} ($r = +0{\cdot}51$) and Mn ($r = +0{\cdot}18$) suggests that a minor amount of vanadium in these sediments probably is associated with the oxides/hydroxides phase of iron and manganese. Factor analysis results of the chemical data of these sediments showed the existence of 'Fe-Mn' oxides/hydroxides phase, having positive loadings of Fe, V, Mn and As (see Chapter Five). Amongst clay mineral species, illite is the only clay mineral which showed a medium strong positive correlation ($r = +0{\cdot}21$) with vanadium, which is significant at the 0·1% level. The other clay minerals, e.g. chlorite ($r = +0{\cdot}14$), and mixed-layer ($r = +0{\cdot}08$) showed positive correlations but very weak. The geochemical correlations of vanadium in the clay fraction of these sediments, as shown in the Appendix (7.2D), shows a very strong positive correlation of vanadium with chlorite (r = +0·35; significant at the 0·01% level) and a medium strong positive correlation with illite (r = +0·26), significant at the 0·05% level. These correlations confirm that vanadium in the studied sediments is mainly associated with these clay minerals. The vanadium of the (W.B.) sediments shows negative correlations with organic carbon, indicating no relationship.

It may be concluded from the above observations that in the (W.K.B.) sediments a significant amount of vanadium (76%) is associated with clays mainly by substitution in the lattices of the clay minerals. Some of the vanadium is also associated with iron-oxides/hydroxides as coatings on the clay minerals. A small fraction of vanadium is also associated with organic carbon, sulphides and pyrite present in the sediments.

The (W.B.) sediments contain vanadium only in two phases: namely clays in their lattices and oxides/hydroxides of Fe-Mn. Organic carbon does not show any relationship with vanadium, and sulphide minerals only showed a very weak association.

b) Chromium

Table (4.3b)

	(W.K.B.)	(W.B.)
Range	60 - 171* p.p.m.	42 - 219+ p.p.m.
Average	118 p.p.m.	110 p.p.m.
Carbonate free: Average	166 p.p.m.	157 p.p.m.
Clay fraction: Average	192 p.p.m.	191 p.p.m.
Highest in Bulk rock	150 p.p.m. (K.F.)	132 p.p.m. (L.O.C.)
Lowest " " "	93 p.p.m. (U.O.C.)	94 p.p.m. (M.O.C.)

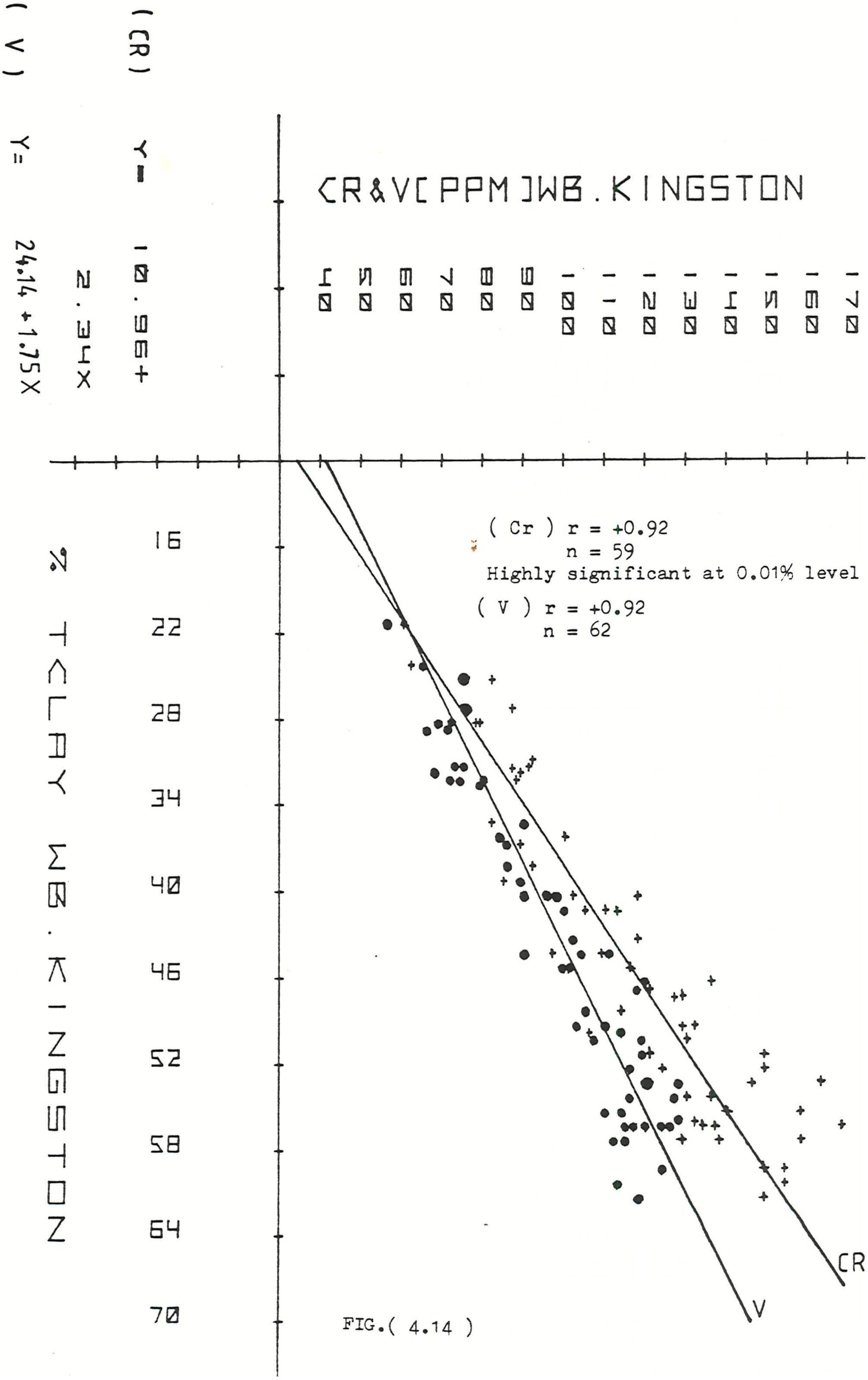
* Sample WBK-28 showed the highest concentration of chromium.

\+ Sample BR-1734 " " " " " "

The sediments of the Winterborne Kingston Borehole, on the whole, showed relatively higher abundance of Cr, as is shown in Tables (4.3b and 4.3). The clay fraction ($<2\mu$) samples of both the borehole sediments showed much higher abundances of Cr as compared to the bulk rock samples.

The stratigraphic distribution of Cr in the studied sequences is shown in Tables (4.1A and 4.2A). The lower concentration of Cr in sediments of the (U.O.C.) of the (W.K.B.) sediments may be related to the source rock. It is a well-known fact that basic and ultrabasic igneous rocks contribute higher amounts of Cr as compared to the acidic or intermediate type of rocks. The depletion of Cr in these sediments may also be associated with the lower concentrations of components, e.g. total clays, organic carbon, pyrite and illite, which are shown in Table (4.1B). The abundant amount of smectite (montmorillonite-illite) present in the Upper Oxford Clay sediments may be another reason for lesser concentration of Cr in these sediments. GOLDBERG and ARRHENIUS (1958) mentioned that not much Cr can occupy the exchangeable positions of clay minerals. HIRST (1962) mentioned the preferred association of Cr with illite. The Cr values in this study show stronger correlations with the elements K, Al, Rb and clay mineral illite, as compared to its correlations with Fe^{+2} and Mg, as shown in Appendix (4.1C), indicating its preferred association with illite as opposed to smectite. The enrichment of Cr in sediments of the Kellaways Formation suggests that a significant amount of Cr was brought into the depositional environments, in association with iron-oxides/organic matter, or more Cr was being released due to intense chemical weathering probably taking place in the same area.

HIRST (1962) studied Cr/Al and Cr/Mg ratios and noticed a moderately constant ratio of Cr/Al, indicating association of Cr with clays. He noticed the highest value of the Cr/Mg ratio in the sediments containing the lower amounts of montmorillonite, from which he concluded the lesser preference of Cr for montmorillonite. The Cr/Al ratios in all parts of the Oxford Clay and Kellaways Formations are moderately constant, as shown in Tables (4.1C and 4.2C). They indicate a strong relationship of Cr with 'aluminosilicates', particularly clays. The sediments of the (L.O.C.) and (K.F.) show the lower concentration of smectite and the higher values of Cr/Mg ratios, as shown in Tables (4.1B and 4.1C), indicating a lesser degree of preference of Cr towards smectite (montmorillonite-illite). Illite is formed under reducing conditions which probably allow the retention of Cr as Cr^{3+} and its inclusion in the lattices of illite. The montmorillonite is formed under oxidising and alkaline conditions where 'Cr' may be



(Cr) r = +0.92
n = 59
Highly significant at 0.01% level

(V) r = +0.92
n = 62

FIG.(4.14)

converted to the anionic complex (CrO_2^-) and is removed in solution (HIRST, 1962).

The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows a very strong positive correlation of Cr (at the 0·01% level) with depth and typical lithophile elements, e.g. Si, Ti, Al Mg, Na, K, V, Ni, Ba, Th, Cu, Rb, Zr, Nb, H_2O and detrital minerals, e.g. illite, kaolinite, chlorite and total clays, suggesting that Cr of these sediments mainly resides in the clays. The distribution of Cr in the sediments and its strong association with clay minerals, particularly illite and total clays, have been described by many workers including NICHOLLS and LORING (1960), FRÖHLICH (1960), HIRST (1962 & 1967), TOURTELOT (1964), GAD et al. (1969), CURTIS (1969) and CHESTER & HUGHES (1967). The higher concentration of Cr in the clay fraction of these sediments and the results of a leaching study of the bulk rock (CHESTER and HUGHES, op.cit.), which showed that 78% Cr in the (W.K.B.) sediments and 88% Cr in the (W.B.) sediments are associated with the lattice-held fractions of the respective sediments. This observation strongly confirms that most of the Cr of these sediments is present in clays, particularly illite. The strong relationship of Cr and total clays is very well illustrated by Figure (4.14), which shows a strong positive correlation of Cr with total clays ($r = +0{\cdot}92$) and an intercept of+10·96 p.p.m., indicating that this amount of Cr is not associated with clays. The average Cr associated with clays may be obtained by subtracting the value of the intercept (10·96) from the average contents of Cr (118 p.p.m.), giving 107 p.p.m., which corresponds to 91% of the total Cr present in the sediments.

The (W.K.B.) sediments,on leaching with the acid-reducing reagents, show higher amounts of Cr (22%) leached as compared to the Warlingham Borehole sediments Cr (12%). The higher amount of Cr leached in the (W.K.B.) sediments suggests that more Cr is present in non-lattice-held positions, possibly adsorbed onto the iron-oxides/hydroxides. The positive correlation of Cr with the residual iron-oxide ($r = +0{\cdot}27$) in these sediments confirms this association.

The very strong positive correlation of Cr with organic carbon ($r = +0{\cdot}51$), highly significant at the 0·01% level, indicates a strong association with organic carbon, as previously well documented by NICHOLLS and LORING (1960), WEDEPOHL (1964), HIRST (1967), GAD et al. (1969) and CHOWDHURY (1980). The strong relationship of Cr and organic carbon is shown in Figure (4.15). Cr also shows a very strong positive correlation, significant at the 0·01% level, with Ni (r = +0·67) and Cu (r = +0·59). It also shows a positive, though weak, correlation with Mo (r = +0·27), S (r = +0·03) and Fe^{+2}(r = +0·05), suggesting an association with the sulphide phase; pyrite is present abundantly in all samples. GAD et al. (1969) and SPENCER (1966) mentioned the association of a minor amount of Cr in pyrite. The correlations of Cr with Cu and Ni may be due to closely similar ionic radii of these metals (Cr = 0·70Å; Cu = 0·72Å; Ni = 0·69Å), which might have facilitated this substitution in the sulphides present.

The (W.B.) sediments in Table (4.3b) show the highest and lowest concentration of Cr in the sediments of the Lower and Middle Oxford Clay respectively. The highest concentration of Cr in the Lower Oxford Clay sediments may be due to higher abundances of organic carbon (3·93%), pyrite (1·94%) and total clays (54·43%), being the most likely phases for the residence of Cr. The sediments of (U.O.C.) and (K.F.) show the highest value of the Cr/Al ratio (0·0018), which may be due to a higher concentration of illite in these sediments. According to HIRST (1962), Cr shows a preferred association with illite in clays. The highest value of the Cr/Mg ratio (0·019) in the (K.F.) sediments indicates the preferred association of Cr with illite, as these sediments contain the lowest amount (10·40%) of mixed-layer (illite-montmorillonite) clay minerals.

The correlations of Cr with other chemical elements, minerals and organic carbon of the (W.B.) sediments are shown in the Appendix (4.2C). These correlations indicate that Cr in these sediments mainly resides in clays, particularly illite. The correlation coefficient of Cr with total clays (r = +0·44) is the highest, confirming its strong association with clays. The association of Cr with clays is also explained by its positive correlations with lithophile elements, e.g. Al, V, Fe, Ti, Na, K, Th, Rb, Y, Nb and H_2O^+, all being significant at the 0·1 - 5% levels. Some Cr is also associated with organic carbon, which is indicated by its strong positive correlation with organic carbon (r = +0·35), significant at the 0·01% level. A minor amount of

Cr in these sediments is also associated with the sulphide phase minerals, i.e. pyrite. This relationship is indicated by the very strong positive correlation of Cr with Fe_2O_3(total iron), Fe^{+2}, Mo, S and pyrite, all being significant at the 0•01% level.

It may be summarised, that Cr in the (W.K.B.) sediments mainly occurs in the lattices of clays (approximately 91% of the total Cr), the remaining amount of Cr is associated with organic carbon and the minerals of the sulphide phase. The (W.B.) sediments contain Cr, mainly in the lattices of clays (approximately 88% of the total Cr is associated with the lattice-held fraction), the remaining amount of Cr is associated with organic carbon and sulphide minerals, particularly pyrite.

c) Nickel

Table (4.3c)

		(W.K.B.)	(W.B.)
Bulk rock	Range	31 - 71* p.p.m.	12 - 66+ p.p.m.
	Average	53 p.p.m.	42 p.p.m.
Carbonate free: Average		75 p.p.m.	60 p.p.m.
Clay fraction: Average		70 p.p.m.	73 p.p.m.
Highest in Bulk rock		64 p.p.m. (L.O.C.)	47 p.p.m. (L.O.C.)
Lowest " " "		40 p.p.m. (U.O.C.)	37 p.p.m. (K.F.)

* Sample WBK-42 showed the highest concentration of Nickel.
\+ Sample BR-1771 " " " " " "

The Winterborne Kingston Borehole sediments showed higher amount of Ni as compared to the Warlingham Borehole sediments, which show a higher concentration of Ni in the Clay fraction samples, as shown in Table (4.3c). The abundances of Ni in the sediments of both the boreholes are compared with the reported values of Ni in sediments by other workers in Table (4.3), which shows good agreement with the reported values of Ni.

The variation of Ni abundances in the sediments of both the boreholes seems to be controlled by the abundances of total clays, organic carbon and sulphide minerals. The maximum concentration of Ni in the sediments of the (L.O.C.) of the (W.K.B.) is strongly correlated

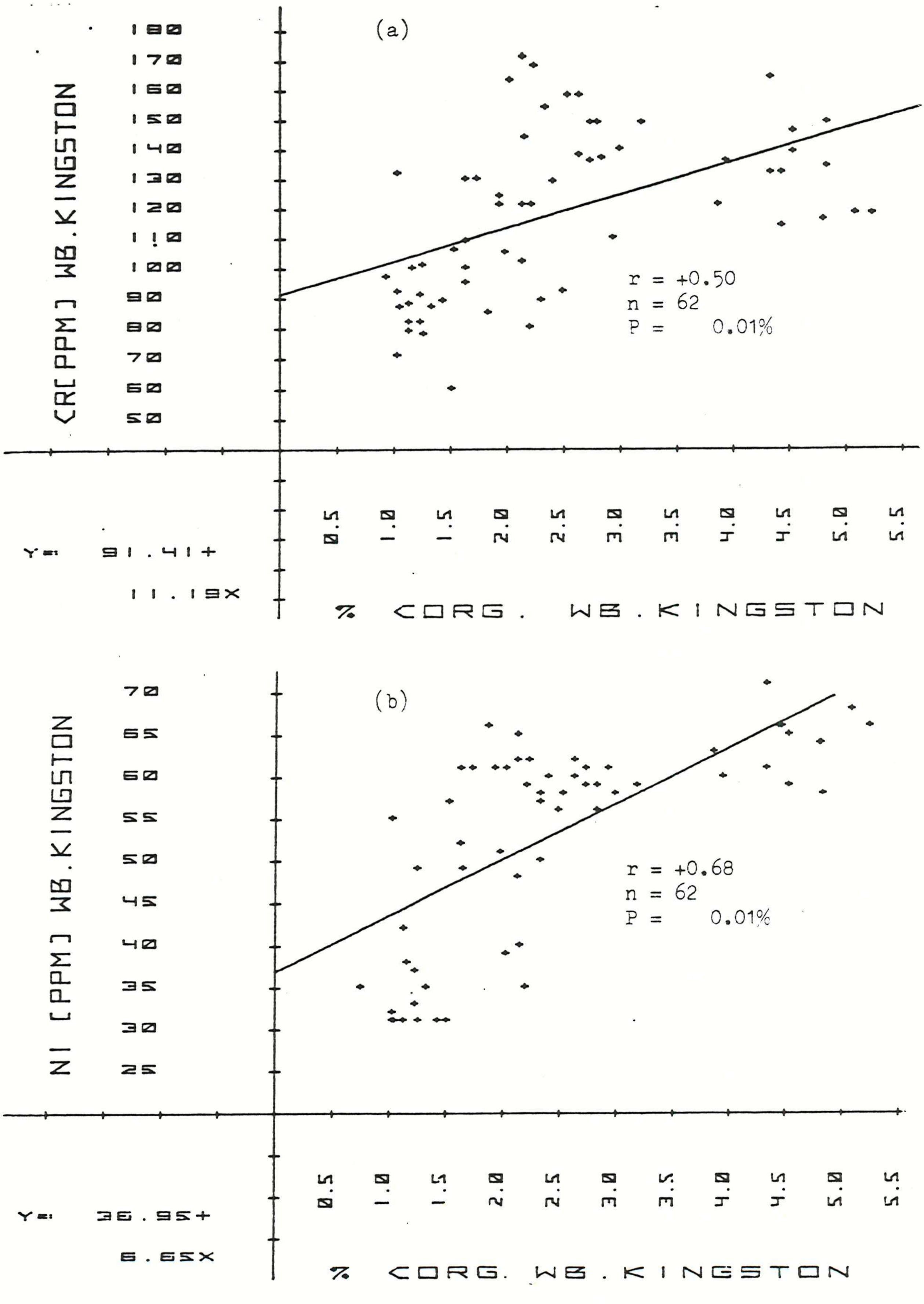

(a)
CR[PPM] WB.KINGSTON
180
170
160
150
140
130
120
110
100
90
80
70
60
50
r = +0.50
n = 62
P = 0.01%
Y= 91.41+
11.19X
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
% CORG. WB.KINGSTON
(b)
NI [PPM] WB.KINGSTON
70
65
60
55
50
45
40
35
30
25
r = +0.68
n = 62
P = 0.01%
Y= 36.95+
6.65X
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
% CORG. WB.KINGSTON

FIG.(4.15)

with the highest abundances of total clays (50·28%), pyrite (3·89%) and organic carbon (4·32%). Similarly, the lowest concentration of Ni (40 p.p.m.) in the (U.O.C.) of the same borehole sediments shows a strong correlation with the lowest abundances of these three phases, 33·26%, 2·25% and 1·50% respectively. The highest concentration of Ni (47 p.p.m.) in the (L.O.C.) of the (W.B.) sediments is associated with the highest abundances of total clays (54·43%), and organic carbon (3·93%), and a relatively lower amount of pyrite (1·94%). The lowest concentration of Ni is present in the sediments of the (K.F.), which also contain the lowest abundance of total clays (42·70%), second highest amount of organic carbon (3·28%), and the highest amount of pyrite (3·03%). These relationships of Ni in these sediments tend to suggest that the abundance of Ni is mainly controlled by total clays and organic carbon, as shown in Figures (4.15b and 4.16a).

NICHOLLS and LORING (1962) observed an antipathetic relationship of the Ni/C_{org} ratios and the contents of organic carbon in the British Carboniferous sediments. They interpreted that this relationship indicates that some of the Ni was incorporated in the sediments by a process independent of organic matter. A similar relationship of Ni/C_{org} ratios and the contents of organic carbon exists in the studied sediments of the two boreholes, which is shown in Tables (4.1B and 4.2B) and (4.1C and 4.2C), suggesting a similar independent process, as mentioned by NICHOLLS and LORING (op.cit.) Because Ni in the present study exhibited a strong relationship with clays, so Ni/Al ratios for both the borehole sediments were also determined, and are shown in Tables (4.1C and 4.2C). These tables show a sympathetic relationship between the Ni/Al ratios and the concentration of Ni in these sediments, confirming the strong relationship between the species of clay minerals present in these sediments and Ni. The distribution of Ni and mineral abundances in the stratigraphic sequences of both the boreholes are given in Tables (4.1A, 4.2A & 4.1B and 4.2B).

The relationship of Ni with organic carbon, clay minerals, sulphide minerals and 'Fe-Mn' oxides/hydroxides in the sediments of reducing environments has been studied by many workers, including NICHOLLS and LORING (1962), WEDEPOHL (1964), GAD et al. (1969), COSGROVE (1973), HIRST (1974), CALVERT (1976), KRAUSKOPF (1979) and CHOWDHURY (1980), who showed a strong relationship of Ni with organic carbon and clay minerals in the Corallian mud-rocks from the Dorset coast. SULAIMAN (1972) mentioned the association of Ni^{2+} with organic carbon, pyrite, clay minerals and Fe-Mn hydroxides during the geochemical studies of the Namurian argillite from Ireland.

The relationship of Ni with the components mentioned above will be examined in the light of results of the leaching study, multivariant correlations and R-mode factor analysis of the chemical data of bulk rock samples of both the boreholes. The leaching study results of the representative samples of the (W.K.B.) sediments, by acetic acid and hydroxylamine hydrochloride (CHESTER and HUGHES, 1967), indicated that 53% Ni of these sediments is associated with the lattice-held fraction, i.e. clays + detrital components, and 47% with other phases. This observation agrees with the results obtained by other statistical analyses, e.g. multivariant correlation and R-mode factor analysis of the chemical data. The correlation coefficient matrix in Appendix (4.1C) shows a very strong positive correlation of Ni with total clays (r = +0·81), which is highly significant at the 0·01% level. The R-mode factor analysis in Chapter Five also shows a very strong positive loading (+0·69) of Ni in 'FACTOR(F-1)'representing the clay factor.

The leaching study results of the representative samples from the (W.B.) sediments show only 39% Ni in the lattice-held fraction, and the remaining 61% Ni in other phases. The Ni contents of these sediments show weak positive correlation with clays (r = +0·25) and a very weak positive correlation (r = +0·11) with pyrite. An antipathetic relationship of Ni with pyrite and organic carbon exists in the sediments of the (K.F.), which clearly indicates that in the (W.B.) sediments different parameters existed for the control of Ni.

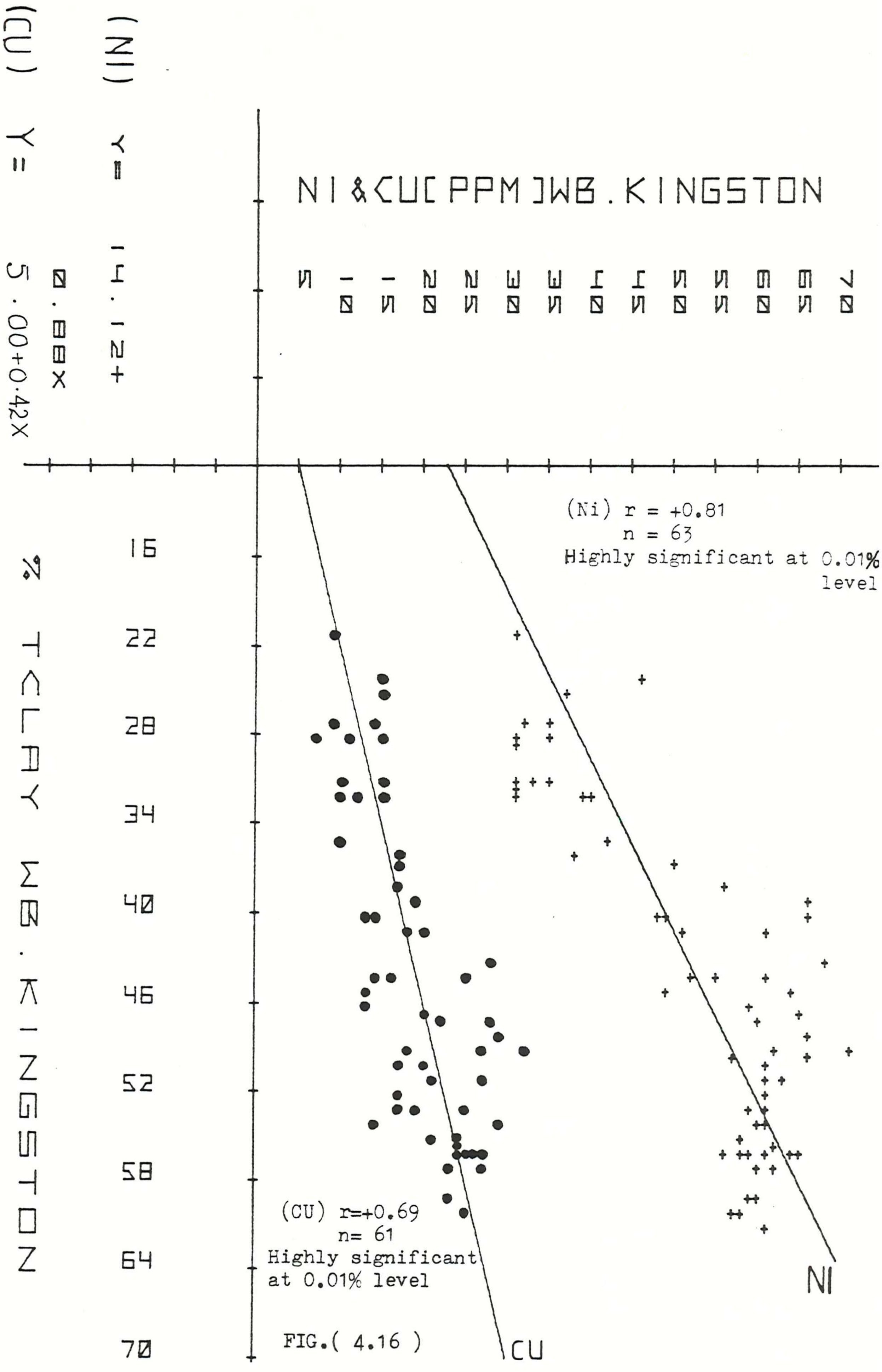
The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows very strong positive correlations of Ni with detrital (lithophile) elements, e.g. Ti, Al, Fe_2O_3, Mg, K, V, Cr, Ba, Th, Rb, highly significant at the 0·01% level, indicating that Ni in these sediments is strongly associated with the lattice-held fraction. The same correlation matrix shows very strong positive correlations of Ni with clay minerals, e.g. illite(r = +0·85), kaolinite(r = +0·91) and chlorite (r = +0·69), and also with total clays (r = +0·81), confirming the above conclusions. Figure (4.16a) shows the very strong relationship of Ni with total clays. This figure gives an intercept of+14 p.p.m., indicating that this amount of Ni is not associated with clays. The association of Ni with clay minerals has been studied by many workers, as mentioned earlier. NICHOLLS and LORING (1962) stated that a considerable amount of Ni is bound in clay minerals. GAD et al.(1969) mentioned that detrital components of all the shales contain approximately 50 p.p.m. of Ni. SULAIMAN (1972) mentioned that Ni replaces Fe^{2+} or Mg^{2+} in clay minerals, especially chlorite. He found a positive correlation of Ni with chlorite and illite/montmorillonite mixed-layer, from which he explained that its correlation with chlorite is due to replacement of Mg^{2+} and Fe^{2+} by Ni^{2+}, and with illite/montmorillonite mixed-layer due to adsorption. The same author reported adsorption of Ni^{2+} on kaolinite. CHOWDHURY (1980) stated that the ionic radius of Ni^{2+} (0·77Å) favours the occupation of the octahedral site in clay mineral. The same author mentioned that a significant amount of Ni (about 10% of total) was extracted from the clay fraction of montmorillonite-rich samples. He further stated that the occurrence of relatively higher amounts of extractable Ni in the clay fraction of iron-rich samples indicates that Ni is present in the iron-oxide coatings. The very strong positive correlations of Ni with chlorite, illite and kaolinite of these sediments may be explained in the light of observations described above.

The remaining amount of Ni is associated with pyrite and organic carbon, as is shown in Figure (4.15a), and is suggested by its very strong positive correlations with organic carbon ($r = +0{\cdot}68$), S ($r = +0{\cdot}61$), Fe^{+2} ($r = +0{\cdot}62$), Cu ($r = +0{\cdot}78$), Mo ($r = +0{\cdot}49$) and pyrite ($r = +0{\cdot}61$), all being highly significant at the 0·01% level. Many authors, including NICHOLLS and LORING (1962), WEDEPOHL (1964), GAD et al. (1969), VOLKOV and FOMINA (1974),and CALVERT (1976) found a very strong positive correlation of Ni^{2+} and organic carbon in the sediments studied by them. GAD et al. (op.cit.) stated that the relationship of Ni^{2+} with organic carbon is due to organic complexing or biological activity. CALVERT (op.cit.) stated that Ni^{2+} forms complexes with organic matter and could be adsorbed onto degraded organic matter. A very strong association of Ni^{2+} with pyrite has been mentioned by many authors, including NICHOLLS and LORING (1962), LE RICHE (1959), and BUTUZOVA (1968). BUTUZOVA (op.cit.) stated that minor elements Ni, Cu, As, Pb are accumulated in iron sulphide. The ionic radii of Ni^{2+} (0·77Å), being close to the ionic radii of Fe^{+2} (0·86Å), may facilitate the co-precipitation of Ni^{2+} with pyrite.

Some of the remaining amount of Ni seems to be associated with the Fe-oxides/hydroxide phase, which exists in the studied sediments. KRAUSKOPF (1979) stated that Ni may be associated with iron-hydroxides by adsorption. SULAIMAN (1972) mentioned the association of Ni with Fe-Mn hydroxides in the Namurian argillites. The correlation coefficient matrix in Appendix (4.1C) shows a medium strong positive correlation of Ni with the residual Fe_2O_3($r = +0{\cdot}22$), significant at 5% level, which explains the probable association of Ni with the iron-oxides.

The correlation coefficient matrix for the (W.B.) samples in Appendix (4.2C) shows a very strong positive correlation of Ni with Pb ($r = +0{\cdot}92$), Ga ($r = +0{\cdot}91$), Zn ($r = +0{\cdot}59$), As ($r = +0{\cdot}62$), Cu ($r = +0{\cdot}90$), all being highly significant at the 0·01% level, suggesting co-precipitation of Ni with sulphide complexes of these elements. The only detectable sulphide in these sediments is pyrite. The very strong positive correlations of Ni, as mentioned above, may suggest that, on a very localized scale, complex/complexes of these metals were precipitated with the co-precipitation of Ni, producing a minor amount that escaped detection by X.R.D. The same correlation matrix shows medium positive correlations of Ni with Ti, Al, Fe_2O_3, K, V, Cr, La, Ce, Th, Rb, Y, Nb, H_2O, illite and total clays, all being significant at the 5% level; suggesting that some of the Ni is associated with clay minerals in the manner explained earlier. A weak positive correlation of Ni with S ($r = +0{\cdot}11$), Mo ($r = +0{\cdot}14$), organic carbon ($r = +0{\cdot}14$), Fe^{+2} ($r = +0{\cdot}11$) and pyrite ($r = +0{\cdot}11$), suggests that some Ni^{2+} is also associated with organic carbon as adsorbed and some with pyrite as co-precipitated.

In summary, the (W.K.B.) sediments show that Ni is mainly associated with clay minerals (Fig.4.16), having only minor relationships with organic carbon, Fe-oxides and pyrite. In contrast the (W.B.) sediments show a major association between Ni and sulphides, with only minor relationships with clays and organic carbon.



(Ni) r = +0.81
n = 63
Highly significant at 0.01% level

(CU) r=+0.69
n= 61
Highly significant at 0.01% level

FIG.(4.16)

d) <u>Copper</u>

Table (4.3d)

		(W.K.B.)	(W.B.)
Bulk rock	Range	6 - 36* p.p.m.	3 - 48+ p.p.m.
	Average	19 p.p.m.	19 p.p.m.
Carbonate free: Average		27 p.p.m.	26 p.p.m.
Clay fraction: Average		26 p.p.m.	27 p.p.m.
Highest in the Bulk rock		27 p.p.m.(L.O.C.)	24 p.p.m.(L.O.C.)
Lowest " " " "		13 p.p.m.(U.O.C.)	17 p.p.m.(U.O.C.)

* Sample WBK-45 showed the highest concentration of copper.
+ Sample BK-1721 " " " " " "

The sediments of the (W.K.B.) and (W.B.) show equal amounts of Cu in the bulk rock samples as well as in the clay fraction samples, as shown in Table (4.3d).

The highest concentration of Cu (36 p.p.m.) in the (W.K.B.) sediments is shown by sample WBK-45, which also has the highest abundance of organic carbon (5·21%), and significantly higher values of pyrite (4·8%) and total clays (40%), In the (W.B.) sediments the highest concentration of Cu (48 p.p.m.) is shown by sample BR-1721, which contains the highest abundance of organic carbon (11·35%) and significantly high concentrations of pyrite (4·19%) and total clays (48·48%). The lowest content of Cu (3 p.p.m.) in the (W.B.) sediments is present in sample BR-1811, which contains no organic carbon, and the lowest amounts of pyrite (0·4%) and total clays (11·15%). These observations suggest that a very strong relationship exists between organic carbon, pyrite and total clays and Cu in the sediments of the two boreholes.

The stratigraphic distribution of Cu and mineral phases for the (W.K.B.) sediments is given in Tables (4.1A and 4.IB). These tables show that the highest concentration of Cu (27 p.p.m.) occurs in the sediments of the (L.O.C.), which also contain the highest abundances of pyrite (3·89%) and organic carbon (4·32%), and significantly higher amounts of total clays (50·28%) and illite (60·4%). The lowest concentration of Cu (13 p.p.m.) occurs in the sediments of the (U.O.C.), which also contain the lowest abundances of pyrite (2·25%), organic carbon (1·50%), total clays (33•26%) and illite (42•60%). The above observations strongly suggest that the Cu concentration exhibits a preferred association with pyrite, organic carbon and clays.

The stratigraphic distribution of Cu and mineral phases for the (W.B.) sediments is given in Tables (4.2A and 4.2B). These tables show the highest concentrations of Cu (24 p.p.m.), organic carbon (3•93%) and total clays (54•43%), and a significantly higher amount of pyrite (1•94%) and illite (65•41%) in the (L.O.C.). The lowest concentration of Cu (17 p.p.m.) exists in the sediments of the (U.O.C. - M.O.C.). The (U.O.C.) sediments also contain the lowest abundances of organic carbon (1•57%), pyrite (1•04%) and total clays (40•29%); similar lowering trends of these components are shown by the sediments of the (M.O.C.). These trends of distribution of Cu and mineral phases in these sediments suggest, that Cu shows a preferred association with organic carbon and clay abundances of these sediments. The association of Cu with pyrite in these sediments seems to be a subordinate type. The average contents of Cu in the bulk rock and clay fraction ($> 2\mu$) samples are shown in Table (4.3), which indicates a depleted amount of Cu in the sediments of both boreholes, as compared to the reported abundances of Cu in sediments by other workers.

VOGT and KOSTER (1978) mentioned that montmorillonite contains relatively lower amounts of Cu than other clay minerals. The lowest concentration of Cu (13 p.p.m.) in the (U.O.C.) sediments may be due to the highest concentration of smectite (45•16%) and lowest amount of illite (42•6%). Most of the trace elements, including Cu, Ni, Nb, Mo, Rb, Y, V, Cr, Th, show their lowest concentrations in the (U.O.C.) sediments, which are rich in smectite (montmorillonite-illite). This may suggest that precursor source rocks of the montmorillonite-rich Upper Oxford Clay were depleted in the contents of these elements. CHOWDHURY (1980) found a similar association of minor elements and montmorillonite in the Corallian mud-rocks from the Dorset coast. He explained that it indicates the source rock was either an intermediate or an acidic igneous type. Similar rock types may have contributed to the Upper Oxford Clay of the Winterborne Kingston Borehole.

The association of Cu with clay minerals, organic carbon, sulphide minerals and oxides/hydroxides of Fe-Mn have been studied by many workers. HIRST (1962) stated that minor elements e.g. Cu, Pb

Ba, Ga and Ni entered the basin of deposition mainly combined structurally in the lattices of the degraded clay minerals. The same author further stated that Cu, Cr, Ni, Pb and Ba are associated with illite and montmorillonite in general, but Cu and Cr show a preferred association with illite. HIRST (op.cit.) stated that in the sediments of the 'Gulf of Paria', the Cu is associated with clays because the Cu/Al ratios remain remarkably constant. The Cu/Al ratios for the different divisions of the studied sequences are shown in Tables (4.1C and 4.2C). These tables show that the Cu/Al ratios for the sediments of both boreholes show fairly constant trends, with the exception of the Lower Oxford Clay sediments of the (W.K.B.), which have showed the highest value of this ratio ($3{\cdot}97 \times 10^3$), suggesting an extra association of Cu with clays. The sediments of the (L.O.C.) contain the highest amount of illite (60·38%), which may therefore hold the extra Cu as suggested by HIRST (1961). The sediments of the (L.O.C.) of the (W.B.) also show the highest value of Cu/Al ratio ($3{\cdot}00 \times 10^3$) and illite (35·60%). NICHOLLS and LORING (1962) mentioned that the bulk of Cu is associated with silicates (including quartz). STEPHENS et al. (1975) noted positive correlations of Cu with Si, Al, Fe, Mg, Rb, Zr, Zn, Pb, K, Ti, Na and Y. The correlations of Cu with Si, Al and Rb suggest its association with aluminosilicates. CHOWDHURY (1980) mentioned that the bulk of Cu of the coastal Corallian samples is associated with illite. The same author noted that Cu in the clay fraction chemistry correlated with Al, Fe, Mg, from which he explained that Cu is held in the octahedral site in the clay minerals by proxying for Al^{3+}, Fe^{3+} and Mg^{2+}.

The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows a very strong positive correlation of Cu with the typical lithophile elements, e.g. Ti, Al, Fe (total iron), K, V, Cr, Ni, Ba, Rb, all being significant at the 0·01% level. The same Appendix also shows a very strong positive correlation of Cu with detrital minerals, e.g. illite ($r = +0{\cdot}70$), kaolinite ($r = +0{\cdot}78$), chlorite ($r = +0{\cdot}58$) and total clays ($r = +0{\cdot}65$), all being highly significant at the 0·01% level. These correlations strongly suggest that a significant amount of Cu is associated with clay minerals in their lattices. A very strong positive correlation of Cu with total clays ($r = +0{\cdot}69$) is illustrated by Figure (4.16), which shows an intercept of a value of+5 p.p.m., indicating that 5 p.p.m. of the total

Cu is not associated with clays, and is present in other phases. The average amount of Cu associated with clays is 14 p.p.m. (i.e. 19 - 5 = 14 p.p.m.), which is 74% of the total contents of Cu present in these sediments. This result shows fairly good agreement with the 66% Cu determined in the lattice-held fraction (aluminosilicates) by the leaching study (CHESTER & HUGHES, 1967).

The association of Cu with organic carbon and sulphide minerals has been studied by many workers, including CALVERT (1976), GAD et al. (1969), HIRST (1974), WEDEPOHL (1974), STEPHENS et al.(1975), and FLEISCHER (1955). These authors mentioned the association of Cu with organic carbon by adsorption and reaction with degraded organic matter (WEDEPOHL, 1974).

The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows a very strong positive correlation of Cu with S, Mo, Ni, Fe^{+2}, organic carbon and pyrite, all being highly significant at the 0·01% level, suggesting that the non-detrital Cu is associated with organic carbon and pyrite. This association is also shown in Figure (4.17a & b). A minor amount of Cu seems to be associated with the iron-oxide, which is indicated by the positive correlation of Cu with the residual Fe_2O_3($r = +0{\cdot}59$). KRAUSKOPF (1956) showed that Cu is effectively adsorbed by $Fe(OH)_3$, $Mn(OH)_4$ and clay minerals. The strong positive correlation of Cu with detrital kaolinite ($r = +0{\cdot}78$) suggests that some Cu (non-lattice held) probably precipitated on iron-oxide film coatings on the grains of kaolinite.

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) shows very strong positive correlations of Cu with Pb, As, Ga, Zn and Ni, suggesting that Cu, Pb and Zn may be present either in the form of an admixture of other minerals such as chalcopyrite, galena and sphalerite, as pointed out by FLEISCHER (1955), or as small amounts in solid solutions with pyrite, as mentioned by DEER et al. (1962). STEPHENS et al. (1975) mentioned the occurrence of a group of metals, i.e. Fe, Cu, Pb and Zn in the studied sediments. The same Appendix shows a medium strong positive correlation of Cu with lithophile elements and clay minerals (kaolinite and chlorite) and total clays, significant at the 5% level, suggesting that some Cu is associated with clays. The same correlation coefficient shows medium strong positive correlation of Cu with S, P, Mo, organic carbon, H_2O, Fe^{+2} and pyrite, significant at the 5% level, indicating that a minor amount of Cu is also associated with pyrite. The low degree of correlation of Cu with pyrite (r = +0·19; at the 5% level) and its very strong positive correlation with metals Pb, Ga, Ni, Zn, and As, highly significant at the 0·01% level, suggest that a significant amount of Cu is present in the form of an admixture of other minerals (FLEISCHER, 1955). This view is further confirmed by the factor analysis of the chemical data of these samples described in Chapter Five, which shows very high loadings of minor elements, e.g. Pb, Ga, Zn, Cu, Ni and As in 'FACTOR (F-2)' and no loading of Cu in 'FACTOR (F-3)', which represents sulphide, i.e. pyrite.

It may be concluded that Cu in the (W.K.B.) sediments is associated mainly with clays, showing its preferred association with illite; a minor amount is associated with organic carbon, pyrite and a very small amount with the Fe-oxides/hydroxides. The Cu contents of the (W.B.) are mainly present in the sulphides, organic carbon and total clays.

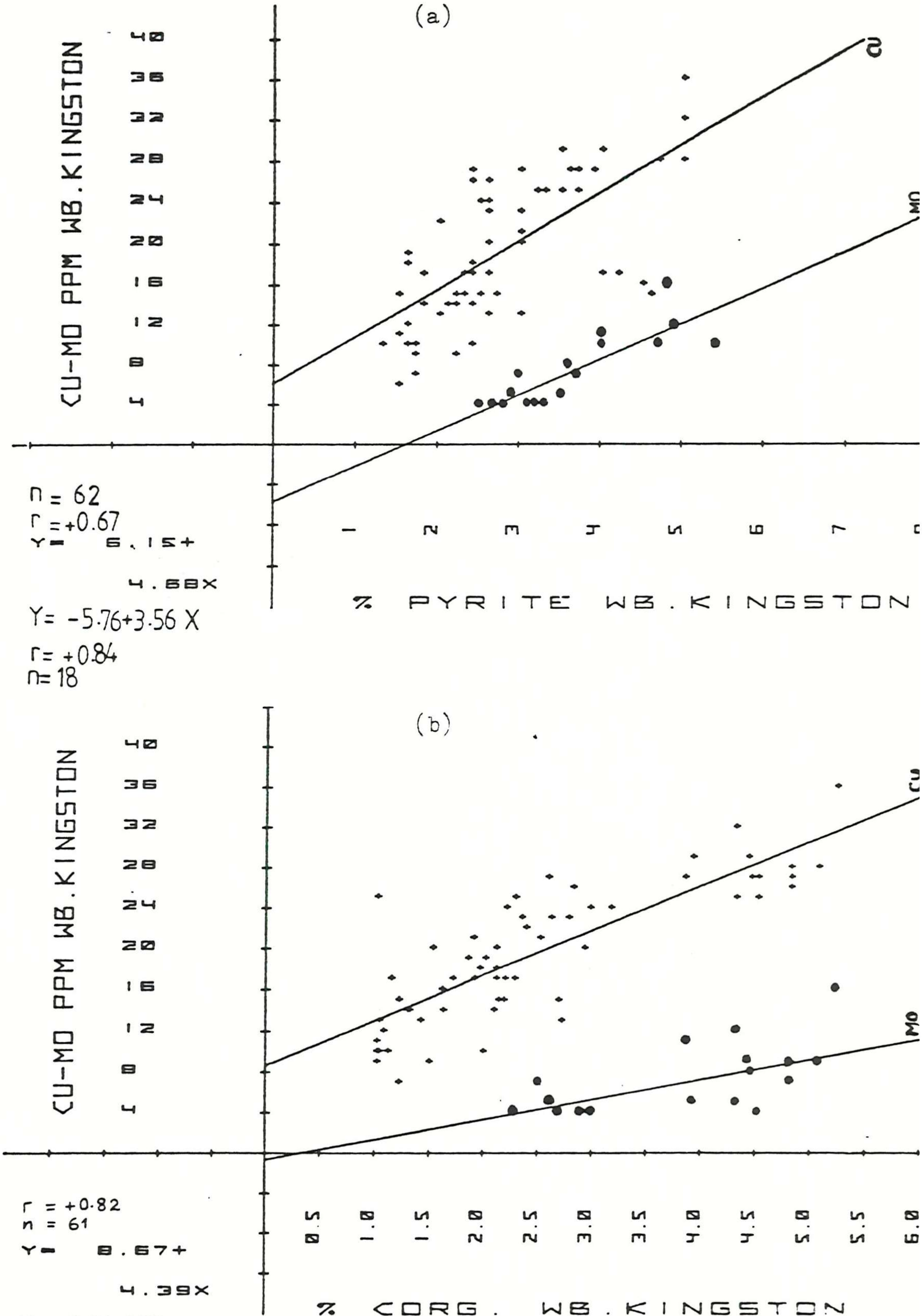
e) Molybdenum

Table (4.3e)

		(W.K.B.)	(W.B.)
Bulk rock	Range	0 - 16* p.p.m.	0 - 38+ p.p.m.
	Average	7 p.p.m.	10 p.p.m.
Carbonate free: Average		-	-
Clay fraction: Average		4·5 p.p.m.	1 p.p.m.
Highest in Bulk rock		8 p.p.m. (L.O.C.)	6 p.p.m. (K.F.)
Lowest " " "		0 p.p.m. (U.O.C.)	0·2 p.p.m. (U.O.C.)

* Sample WBK-45 showed the highest amount of Molybdenum.
\+ Sample BR-1762 " " " " " "

Molybdenum, in the majority of samples of the two borehole sediments was below the detection limit (4 p.p.m.). Only 18 samples from the (W.K.B.) and 14 from the (W.B.) sediments show a concentration of Mo higher than the detection limit. Sample WBK-45, with the highest Mo value of 16 p.p.m., also contains the highest abundance of organic



n = 62
r = +0.67
(CU) Y= 6.15+ 4.68X

(MO) Y= -5.76+3.56 X
r= +0.84
n= 18

r = +0.82
n = 61
(CU) Y= 8.67+ 4.39X

(MO) Y= -0.65+1.98
r = +0.56
n = 18

FIG.(4.17)

carbon (5·21%) and a significantly high amount of pyrite (4·8%). Similarly, sample BR-1762 of the (W.B.) sediments, with the highest Mo value of 38 p.p.m., contains the highest abundance of pyrite (12·70%) and a significantly high amount of organic carbon (5·38%). The average value of the abundances of 12 clay fraction ($< 2\mu$) samples of each borehole sediments is much lower than the average value of Mo concentrations shown by the bulk rock samples of both the boreholes (as shown in Tables (4.3d and 4.3). The sediments of both the boreholes contain significantly higher amounts of Mo as compared to the reported concentration of Mo in shales and sediments by other workers, which is shown in Table (4.3). GAD et al. (1969) reported a strong correlation between Mo, organic carbon and strong reducing environments. DOFF (1969) mentioned concentrations of S, Mo, Pb, Zn, Ni, Cr and C_{org} in the sediments of anoxic environments. KRAUSKOPF (1967) stated that sediments of strong reducing environments will show higher values of the Fe_2O_3/Al_2O_3 ratio, as compared to the value of the same ratio of the average shales. The sediments of the two boreholes showed the highest concentrations of S, Mo, Pb, Zn, Ni, Cr and C_{org}, as is shown in Table (4.3). The Fe_2O_3/Al_2O_3 ratio of the sediments of the Winterborne Kingston Borehole is 0·497, much higher than the value (0·387) of the average shales of KRAUSKOPF (1979). These observations strongly support that the studied sediments were deposited under strong reducing conditions. From these observations, it is expected that major amounts of Mo in these sediments must be associated with C_{org} and sulphide minerals; components generally concentrated under reducing conditions.

The stratigraphic distribution of Mo in the Winterborne Kingston Borehole sediments shows its highest (8 p.p.m.) concentration in the sediments of the Lower Oxford Clay, which also contain the highest amounts of organic carbon (4·32%) and pyrite (3·89%). The lowest concentrations of Mo, organic carbon (1·50%) and pyrite (2·25%) are present in the sediments of the Upper Oxford Clay. The concentration of Mo in the Warlingham Borehole sediments does not follow the same trends as demonstrated by the Winterborne Kingston Borehole sediments. The trend is opposite, and the highest concentration of Mo (6 p.p.m.) occurs in the sediments of the Kellaways Formation which contain the highest amount of pyrite (3·03%) and second highest amount of organic carbon (2·28%). According to HIRST (1962) concentration of Mo takes place in the near-shore sediments. The lowest concentration of Mo is associated with the lowest concentrations of organic carbon and pyrite in the Upper Oxford Clay sediments. From these observations it may be postulated that Mo concentration in the Winterborne Kingston Borehole sediments is controlled equally by the abundances of organic carbon and pyrite. A very strong association of Mo with organic carbon and pyrite has been mentioned by GAD et al. (1969), PILIPCHUK & VOLKOV (1974), NODDACK and NODDACK (1955), LE.RICHE (1959), CALVERT (1976) and PRICE (1976). The concentration of Mo in the Warlingham Borehole sediments seems to be controlled mainly by pyrite and a minor amount of organic carbon. This conclusion is based on the antipathetic relationship between Mo and organic carbon, and the pathetic relationship of Mo and pyrite in the sediments of the Lower Oxford Clay and Kellaways Formation respectively, which is also shown in Tables (4.2A & 4.2B). LE.RICHE (1959) stated that if high Mo concentrations do not correlate with high organic carbon values, then two different types of organic carbon are present in the sediments. The Mo and organic carbon relationship of the Warlingham Borehole sediments suggests the presence of two different types of organic carbon: one possibly land derived and the other strictly marine.

The correlation coefficient matrix for the Winterborne Kingston Borehole sediments in Appendix (4.1C) shows very strong positive correlations of Mo with S, Ni, Pb, Zn, H_2O, Fe^{+2}, C_{org}, pyrite and kaolinite, all being highly significant at the 0·01% level. The same correlation matrix shows medium positive correlations of Mo with lithophile elements, e.g. Ti, Al, Fe_2O_3, K, P, Cr, Ba and minerals e.g. illite, chlorite and total clays, all being significant at the 5% level. Molybdenum shows its negative correlations with Si, Zr, Ca, Mn, As and smectite. These correlations strongly suggest that Mo of the (W.K.B.) sediments is associated with organic carbon and pyrite, as suggested by other workers and mentioned earlier. The strong association of Mo with organic carbon ($r = +0{\cdot}56$), and very strong relationship with pyrite ($r = +0{\cdot}84$) are illustrated in Figures (4.17a and 4.17b).

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) shows very strong positive correlations of Mo with

S (r = +0·77), P_2O_5 (r = +0·60), C_{org} (r = +0·68), Fe^{+2} (r = +0·77) and pyrite (r = +0·77), all being highly significant at the 0·01% level. It shows a weak positive correlation with depth, Fe_2O_3, Cr, Ba, La, Ce, Ni, Y, H_2O, kaolinite and total clays, all being significant at the 5% level. The very strong positive correlations of Mo with S, Fe^{+2} and pyrite suggest that a major amount of Mo is associated with pyrite.

It may be concluded that Mo, in the (W.K.B.) sediments is mainly associated with pyrite and some amount with organic carbon; this conclusion is also confirmed by the factor analysis of the chemical data of these sediments, which shows very strong loadings of Mo and C_{org} in the FACTOR (F-2), representing the pyrite and organic carbon phases (see Chapter Five).

The concentration of Mo in the (W.B.) sediments is controlled mainly by the sulphide phase, i.e. pyrite, and a minor amount is associated with organic carbon. Factor analysis of the chemical data of these sediments also suggested similar controls (in FACTOR, F-3), which show a very high loading of Mo with a comparatively low loading of organic carbon.

f) Rubidium

Table (4.3f)

		(W.K.B.)	(W.B.)
Bulk rock	Range	* 45 - 149 p.p.m.	+ 40 - 240 p.p.m.
	Average	99 p.p.m.	132 p.p.m.
Carbonate free: Average		138 p.p.m.	186 p.p.m.
Clay fraction: Average		224 p.p.m.	260 p.p.m.
Highest in Bulk rock		135 p.p.m. (K.F.)	158 p.p.m. (L.O.C.)
Lowest " " "		69 p.p.m. (U.O.C.)	117 p.p.m. (K.F.)

* Sample WBK-56 showed the highest concentration of robidium.
\+ Sample BR-1771 " " " " " "

The sediments of the (W.K.B.) in Table (4.3f) show a relatively lower abundance of Rb as compared with the (W.B.) sediments, which have shown a higher abundance of Rb than the reported abundance of Rb in shales and other sedimentary rocks by other workers, as shown in Table (4.3). NICHOLLS and LORING (1962) also found a lower concentration of Rb in the British Carboniferous sediments. The average value of Rb in the (W.B.) sediments shows a close agreement with the average value of Rb reported by TUREKIAN and WEDEPOHL (1961) in shales. The stratigraphic distribution of Rb in the sediments of the two boreholes does not show similar trends. The sediments of the (W.K.B.) contain the highest and lowest abundances of Rb in the sediments of the (K.F.) and (U.O.C.) respectively, but the (W.B.) sediments show the highest and lowest abundances of Rb in the (L.O.C.) and (K.F.) respectively, as shown in Table (4.3f).

The higher concentration of Rb reflects the higher abundance of K; the highest abundances of K in the (K.F.) of the (W.K.B.) sediments as shown in Table (4.1A) and those in the (L.O.C.) of the (W.B.) sediments in Table (4.2A) confirm the above view. The variations of Rb concentration also exhibit the variations in the clay mineral species present in the sediments. CHOWDHURY (1980) reported higher abundances of Rb and K with higher concentration of illite in the Corallian mud-rocks from the Dorset coast. The overall lower concentration of Rb in the (W.K.B.) as compared with the (W.B.) sediments can be related to the amounts of total clays, and the type of clay mineral species (particularly illite), present in these sediments. The (W.B.) sediments contain relatively higher abundances of total clays (45·51%) and illite (65·53%) when compared to the abundances (44·18%) and (53·5%) of the respective components in the (W.K.B.) sediments. The relationship of Rb in the studied sediments with the components, e.g. total clays, illite and K, becomes more clear when the distribution trends of these components in the stratigraphic sequence are carefully examined in the Tables (4.1A & 4.1B) and (4.2A & 4.2B) respectively, which show a sympathetic relationship between all these phases.

In particular, the strong relationship between the concentrations of Rb and total clays is very well illustrated by two samples, one from the (W.K.B.) sediments, i.e. WBK-56, which showed the highest abundance of Rb (149 p.p.m.), and total clays (60·6%), and the other sample, BR-1771, from the (W.B.) sediments, which also showed the highest concentrations of Rb (240 p.p.m.) and total clays (75·98%).

GOLDSCHMIDT (1954) stated that the residual sediments such as sandstones and quartz contain a lower amount of Rb in comparison to the argillaceous sediments. The sediments of the (U.O.C.) of the (W.K.B.) and of the (K.F.) of the (W.B.) showed the lowest concentrations of Rb, as shown in Table (4.3f). These sediments contain the highest amounts of quartz, as shown in Tables (4.1B & 4.2B). The lowest concentration of Rb may be related to higher contents of quartz, as suggested by GOLDSCHMIDT (op.cit.)

The enrichment or depletion of Rb in sedimentary rocks may also reflect the type of weathering that prevailed in the area of provenance. A lower concentration of Rb in the sediments is generally associated with physical weathering, which provides a small amount of Rb for incorporation in clay minerals. On the other hand, chemical weathering provides abundant Rb from the fresh rocks for incorporation in clay minerals. The distribution of Rb in the sediments of the two boreholes tends to suggest that at the time of deposition of (U.O.C.) of the (W.K.B.) sediments, the weathering conditions in the area of provenance were more of a physical type, and in the case of the (W.B.) sediments a pronounced chemical weathering condition existed at the time of deposition of the (L.O.C.) sediments, which contain the highest abundance of Rb. CHOWDHURY (1980) stated that deep chemical weathering was operative in the source area during the time the Oxford Clay was being deposited.

GOLDSCHMIDT (1954) stated that the geochemistry of Rb is very much related to that of K. The ionic radius of Rb^+(1·57Å) is very close to that of K^+(1·46Å), which facilitates substitution. KRAUSKOPF (1979) also stated the same views about the substitution of Rb in K-bearing minerals. ELDERFIELD (1976) stated that Rb has a very low hydration energy, and it is expected to be fixed in the inter-layer positions of micas and possibly chlorite. GOLDSCHMIDT (op.cit.) stated that if clays show dissimilar results of Rb, the individual Rb values reflect the variations of the clay mineral species, as has been observed in the sediments of the (K.F.) of the Winterborne Kingston Borehole, and the (L.O.C.) of the Warlingham Borehole. DEGENS et al. (1957) stated that the Rb^+ ion, being slightly larger than K^+, can substitute for K^+ in the inter-layer positions of minerals such as mica, montmorillonite and illite, but not in kaolinite since it does not have a structural position for Rb.

WELBY (1958) stated that a high Rb/K ratio in sediments indicates the enrichment of Rb relative to K during the weathering and transportation cycle. He further stated that K is subsequently adsorbed by the clay minerals in a marine environment. The trends of Rb/K and K/Rb ratios in the studied sequences are shown in Tables (4.1C & 4.2C). The sediments of the (W.K.B.) showed the lowest and highest values of the Rb/K ratios in the sediments of the (U.O.C.) and (L.O.C.) respectively. The sediments of the (W.B.) also displayed similar trends of this ratio. This study suggests that Rb enrichment of the sediments showing higher values of Rb/K ratios took place during the weathering and transportation, as suggested by WELBY,(op.cit.).

The correlation coefficient matrix of the Winterborne Kingston Borehole sediments shown in Appendix (4.1C) shows a very strong positive correlation of Rb, highly significant at the 0·01% confidence level, with depth and typically lithophile elements, e.g. Si, Ti, Al, Mg, Na, K, V, Cr, Ni, Ba, Ce, Th, Cu, Zr, Nb, H_2O, and also detrital minerals, e.g. illite, kaolinite, chlorite, organic carbon and total clays. The same Appendix (4.1C) shows very strong negative correlations of Rb, highly significant at the 0·01% level, with Ca, Mn, CO_2, calcite and smectite. These correlations confirm the lithogenous origin of Rb and its association with the detrital component (i.e. total clays) of these sediments. HIRST and KAYE(1971) found a very strong positive correlation of Rb with Ti, Mg, Al, K, V, Cr, Ni, Cu, Ba and organic carbon. The very strong positive correlation of Rb with total clays ($r = +0{\cdot}93$), highly significant at the 0·01% level, is shown in Figure (4.18a). This figure shows an intercept of 18·65 p.p.m., suggesting that this amount of Rb is not associated with clays. The average amount of Rb associated with total clays is 80·35 p.p.m., (i.e.90 p.p.m. - 18·65 p.p.m. = 80·35 p.p.m.), which is approximately 81% of the total Rb present in the sediments. The remaining amount of Rb may be associated with other phases, e.g. organic carbon, as suggested by HIRST and KAYE (op.cit.).

The correlation coefficient matrix of the Warlingham Borehole sediments is given in Appendix (4.2C), which shows a very strong positive correlation of Rb with the lithophile elements, e.g. Ti, Al, Na, K, V, Ce, Th, Y, H_2O and total clays, highly significant at the 0·01% level. The same Appendix shows a medium strong positive correlation of Rb with depth, Si, Fe_2O_3(total iron), Cr, Ba, La, Ga, Cu, Ni, Nb and organic carbon, significant at the 0·1 - 5% levels. These sediments also show a very strong negative correlation, significant at the 0·01% level, of Rb with Ca, CO_2, and a medium strong negative correlation of Rb with Mn, As, mixed-layer clay minerals, quartz, dolomite and calcite. These correlations are very similar to those of the sediments of the Winterborne Kingston Borehole, and thus suggest that Rb in the Warlingham Borehole sediments is also associated mainly with total clays (r = +0·93), with a minor amount associated with other phases such as organic carbon (r = +0·40).

g) <u>Barium</u>

Table (4.3g)

		(W.K.B.)	(W.B.)
Bulk rock	Range	110 - 389* p.p.m.	75 - 428+ p.p.m.
	Average	214 p.p.m.	265 p.p.m.
Carbonate free: Average		298 p.p.m.	365 p.p.m.
Clay fraction: Average		421 p.p.m.	458 p.p.m.
Highest in Bulk rock		370 p.p.m. (K.F.)	407 p.p.m. (K.F.)
Lowest " " "		252 p.p.m.(U.O.C.)	335 p.p.m.(U.O.C.)

* Sample WBK-65 showed the highest concentration of Barium.
\+ Sample BR-1831 " " " " "

The average contents of Ba of the (W.B.) sediments on an absolute and a carbonate free basis are relatively higher than those of the (W.B.K.) sediments, as shown in Table (4.3g). The clay fraction samples of both the boreholes show enrichment of Ba abundances over the concentrations of Ba in bulk rock samples. The clay fraction samples of the (W.B.) sediments showed a higher abundance of Ba as compared to the (W.B.K.) samples, as shown in Table (4.3g).. In the (W.K.B.) sediments, sample WBK-65 showed the highest concentration of Ba(389ppm), this sample also contains appreciably higher abundances of total clays (56·3%), illite (64%) and kaolinite (22%). In the (W.B.) sediments, sample BR-1831 showed an exceptionally high concentration of Ba (844 p.p.m.), associated with significantly higher amounts of total clays (48·21%), illite (59%) and kaolinite (26%); these associations suggest a strong relationship of Ba with these clays. The highest concentration of Ba in both the borehole sediments is present in the sediments of (K.F.) and the lowest in the (U.O.C.) sediments, as is shown in Table (4.3g). From these trends it is indicated that distribution of Ba in the sediments of both the boreholes is largely controlled by the abundances of total clays and specific clay mineral species, e.g. illite and kaolinite; which have played a very significant role in the control of Ba in these sediments.

The enrichment of Ba in the clay fraction samples of both the boreholes clearly indicates that most of the Ba in these sediments is associated with clays. The very strong positive correlation of Ba at the 0·01% level, with detrital components, including illite, kaolinite, chlorite and total clays, as shown in the correlation coefficient matrix in Appendix (4.1C), confirms the above views. In the (W.K.B.) sediments Ba showed the highest value of the correlation coefficient ($r = +0{\cdot}80$) for illite, indicating its preferred association with illite. The (W.B.) sediments show a very strong positive correlation of Ba, in Appendix (4.2C), significant at the 0·01% level, with kaolinite ($r = +0{\cdot}62$), total clays ($r = +0{\cdot}41$) and chlorite ($r = +0{\cdot}19$). These correlations suggest a strong relationship of Ba with kaolinite, chlorite and total clays. SULAIMAN (1972) studied the K/Ba ratio for the Namurian Argillites of Ireland and noticed that the lowest value of this ratio exists in the kaolinite-rich province of his sediments. The K/Ba ratio for the (W.B.) sediments shows its lowest value (46·93) in the sediments of the (K.F.), which contains the highest average amounts of kaolinite (23·70%) and Ba (306 p.p.m.). The stratigraphic distribution of Ba and kaolinite, and K/Ba ratios, are given in Tables (4.2A, 4.2B & 4.2C) respectively. The enrichment of Ba in these sediments is due to the preferential substitution of Ba^{2+}(1·44Å) for K^{+}(1·46Å) due to their similar ionic radii (RANKAMA and SAHAMA, 1950; and GOLDSCHMIDT, 1954). According to GOLDSCHMIDT (op.cit.) the precipitation of very insoluble barite ($BaSO_4$) is often found as concretions in hydrolysates and shales. According to the same author the precipitation of Ba takes place in oxidate sediments, particularly those rich in Mn-dioxide, due to absorption of Ba^{2+} cations by the negatively charged colloidal particles of Mn precipitate. SULAIMAN (1972) explained the correlation of Ba with kaolinite as a result of possible precipitation of barite ($BaSO_4$). The same author further suggested that the association of Ba and kaolinite may be the result of interaction of acidic solutions on the K and Ba bearing minerals, in which K, being relatively mobile, was removed and Ba was left behind, to be adsorbed onto the kaolinite grains. Formation of insoluble compounds of Ba, e.g. barite ($BaSO_4$) in the studied sediments is possible under the processes explained above.

The sediments of the (K.F.) contain minor amounts of K-feldspar in which substitution of Ba^{2+} (1·44Å) for K^+ (1·46Å) is easily possible. The acidic nature of these sediments is reflected by the pH values of these sediments, shown in Table (4.3B). The pH was determined in representative samples from the Warlingham Borehole sediments, including samples from the (K.F.) which contains the highest amount of kaolinite. SULAIMAN (1972) followed the method of pH determination in sediments proposed by BEAR (1964), and determined the pH of samples of Namurian argillites of Ireland containing the highest amounts of kaolinite, to see the trends between the values of pH and kaolinite. He concluded that percolating solutions were acidic and related to the abundances of kaolinite. PEREL'MAN (1967) reported that in the weathering of shales, coals and clays, leaching solutions can be strongly acidic (the pH drops from 6·9 to 2·9). BUTT (1971)in a reconnaissance geochemical study of the bed-rocks, as well as soils and waters in Northern Ireland, mentioned that the percolating solutions in the near-shore area should be generally on the acid pH side. The pH values of the (K.F.) samples range between 7·05 and 5·90, indicating a neutral-acidic nature, and reflecting the pH conditions under which these sediments were deposited (SULAIMAN, 1972). From this evidence, it is indicated that percolating solutions at the time of deposition of the Kellaways Formation sediments were acidic.

The association of Ba with kaolinite in the (W.B.) sediments can be easily explained in the light of the above facts. The association

TABLE (4.3B): Determination of pH in the Sediments of the Oxford Clay and Kellaways Formations from the Warlingham Borehole

	Sample No.	pH	% Pyrite	% Calcite
(U.O.C.)	BR-154	9.35	1.72	12.05
	BR-246	8.85	0.73	38.19
	BR-543	9.25	0.90	21.08
	BR-812	9.25	0.93	51.14
(M.O.C.)	BR-958	9.15	5.18	22.60
	BR-1157	8.95	1.53	20.64
	BR-1377	9.00	1.81	26.07
(L.O.C.)	BR-1583	9.00	2.08	20.35
	BR-1683	8.75	1.72	17.61
(K.F.)	BR-1762	7.05	12.70	17.04
	BR-1852	5.90	0.56	0.00

Note: 1. Samples were standardized at 23.5°C temp. and 7 pH solution.

2. pH was determined by following the method used by BEAR (1968) and SULAIMAN (1972).

may also be explained in the light of NICHOLLS and LORING's (1962) findings, who stated that Ba was adsorbed by the negatively charged iron-monosulphide to disulphide; the Ba was retained in the rock, though not necessarily in the sulphides. MOHR (1959a) reported a small amount of Ba associated with pyrite. The Ba of the (W.B.) sediments shows a positive correlation with C_{org} ($r = +0{\cdot}24$), sulphur ($r = +0{\cdot}16$), Fe^{+2} ($r = +0{\cdot}12$) and pyrite ($r = +0{\cdot}13$), all shown in Appendix (4.2C), suggesting association of Ba with pyrite; which shows its highest concentration (3·03%) in the sediments of the (K.F.). The kaolinite grains, being coarser, settled rapidly along with other detritus, and due to abundantly available biological organisms and organic matter within the environments, strong reducing conditions were created; probably within the freshly deposited sediments, and thus the formation of iron-sulphide (pyrite) was facilitated. The relationship of Ba with the abundances of total clays and kaolinite is very well illustrated by sample BR-129, which shows the lowest concentrations of Ba (75 p.p.m.), total clays(18·34%) and kaolinite (0%). From these observations it becomes clear that Ba in the (W.B.) sediments is associated mainly with clay minerals, particularly with kaolinite and chlorite, and a minor amount seems to be associated with sulphide minerals. The sediments of the (W.K.B.) contain Ba in total clays with illite having its preferred association.

The average contents of Ba in the sediments of both the boreholes are considerably lower than its values in the average shales and other sediments reported by other workers, and shown in Table (4.3). HIRST (1962) also found lower contents of Ba in the clays, to which he attributed the high rate of sedimentation. The lowest concentration of Ba in the sediments of the Upper Oxford Clay in both the boreholes, in particular, appears to be due to high rates of deposition of these sediments. Evidence related to the high rates of deposition of these sediments has been given elsewhere. HIRST (op.cit.) reported higher concentration of Ba in the platform sediments. The sediments of Kellaways Formation of both the boreholes showed the highest values of Ba as compared to the sediments of the Oxford Clay Formation of both the boreholes. The sediments of the Kellaways Formation of the Warlingham Borehole showed exceptionally high values of Ba (407 p.p.m.), quartz (40·7%), Zr (347 p.p.m.), kaolinite (23·70%) and Nb (23 p.p.m.);

all being detrital and heavy, suggesting a near-shore type of environment.

HIRST (1962) observed the constancy of Ba/K and Ba/K + Na ratios in the sediments studied by him, from which he interpreted that it shows the control of illite and montmorillonite over the distribution of Ba. NICHOLLS and LORING (1962) also observed similar constancy of these ratios and interpreted it as a strong association with illite. The Ba/K and Ba/K + Na ratios of both the borehole sediments are shown in Tables (4.1C & 4.2C), which show constancy as described by HIRST (op.cit.) and NICHOLLS and LORING (op.cit.). It suggests that illite, in general, controls the distribution of Ba in these sediments. CAMERON (1957) stated that Ba, like K, is incorporated in sheet minerals at or near the site of weathering. According to GOLDSCHMIDT (1954) the similar ionic radii of divalent Ba^{2+} (1·44Å) and univalent K^+ (1·46Å) allows Ba^{2+} to be captured by the K^+ minerals. The same author stated that a very small amount of Ba^{2+} ions are able to enter the calcium, due to the smaller ionic radius of Ca^+ (1·08Å) as compared to Ba^{2+} (1·44Å). A very strong negative correlation of Ba, significant at the 0·01% level, with Ca, Mg, Mn, calcite and dolomite, and a medium strong negative correlation with Sr, as shown in Appendix (4.2C), clearly confirm that no substitution of Ba^{2+} against Ca^+ took place in these sediments, and most of the Ba is associated with clays. The very strong relationship of Ba with total clays (r = +0·95) is illustrated in Figure (4.18a). A minor amount of Ba in the (W.K.B.) sediments is also associated with the iron-oxides/hydroxides; which is indicated by the medium positive correlation of Ba with Fe^{+3} (r = +0·21), significant at the 0·1% level. In the (W.B.) sediments a minor amount of Ba is associated with the minerals of the sulphide phase, as indicated by the positive correlation of Ba with sulphur (r = +0·16) and other elements of the chalcophile group. Some of the Ba also exists in the form of insoluble compounds of Ba, probably as barite ($BaSO_4$) which, being in very small quantity, might have escaped its detection by X.R.D.

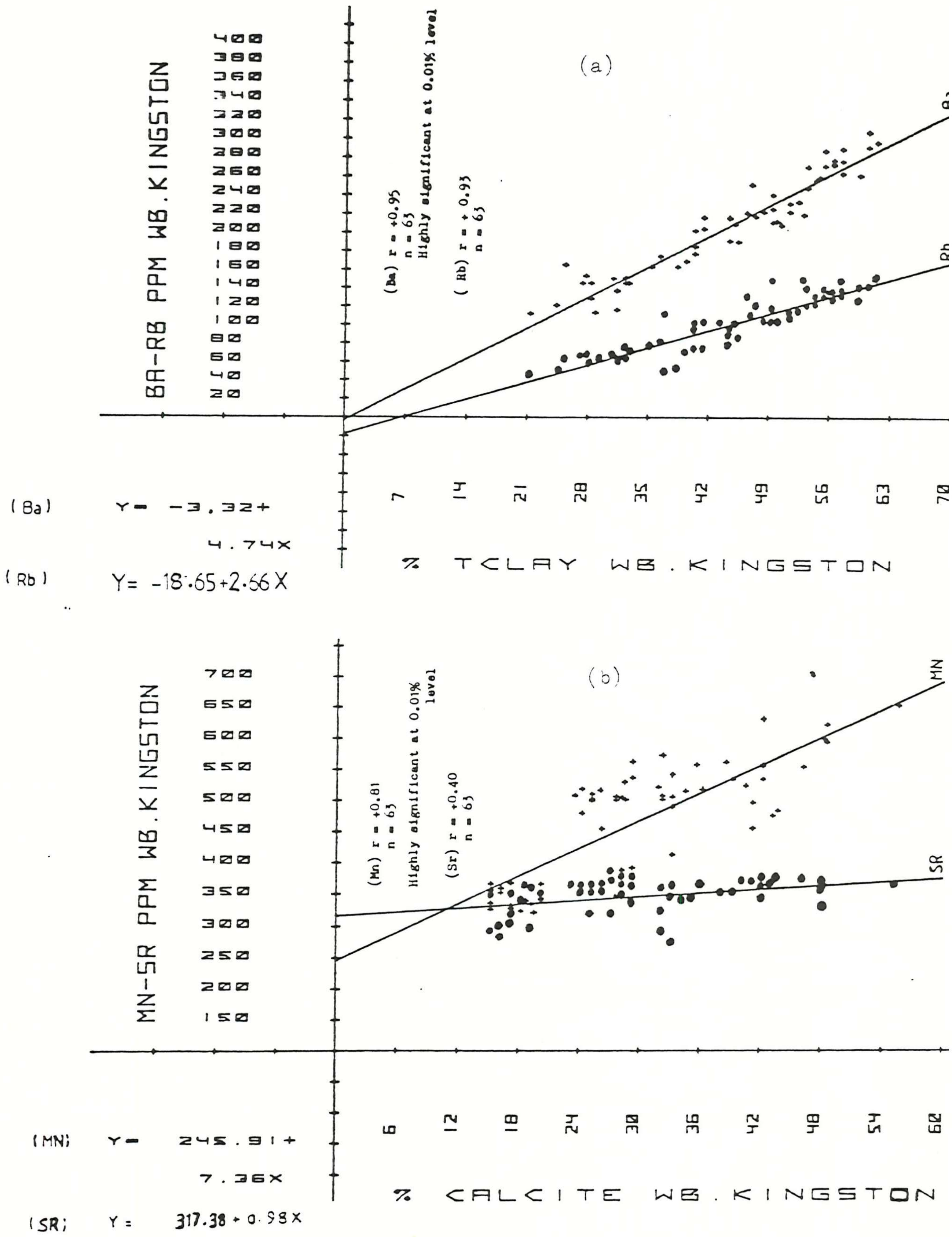
BA-RB PPM WB.KINGSTON
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
(a)
(Ba) r = +0.95
n = 63
Highly significant at 0.01% level
(Rb) r = + 0.93
n = 63
Ba
Rb
7
14
21
28
35
42
49
56
63
70
% TCLAY WB.KINGSTON
(Ba) Y= -3.32+4.74X
(Rb) Y= -18.65+2.66X
MN-SR PPM WB.KINGSTON
150
200
250
300
350
400
450
500
550
600
650
700
(b)
(Mn) r = +0.81
n = 63
Highly significant at 0.01% level
(Sr) r = +0.40
n = 63
MN
SR
6
12
18
24
30
36
42
48
54
60
% CALCITE WB.KINGSTON
(MN) Y= 245.91+7.36X
(SR) Y= 317.38+0.98X

FIG.(4.18)

h) Manganese

Table (4.3h)

		(W.K.B.)	(W.B.)
		*	+
Bulk rock	Range	361 - 647 p.p.m.	62 - 391 p.p.m.
	Average	467 p.p.m.	157 p.p.m.
Carbonate free: Average		691 p.p.m.	244 p.p.m.
Clay fraction: Average		196 p.p.m.	174 p.p.m.
Highest in bulk rock		535 p.p.m.(U.O.C.)	203 p.p.m.(U.O.C.)
Lowest in bulk rock		345 p.p.m. (K.F.)	84 p.p.m. (K.F.)

* Sample WBK-9 showed the highest concentration of Manganese.

\+ Sample BR-444 " " " " " "

The Winterborne Kingston Borehole sediments show enrichment of Mn over its concentration in the Warlingham Borehole sediments, as shown in Table (4.3h). The highest concentration of Mn (647 p.p.m.) in the (W.K.B.) sediments is shown by sample WBK-9, which also contains the highest amounts of calcite (55•3%) and smectite (12•30%). In the (W.B.) sediments the highest concentrations of Mn (391 p.p.m.) and illite (38•81%) are shown by sample BR-444, which also contains a significantly high amount of total carbonates (34%). These observations suggest that manganese in the sediments of both the boreholes is associated mainly with authigenically/diagenetically produced mineral phases, including iron-manganese oxides/hydroxides coated onto the surfaces of clay minerals.

The clay fraction samples of the (W.K.B.) and (W.B.) sediments show Mn values of 196 and 174 p.p.m. respectively. The Mn contents of the clay fraction of the (W.K.B.) sediments represent nearly 42% of the total manganese contents of the bulk rock. The remaining 58% Mn resides in the soluble fraction (mainly carbonates) dissolved by the acid-reducing reagents, i.e. acetic acid + hydroxylamine hydrochloride (CHESTER & HUGHES, 1967). The clay fraction of the (W.B.)sediments shows an enrichment of Mn (174 p.p,m.) over the Mn contents (157 p.p.m.) in the bulk rock, indicating its strong association with the clays. The leaching study results (CHESTER & HUGHES, 1967), described in Chapter Six, show that only 30% Mn is associated with the lattice-held fraction, which is a lower value than 47% shown by the (W.K.B.) sediments. By comparison, it appears that more manganese is associated with clays in the (W.K.B.) sediments. If the percentages of soluble manganese in both the borehole samples are taken into consideration, then it becomes clear that the (W.B.) sediments show about 70% Mn, while the (W.K.B.) sediments show only 53% soluble manganese. The enrichment of Mn in the clay fraction of the (W.B.) samples may be due to the presence of iron-oxides/hydroxides and the association of a significant amount of manganese with these oxides/hydroxides.

The correlation coefficient matrix for both the boreholes (in Appendices 4.1C & 4.2C) shows a much stronger positive correlation of Mn with iron-oxide ($r = +0{\cdot}49$), highly significant at the 0·01% level, in the (W.B.) sediments, as compared to the (W.K.B.) sediments, which show a weak positive correlation of Mn with iron-oxide ($r = +0{\cdot}26$), significant only at the 5% level. This evidence explains the higher contents of Mn in the clay fraction of the (W.B.) sediments. It also confirms the presence of the Fe-Mn oxides/hydroxides in these sediments.

The highest concentration of Mn (535 p.p.m.) and (203 p.p.m.) is present in the Upper Oxford Clay of the (W.K.B.) and (W.B.) sediments respectively. The Upper Oxford clay sediments in the two boreholes also show the highest abundances of carbonates, smectite and mixed-layer clay minerals, as is shown in Tables (4.1B & 4.2B). The lowest concentration of Mn (345 p.p.m.) and (84 p.p.m.) is present in the sediments of the (K.F.) of the (W.K.B.) and the (W.B.) sediments respectively. The Mn contents and the Mn/Fe ratios of the sediments of the (K.F.) of the (W.K.B.) sediments shown in Tables (4.1A & 4.1C) and those of the (W.B.) sediments in Tables (4.2A & 4.2C), suggest that strong reducing conditions probably prevailed constantly below the sediment surface during the deposition of these sediments. The presence of significantly higher amounts of pyrite and organic carbon in these sediments confirms the existence of strong reducing conditions. According to GOLDSCHMIDT (1954), under reducing conditions Mn is mobilized as $Mn(HCO_3)_2$, and under oxidizing conditions it precipitates. The oxidation and reduction of manganese depends strongly on the acidity of the aqueous solutions within the sediments. A combination of low Eh and acidic solutions may result in the leaching of a significant amount of manganese as $Mn(HCO_3)_2$, as suggested by

RANKAMA and SAHAMA (1950). Bacterial degradation of organic matter may add certain acids to make the ground waters acidic, and thus the oxidation/reduction of manganese in the sediments is controlled. The presence of percolating solutions of acidic pH in the sediments of the (K.F.) of the (W.B.) sediments is indicated by the pH values of these sediments, shown in Table (4.4) and described in the study of Ba in this chapter. Under reducing conditions, manganese loosely absorbed by the sediments is leached. The depletion of manganese in the sediments of the (K.F.) may be partly due to the presence of the leaching processes active at the time of deposition or sedimentation. The presence of leaching processes in these sediments has already been described in the geochemistry of iron in these sediments. The poor contents of carbonate minerals in these sediments may also be another valid reason for the depletion of Mn. In carbonate minerals, according to RANKAMA and SAHAMA (1950), the Mn^{2+} (0·91Å) replaces the Ca^{2+} (1·08Å); there being a close similarity of the ionic radii.

The higher concentration of manganese in the Upper Oxford Clay sediments of both the boreholes probably reflects the existence of oxidising conditions, most likely present within the sediments by the entrapped oxygen or at the sediment-water interface. The abundances of carbonates, smectite and mixed-layer clay minerals shown in Tables (4.1B & 4.2B) seem to be the most valid reasons to explain the enrichment of manganese in these sediments, as also explained by RANKAMA and SAHAMA (op.cit.). According to BOSTRÖM (1973), CHESTER and MESSIHA-HANNA (1970) and CHESTER and HUGHES (1967), the enrichment of manganese in the oxidising environments may be due to the presence of authigenically produced manganese oxides. The factor analysis results of the chemical data of the sediments of both boreholes, in Chapter Five, show the existence of the Mn-oxides/Fe-Mn oxides/hydroxides factors in these sediments. Therefore some of the manganese in these sediments may be contributed by these Fe-Mn oxides/hydroxides.

DEER et al. (1962) states that montmorillonite and illite both contain about 770 p.p.m. of manganese. The average values of Mn in the clay fractions of both the borehole sediments, as shown in Table (4.3), are very much lower values than those reported by DEER et al. (op.cit.). The reason for such a big depletion of manganese in the clay fractions of these sediments may be due either to the reported abundances of smectite, illite and mixed-layer clay minerals, shown in Tables (4.1B & 4.2B), or to its presence in the form of Fe-Mn oxides/hydroxides, coated onto the surfaces of the clay minerals. The majority of the clay mineral population is of detrital origin; such minerals during their transportation can easily lose a significant amount of Mn adsorbed onto their surfaces due to leaching processes. Reduction in manganese also takes place after the burial of the clay minerals under the reducing conditions.

HIRST (1962) studied the Mn/Fe ratios and states that much of the variation of the ratio is attributable to their separation at or near the site of weathering. HEWETT (1932) and LJUNGGREN (1953) state that Fe^{+2} in solution is more easily oxidized than Mn^{2+} and is stabilized as Fe_2O_3 or $Fe(OH)_3$, whereas Mn^{2+} oxidizes to $Mn(OH)_3$ $Mn(OH)_4$ or MnO_2. HIRST (op.cit.) states that at the site of weathering Mn, like Fe, may enter the newly developing minerals such as montmorillonite, or it may be co-precipitated with Fe, $Fe(OH)_3$ sols. being +ve charged and $Mn(OH)_4$ sols. being -ve charged. The lowest ratio of Mn/Fe exists in the sediments of the (K.F.) of both the boreholes, as shown in Tables (4.1C & 4.2C); it may be connected with the weathering conditions of these sediments, as proposed by HIRST (op.cit.).

The correlation coefficient matrix of the Winterborne Kingston Borehole sediments in Appendix (4.1C) shows a very strong positive correlation of Mn, significant at the 0·01% level, with Ca, CO_2, calcite and smectite, and its strong positive correlation, significant at the 1 - 5% levels, with As, Sr, P, iron-oxides. This correlation matrix also shows a very strong negative correlation of Mn, highly significant at the 0·01% level, with depth and lithophile elements, e.g. Si, Ti, Al, Na, K, V, Cr, Ni, Ba, Ce, Th, Cu, Rb, Nb and organic carbon, H_2O, illite, kaolinite, chlorite and total clays. These correlations strongly suggest that Mn of the Winterborne Kingston Borehole sediments is associated mainly with the authigenically produced minerals, e.g. calcite, sedimentary apatite and smectite, as explained earlier. A very strong relationship of Mn with calcite is shown in Figure (4.18b). A small amount of manganese is also present in the iron-oxides/hydroxides present in these sediments, being adsorbed onto the surfaces of the clay minerals. The presence of iron-oxides/hydroxides in these sediments is also confirmed by the factor analysis in Chapter Five. Manganese showed the strongest correlation coefficient value with calcite (r = +0·81); this confirms that most of the manganese is associated with the carbonate minerals, particularly calcite, which is illustrated in Figure (4.18b).

The correlation coefficient matrix in Appendix (4.2C) for the Warlingham Borehole sediments indicates a very strong positive correlation of Mn, significant at the 0·01% level, with Ca, CO_2, total carbonates (calcite + dolomite), iron-oxide, Mg, Sr and dolomite and mixed-layer minerals; also a medium strong positive correlation, significant at the 5% level, with As, V and illite, as shown in the same Appendix. The same correlation coefficient matrix shows a strong to very strong negative correlation of manganese, significant at the 0·01% level, with depth and typical lithophile elements, e.g. Si, Ti, Al, Na, S, P, Ba, Th, Y, Zr, H_2O, Fe^{+2} and kaolinite, organic carbon, quartz and pyrite. These correlations strongly suggest that Mn in these sediments is associated with dolomite, calcite, mixed-layer clay minerals, in which Mn^{2+} (0·91Å) replaced Ca^{2+} (1·08Å), as mentioned by RANKAMA and SAHAMA (1950). A significant amount of manganese in these sediments seems to be associated with the iron-oxides/hydroxides phase. The presence of the iron-oxides/hydroxides phase in these sediments is described in the factor analysis in Chapter Five.

i) Strontium

Table (4.3i)

		(W.K.B.)	(W.B.)
Bulk rock	Range	281 - 390* p.p.m.	191 - 391+ p.p.m.
	Average	347 p.p.m.	256 p.p.m.
Clay fraction: Average		151 p.p.m.	105 p.p.m.
Highest in the Bulk rock		361 " (M/U.O.C.)	283 p.p.m. (M.O.C.)
Lowest " " " "		308 " (K.F.)	171 p.p.m. (K.F.)

* Sample WBK-28 shows the highest concentration of Strontium.
\+ Sample BR-1544 " " " " " "

The abundances of Sr in both the borehole sediments are shown in Table (4.3i). The high concentration of Sr in the sediments of the (W.K.B.) may be due to higher contents of calcite (28·48%) as compared to the (W.B.) sediments (22·52%). The total carbonates (i.e. calcite + dolomite) of the (W.B.) sediments though are slightly higher (29·09%) than the total carbonate (calcite) content of the (W.K.B.) sediments, as mentioned above. According to GOLDSCHMIDT (1954), the amount of Sr in dolomites is usually very small, and thus the comparison based on calcite contents only is probably justified. The clay fraction samples of the (W.K.B.) sediments also show a higher concentration of Sr (151 p.p.m.) when compared with the clay fraction of the (W.B.) sediments (105 p.p.m.) This enrichment of Sr may be due to the presence of very fine-grained calcite, very difficult to remove from the clay fraction, or it may be related to the contents of smectite.

The sediments of the (W.K.B.) and (W.B.) in their lattice-held fractions have shown 31% and 43% respectively of associated strontium. PAPAVASILIOU (1979) also reported ~ 34% Sr associated with the lithogenous fraction of sediments of the 'Deep Sea', from the Indian Ocean. The lower concentration of Sr (31%) in the lattice-held (lithogenous) fraction of the (W.K.B.) sediments may be due to a lower abundance of the clay minerals in which the Sr resides.

From the correlation coefficient matrix in Appendix (4.1C) it can be seen that, amongst the clay mineral species, smectite is the only mineral which shows a very strong positive correlation (r = +0·32) with strontium, significant at the 0·01% level. The amount of smectite in the bulk rock is only 8·52%, as is shown in Appendix (4.1B), which roughly represents 20% of the total clay contents (44·18% of the sediments). This explains the lower contents of Sr in the lattice-held fraction of the Winterborne Kingston Borehole sediments. The higher concentration of Sr (43%) in the lattice-held fraction of the Warlingham Borehole sediments is due to its residence in more than one clay mineral species. The correlation coefficient matrix in Appendix (4.2C) shows its very strong positive correlation with illite (r = +0·34), significant at the 0·01% level, and a medium strong positive correlation with chlorite (r = +0·23), significant at the 0·05% level. A weak positive correlation with mixed-layer(r = +0·08) is also shown, indicating its association with these other clay minerals. If the abundances of these clay minerals are added together, it makes a total of 40·15%, which is 88·22% of the total clays (45·51%) present in these sediments. These two observations suggest that the concentration of Sr in the (W.K.B.) sediments is mainly in calcite and smectite, whilst in the (W.B.) sediments Sr is present in total carbonates (mainly calcite, which shows the highest correlation coefficient value: r = +0·48), and it is also present in the clay minerals (illite, chlorite and mixed-layer minerals).

A minor amount of Sr seems to be associated with the oxides/hydroxides of manganese/iron. According to GOLDSCHMIDT (1954), oxidate sediments concentrate Sr, like Ba, in the manganese dioxide sediments. The relationship of Sr with manganese is indicated by its positive correlation with manganese in the sediments of both the boreholes, as can be seen in the correlation coefficient matrices, Appendices (4.1C & 4.2C). The Winterborne Kingston Borehole sediments show a relatively stronger correlation of Sr with Mn (r = +0·33), significant at the 0·01% level. This correlation suggests that either some Sr is associated with the oxides/hydroxides of manganese/iron, as mentioned by GOLDSCHMIDT (1954), or it may be due to the well-known relationship of manganese and strontium with the carbonate minerals, which has been explained earlier in the study of manganese. Factor analysis clarifies that Sr is probably not associated with the oxides/hydroxides of manganese-iron in these sediments as strontium does not show a loading in the oxides/hydroxides factor in Table(5.1.1) in Chapter Five. It shows its weak negative loading with the elements of reducing environments, e.g. U. Mo and C_{org}. This association is not unexpected; DOFF (1969) has reported a higher concentration of Sr (241 p.p.m.) in the anoxic sediments as compared to the oxic sediments (230 p.p.m.). The lowest concentration of Sr is shown by the sediments of the (K.F.) of both the boreholes, as is shown in Table (4.3h). The sediments of the (K.F.) of the (W.K.B.) show a depleted amount of Sr (308 p.p.m.) and Na_2O (0·72%) and highly increased amounts of K_2O (2·59%), Ba (306 p.p.m.) and Rb (135 p.p.m.). According to SPENCER (1966), the decrease of Sr and Na with the increase of K, Ba, and Rb in sediments exhibits the increased influence of the ion-exchange. According to TUREKIAN and KULP (1956), in shales the effect of ion-exchange capacity of the clay minerals has a marked effect on the concentration of Sr relative to Ca, owing to the smaller ionic potential of Sr^{2+} (1·57Φ) as compared to Ca^{2+} (1·89Φ), as mentioned by RANKAMA and SAHAMA (1950). The observed increase in

K, Ba and Rb in the sediments of the Kellaways Formation indicates that these elements were substituted for Sr^{2+}, being very close in ionic radii to Sr^{2+} (1·21Å), with K^{+}(1·46Å), Rb (1·57Å) and Ba^{2+} (1·44Å).

NICHOLLS and LORING (1962) observed the Sr/K and Sr/Ca ratios to investigate the possible proportions of Sr associated with clays and carbonates. The Sr/K ratios in the present study show the highest (0·0166) and lowest (0·0118) values in the sediments of the Upper Oxford Clay and Kellaways Formation, suggesting the maximum and minimum substitution of Sr in the respective sediments. These sediments also show the highest and lowest concentrations of smectite and calcite, as shown in Table (4.1B), which also supports the views expressed above. The Sr/K ratio in the (W.B.) sediments shows the highest (0·0104) and lowest (0·0079) values in the sediments of the Lower Oxford Clay and the Kellaways Formation respectively, indicating that maximum and minimum substitution of Sr took place in the respective sediments. The abundances of illite (65·41%) and calcite (18%) are higher in the Lower Oxford Clay when compared with the abundances of illite (62%) and calcite (10%) in the sediments of the Kellaways Formation. These observations explain the variations of the Sr/K ratios and the possible substitution of Sr in these sediments. The stratigraphic variations of the mineral abundances and Sr/K ratios are shown in Tables (4.1A, 4.2A and 4.1C, 4.2C).

The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows a strong positive correlation of Sr with Ca, P, Mn, CO_2, calcite and smectite, significant at the 1% level, strongly indicating that Sr is located in carbonates, sedimentary phosphates, oxides/hydroxides of manganese. The very strong relationship of Sr with carbonate minerals, particularly calcite, is shown in Figure (4.18b), which may be due to its well-known substitution for Ca^{2+}. The association of Sr with carbonates, particularly with calcite of biogenous origin, has been mentioned by PAPAVASILIOU (1979). CHESTER (1965) stated that Sr is of biogenous origin and is supplied by the calcareous marine organisms. TUREKIAN (1964) stated that foraminiferal tests and coccolithic tests may contain 1200 p.p.m. and 1000-1750 p.p.m. of strontium. BOSTRÖM et al. (1974b) reports that plankton contain about 7600 p.p.m. of Sr. PAPAVASILIOU (1979) reported 1339 p.p.m. of Sr in the calcite of biogenous origin. COSGROVE (1973) reports association of Sr with the carbonate minerals of Red bed mud-stones.

From the above details, it becomes clear that an adequate supply of Sr was available at all times, from the biogenous agencies, e.g. forams, coccoliths and molluscs flourishing in the environments under which these sediments were deposited. The abundant contents of fossils of the foraminifera, coccoliths and molluscs in these sediments are well documented by ARKELL (1933), CALLOMON (1968), CORDEY (1962), BARNARD (1952 & 1953), and ROOD et al. (1971). The enrichment of Sr in certain parts of the Oxford Clay sediments may be related to the abundances of fossil remains of the described organisms.

The positive correlation of Sr with smectite (r = +0·32) may be due to its substitution for either K^+ or Ca^{2+} in the inter-layer position of smectite. According to TUREKIAN and KULP (1956), Sr^{2+} substitutes quantitatively for potassic minerals and is usually found in Ca^{2+}-rich minerals.

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) shows a very strong positive correlation of Sr with calcite (r = +0·48), L.O.I (r = +0·52), Ca (r = +0·37), CO_2(r = +0·37), illite (r = 0·34) and total carbonates (r = +0·39), significant at the 0·01% level; and also a weak positive correlation with elements, e.g. Al, Fe, Mg, K, Mn, Rb, Fe^+, H_2O and minerals, chlorite and total clays, being significant at the 5% level. The same Appendix shows a very strong negative correlation of Sr with Si, Zr, Nb, quartz and kaolinite, all highly significant at the 0·01% level, confirming a non-detrital origin of Sr.

These correlations suggest that Sr in these sediments resides mainly in calcite (r = +0·48). A significant proportion is associated with illite (r = +0·32) and chlorite (r = +0·23) in the inter-layer positions by its substitution for K^+ or Ca^{2+}, as has been explained earlier. A small fraction of Sr seems to be associated with the oxides/hydroxides of Mn-Fe; this relationship is illustrated by the positive correlation of Sr with Mn (r = +0·29) and iron-oxide (r = +0·18).

The association of Sr with clays has been mentioned by a number of research workers. GOLDSCHMIDT (1954) mentioned that in hydrolysates and in clay minerals of soils, the Sr may be fixed on a very moderate scale by 'base exchange', due to the close geochemical relationship between Sr^{2+} (1·27Å) and K^+ (1·33Å). NICHOLLS and LORING (1962), SULAIMAN (1972), GAD et al. (1969) and SPENCER (1966), all these authors have mentioned very strong association of Sr with clay minerals.

j) Lead

Table (4.3j)

		(W.K.B.)	(W.B.)
Bulk rock	Range	18 - 166* p.p.m.	4 - 28+ p.p.m.
	Average	51 p.p.m.	18 p.p.m.
Carbonate free: Average		76 p.p.m.	26 p.p.m.
Clay fraction: Average		84 p.p.m.	25 p.p.m.
Highest in Bulk rock		73 p.p.m. (L.O.C.)	19 p.p.m. (U.O.C.)
Lowest " " "		34 p.p.m. (K.F.)	17 p.p.m. (K.F.)

* Sample WBK-17 showed the highest amount of Lead.
+ Sample BR-958 " " " " " "

The abundances of Pb in the bulk rock and clay fractions ($< 2\mu$) of both the borehole sediments are shown in Table (4.3j). The sediments of the (W.K.B.) in both the bulk rock and clay fractions show exceptionally high values of Pb, as compared to the sediments of the (W.B.), and also the average shales of KRAUSKOPF (1979) and WEDEPOHL (1961), as shown in Table (4.3). The high abundance of Pb in the (W.K.B.) sediments has shown a very strong association with the high abundances of pyrite, organic carbon, kaolinite, chlorite and smectite, along with the elements, e.g. Zn, Ni, Mn, S and Fe_2O_3(total iron), as shown in Appendix (4.1B). The highest and lowest concentrations of Pb in the (L.O.C.) and (K.F.) of these sediments also reflect the same sympathetic relationship with the described components as shown in Table (4.1A). The sympathetic relationship of Pb with mineral phases and elements described above is well illustrated by the examination of the chemical and mineralogical analysis of sample WBK-17 from the (W.K.B.) sediments. Sample WBK-17 showed the highest concentration of Pb (166 p.p.m.) with very high amounts of pyrite (4·6%), smectite (45%), and appreciably high values of kaolinite (8%), calcite (48·3%), indicating a strong relationship of Pb with these components in this sample. CHOWDHURY (1980) reported high Pb(36 ppm) associated with high abundances of pyrite and illite in the Corallian mud-rocks from the Dorset coast. The association of Pb with pyrite may be due to co-precipitation as the concentration of Pb and genesis of pyrite both proceed under the reducing conditions in sediments. The association of Pb with pyrite has been mentioned by many workers including AUGER (1941) and CARSTENS (1942a); DOFF (1969) mentioned that Pb is highly concentrated under anoxic(reducing) conditions. The association of Pb with organic carbon may be due to the fact that both concentrate under the reducing conditions, or it may be due to the great adsorbtive ability of Pb on organic carbon, as mentioned by KRAUSKOPF (1956). The relationship of Pb with organic carbon may also be due to the contribution of some Pb by planktons, as pointed out by BÖSTROM et al. (1974). The association of Pb with smectite may be due to the possible substitution of Pb^{2+} (1·26Å) for K^{+}(1·46A) in the inter-layer position of smectite, due to the similarity of the ionic radii. CHOWDHURY (1980) mentioned the substitution of Pb^{2+} (1·26A) for K^{+} (1·46A) in the inter-layer position of montmorillonitic rich samples in the Corallian mud-rocks from the Dorset coast. The association of Pb with carbonate minerals may be due to co-precipitation of Pb in carbonate apatite. This relationship may also be based purely on genetic association being a common source of organic organisms and Pb; marine organisms, e.g. diatoms and planktons may contribute respectively P_2O_5 and Pb, as stated by BATURIAN et al. (1967) and BÖSTROM et al. (1974). The association of Pb with the carbonate apatite,probably present in these sediments,is indicated by the very strong positive correlation of Pb with P_2O_5($r = +0{\cdot}41$), highly significant at the 0·01% level, as shown in the Appendix (4.1C).

The correlation coefficient matrix in Appendix (4.1C) for the (W.K B.) sediments indicates very strong positive correlation of Pb with Fe_2O_3(total iron), S, P_2O_5, Zn, Cu, Mo, Fe^{2+} and pyrite, all correlations being highly significant at the 0·01% level, confirming that Pb of the (W.K B.) sediments,in general, is associated with sulphide minerals (pyrite) and a minor amount with clays, either as adsorbed or as substituted in the lattices of smectite. The very strong association of Pb with pyrite is shown in Figure (4.19a), which shows an intercept of a value of +6 p.p.m., indicating the amount of Pb not associated with pyrite, which may be related to other phases such as clays and carbonate minerals. The relationship of Pb with clays and carbonate minerals is indicated by its positive correlations shown in Appendix (4.1C), confirming this association. The average amount of Pb associated with pyrite is 45 p.p.m. (i.e. 51 - 6 p.p.m.); this amount represents 88·23% of total Pb in these sediments. This result agrees with the correlation coefficient trends of Pb with the chalcophile elements, as well as with the results of the leaching study and factor analysis of the chemical data of these sediments. Factor analysis in Chapter Five shows that Factor (F-2) is the only factor which contains the highest loadings of Pb with P_2O_5, C_{org}, S, Fe_2O_3, Zn, Fe^{2+} and Mo. This factor represents the sulphide mineral (pyrite) and organic carbon phases of these sediments. The leaching study by the acetic acid hydroxylamine hydrochloride (CHESTER and HUGHES, 1967) shows that the entire amount of Pb is associated with the non-lithogenous(soluble) fraction. This study suggests that the association of Pb with clays in these sediments is most likely as adsorbed Pb onto the clays, as mentioned by KRAUSKOPF (1956).

The sediments of the (W.B.) showed lower abundances of Pb, associated with the lower abundances of the minerals and elements, than mentioned for the (W.K.B.) sediments, and are shown in the Appendices (4.1B) and (4.2B) respectively. The highest abundance of Pb (19 p.p.m.) in the (W.B.) is present in the sediments of the (U.O.C.) and is associated with the highest abundances of Mg, Ca, V, Mn, As, Zn, Ni, Fe^{3+}, calcite, dolomite, illite and mixed-layer (illite-montmorillonite) clay minerals, which are shown in Tables (4.2A & 4.2B). Unlike this, the highest Pb concentration in the (L.O.C.) sediments of the (W.K.B.) is associated with the highest amounts of S, P, Zn, Cu, Ni, Sr, Mo, Fe^{2+}, pyrite, C_{org} and kaolinite. A very strong sympathetic relationship of Pb with elements, e.g. Mg, Ca, Fe^{3+}, Zn, Mn, Ni, Ga and As is also exhibited by the sediments of the (U.O.C.), which is shown in Table (4.2A).

The evidence described above strongly suggests that Pb in the (W.B.)sediments is controlled by phases other than those in the (W.K.B.) sediments. The very strong positive correlation of Pb with elements, e.g. Fe^{3+}, Zn, Mn, Ni, Ga and As, as shown in Appendix (4.2C) may be due to the strong ability of Pb and these elements to adsorb onto 'Fe-Mn' hydroxides, organic carbon and clays (illite + mixed-layer minerals), as suggested by KRAUSKOPF(1956,p.25). The described relationships of Pb are very well exhibited by the chemical and mineralogical results of sample BR-958, which showed the highest abundance of Pb (28 p.p.m.), associated with the highest abundances of elements, e.g. As (21 p.p.m.), Zn(103 p.p.m.), Cu (24 p.p.m.), Fe^{3+} (3·83%), and significantly very high values of Ga (18 p.p.m.), Ni (51 p.p.m.), Mn (160 p.p.m.) and mineral illite(63%). These observations confirm that Pb in the (W.B.) sediments is largely present as adsorbed onto 'Fe-Mn' hydroxides and clays (illite), along with a group of chalcophile elements (Zn, Cu, Ni, Ga, As, Fe^{3+}), as mentioned by KRAUSKOPF (op.cit.)

The above conclusions,regarding the association of Pb with the 'Fe-Mn' hydroxides in the (W.B.) sediments, agree with the results of the leaching study of these samples and the factor analysis of the chemical data. The leaching study by acid-reducing reagents in Chapter Six shows that the entire amount of Pb is present in the non-lithogenous (soluble) fraction. In Chapter Five, factor analysis shows that Pb is very strongly loaded in association with very strong loadings of Ga, Cu, Ni, Zn and As in Factor (F-2), which is an independent factor. Factors (F-1) and (F-3), which represent total clays and sulphide phases respectively, do not show any loading of Pb,which confirms the conclusions drawn above.

k) Zinc

Table (4.3k)

		(W.K.B.)	(W.B.)
Bulk rock	Range	86 - 1914* p.p.m.	0 - 622+ p.p.m.
	Average	430 p.p.m.	68 p.p.m.
Carbonate free: Average		623 p.p.m.	95 p.p.m.
Clay fraction: Average		253 p.p.m.	88 p.p.m.
Highest in Bulk rock		751 p.p.m.(L.O.C.)	84 p.p.m. (U.O.C.)
Lowest " " "		257 p.p.m. (K.F.)	40 p.p.m. (K.F.)

* Sample WBK-43 showed the highest concentration of Zinc.
+ Sample BR-320 " " " " " "

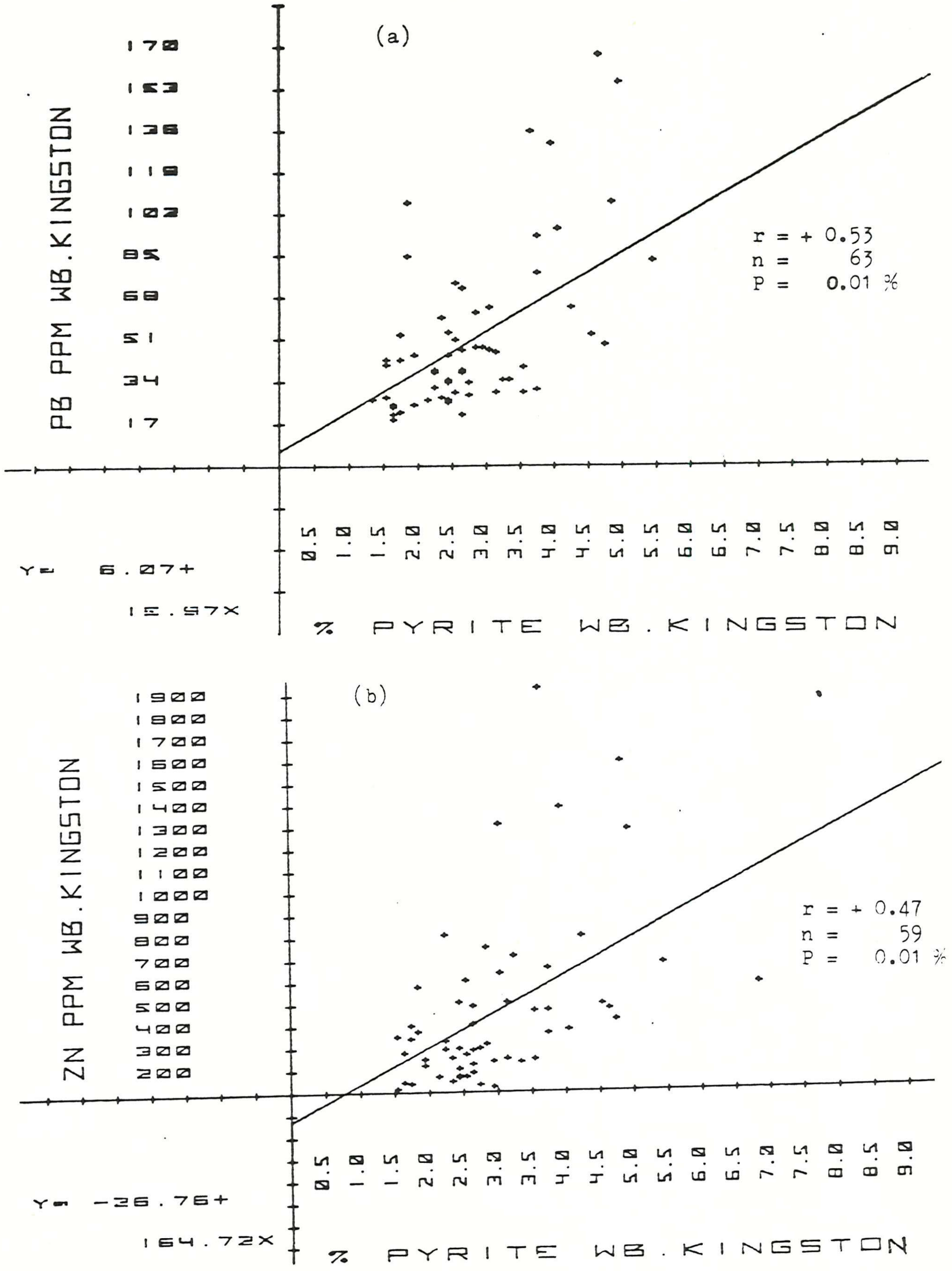

(a)
PB PPM WB.KINGSTON
170
153
136
119
102
85
68
51
34
17
r = + 0.53
n = 63
P = 0.01 %
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Y= 6.07+
15.97X
% PYRITE WB.KINGSTON
(b)
ZN PPM WB.KINGSTON
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
r = + 0.47
n = 59
P = 0.01 %
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Y= -26.76+
164.72X
% PYRITE WB.KINGSTON

FIG.(4.19)

The abundances of Zn in bulk rock and clay fractions of both the boreholes are shown in Table (4.3k). The sediments of the (W.K.B.) showed exceptionally high values of Zn as compared to its values in the sediments of the (W.B.) and reported by other workers, which are shown in Table (4.3). The sediments of the (W.K.B.) show similar trends for the distribution of Zn as they exhibited for Pb. The enrichment of Zn in the (W.K.B.) sediments, like Pb, seems to be related to the exceptionally high abundances of pyrite, organic carbon, kaolinite and chlorite, as shown in Appendix (4.1B). The highest concentration of Zn in these sediments is in the (L.O.C.) which is also associated with the highest abundances of the above described mineral phases and also elements Fe^{+2}, Fe^{+3}, Pb, Cu, Ni, Mo and S, as shown in Table (4.1A). The highest concentration of Zn (1914 p.p.m.) in sample WBK-43 also exhibits its association with very high abundances of phases of organic carbon (4·44%), pyrite (3·6%), kaolinite (18%), chlorite (9%) and total clays (49·4%), and elements, e.g. Pb, Cu, Ni, As and Mn. The lowest concentration of Zn (257 p.p.m.) is shown by the sediments of the (K.F.) of this borehole; which is associated with the lower abundances of the minerals and elements mentioned above. This evidence strongly suggests that the concentration of Zn in the (W.K.B.) sediments, like Pb, is mainly controlled by sulphide minerals (pyrite) and organic carbon; a minor amount is associated with clays. These relationships will be examined later in the light of other analytical results, e.g. multivariant correlations, factor analysis and leaching study. Figure (4.19b) shows a strong positive correlation of Zn with pyrite.

The sediments of the (W.B.) showed comparatively lower values of Zn, which show a relationship with the lower abundances of pyrite, organic carbon, kaolinite, chlorite, but higher concentrations of illite (65·63%),total clays (45·51%) and elements, e.g. Si, Al, Ti, Mg, K, Zr, Nb, Y and As, indicating its close association with clays, particularly with illite. The highest concentration of Zn in the (W.B.) sediments, like Pb, is present in the (U.O.C.). The highest abundance of Zn (84 p.p.m.) in the (U.O.C.) is associated with the highest abundances of elements, e.g. Ca, Mg, V, Mn, Pb, As, Ni, Fe^{+3} and minerals, calcite, dolomite, illite and mixed-layer (illite-montmorillonite) clay minerals, as shown in Tables (4.2A & 4.2B). Sample BR-320 from the (W.B.) sediments showed the highest abundance of Zn (622 p.p.m.) associated with significantly high abundances of illite (73%), chlorite (6%), total clays (48·51%), and elements e.g. Ni (46 p.p.m.) and As (14 p.p.m.). The lowest concentration of Zn (40 p.p.m.) in the (K.F.) of the (W.B.) sediments shows association with the highest values of quartz, pyrite, kaolinite and elements, e.g. Ba, Ce, Zr, Nb, Mo, Fe^{+2}, and lowest values of calcite, dolomite, chlorite, illite and mixed-layer (illite-montmorillonite) clay mineral. This evidence suggests that Zn in the (W.B.) sediments shows sympathetic relationship in mineral phases with carbonates and clay minerals (with the exception of kaolinite), and amongst elements only with Ni, Pb and As.

The associations of Zn in the (W.K.B.), described earlier, and the (W.B.) sediments, mentioned above, become more clear when the correlation trends of Zn with elements and mineral phases for each borehole are studied. The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows very strong positive correlations of Zn with Fe_2O_3, S, P_2O_5, Ni, Pb, Cu, Mo, C_{org}, Fe^{+2} and pyrite, all being highly significant at the 0·01% level. The same correlation matrix shows medium to strong negative correlations of Zn with Si, Ti, Mg, Na, K, V, Ba, Ce, La, Th, Rb, Y, Zr, Nb, Fe^{+3} and minerals, e.g. quartz, smectite and total clays. In these sediments, Zn also showed medium positive correlation with Ni ($r = +0{\cdot}30$), As ($r = +0{\cdot}21$), H_2O ($r = +0{\cdot}15$), illite, kaolinite and chlorite. These correlations strongly suggest that Zn in these sediments is largely associated with sulphide minerals (pyrite) and organic carbon, and a small amount is also related to clay minerals, particularly illite, kaolinite and chlorite. CALVERT (1976) mentioned that clay dependent Zn is located mainly in the lattices of illite(mica) and chlorite. In illite, Zn^{2+}(0·83Å) may substitute for Ca^{2+}(1·08Å), in the inter-layer position, there being close similarity of the radii, or Zn^{2+} (0·83Å) may substitute for Mg^{2+}(0·80Å), Fe^{2+}(0·86Å) or Al^{3+} (0·61Å) in the octahedral position. In chlorite also, Zn may substitute for any of these ions in the inter-layer or octahedral position.

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) indicates the very strong positive correlations of Zn with Pb, Ga, Cu, Ni and As, all being highly significant at the

0·01% level. These correlations suggest that Zn in the (W.B.) sediments is mainly associated with the complexes of these metals. The same Appendix shows weak positive correlations of Zn with lithophile elements, e.g. Ti, Al, Na, K, V, Cr, Ba, Rb and clay minerals, e.g. illite (r = +0·23), chlorite (r = +0·13) and total clays (r = +0·13). The negative correlation exhibited by Zn with P_2O_5, La, Zr, C_{org}, kaolinite, mixed-layer (illite-montmorillonite) clay minerals is also shown in Appendix (4.2C). These correlations suggest that the concentration of Zn in the (W.B.) sediments is, on the whole, controlled by the complexes of metals Pb, Ga, Cu and Ni, as suggested by KRAUSKOPF (1956). Some amount of Zn is also associated with clay minerals, particularly illite and chlorite. The location of Zn in illite and chlorite seems to be in the lattices of these minerals, and this relationship is of a similar nature to that explained earlier in the study of the (W.K.B.) sediments.

The association of Zn with clay minerals, sulphide minerals, organic carbon and Fe-Mn oxides, has been studied and described by many workers. CALVERT (1976) mentioned that clay dependent Zn is mainly located in the lattices of illite (mica) and chlorite. WEDEPOHL (1972) mentioned that the input and concentration of Zn in sediments mainly occurs in association with colloidal iron-oxide and iron-oxide coatings on clay minerals. The highest concentration of Zn in the (U.O.C.) sediments of the (W.B.) is associated with the highest values of Mn (203 p.p.m.) and Fe^{3+} (2·00%), illite (66·5%) and mixed-layer (illite-montmorillonite), indicating that either Zn is concentrated in association with iron-oxides/Fe-Mn oxides, as suggested by WEDEPOHL (op.cit.) and KRAUSKOPF (op.cit.), or it is associated with illite in the lattices as explained earlier. HOROWITZ AND CRONAN (1976) found that only 20% of the total Zn was removed by acid-reducing solutions, and the major amount of Zn was associated with more resistant minerals. CHESTER et al. (1976) also noticed that only 34% of the total Zn was extracted in the soluble phase, and the remaining amount of Zn was associated with the resistant phases. BÖSTROM et al. (1976) stated that the higher values of Zn in the lattice-held fraction could be from the biogenous contribution of Zn, since plankton is enriched in Zn relative to shales. CHOWDHURY (1980) mentioned that Zn may probably be fixed in the octahedral site of clay minerals in the Corallian mud-rocks from the Dorset coast, due to the similarity of the ionic radii of Zn^{2+}(0·83Å), Mg^{2+}(0·80Å), Fe^{2+}(0·86Å) and Al^{3+}(0·61Å). PAPAVASILIOU (1979) reported the association of Zn with detrital/authigenic minerals.

The conclusions derived above regarding the location of Zn in the studied sediments agree with the results of the leaching study and factor analysis of the chemical data of these sediments. The leaching study by acid-reducing reagents (CHESTER and HUGHES, 1967) showed 31% and 32% of total Zn associated with the lattice-held fractions of the (W.B.) and (W.B.K.) sediments, respectively. The results of the factor analysis show very high loadings of Zn, C_{org}, P_2O_5, Pb and Cu in Factor (F-2), representing sulphide and organic carbon in the (W.K.B.) sediments; and in the (W.B.) sediments Zn shows strong loading with Pb, Ga, Cu and Ni in Factor (F-2), representing a complex compound of these metals adsorbed on either Fe-Mn hydroxides or clays, as suggested by KRAUSKOPF (1956).

I) Arsenic

Table (4.3I)

		(W.K.B.)	(W.B.)
Bulk rock	Range	0 - 27* p.p.m.	2 - 63+ p.p.m.
	Average	12 p.p.m.	13 p.p.m.
Carbonate free: Average		17 p.p.m.	20 p.p.m.
Clay fraction: Average		7 p.p.m.	6 p.p.m.
Highest in Bulk rock		15 p.p.m.(M.O.C.)	20 p.p.m. (U.O.C.)
Lowest " " "		9 p.p.m. (K.F.)	6 p.p.m. (L.O.C.)

* Sample WBK-19 showed the highest amount of Arsenic.
+ Sample BR-123 " " " " " "

The contents of As in the bulk rock and clay fraction samples of both the borehole sediments are summarized in Table (4.3I), which shows closely similar concentrations of As in the studied sediments. The clay fraction samples of both boreholes showed much depleted amounts of As, indicating a weak relationship of As with clays. The abundance of As in the bulk rock showed very good agreement with the reported values of As in shales by KRAUSKOPF (1979) and TUREKIAN and WEDEPOHL (1961). The abundances of As reported by COSGROVE (1973) in Red bed mud-rocks and CHOWDHURY (1980) in the Corallian mud-rocks are much higher than those of the sediments of the Oxford Clay and Kellaways Formations. The reason for the relative depletion of As in the studied sediments may be related to its weak association with clays and sulphide minerals and negative correlation with C_{org} in the sediments of both boreholes, as shown in Appendices (4.1C and 4.2C).

The highest concentration of As (15 p.p.m.) in the (M.O.C.) of the (W.K.B.) sediments is associated with the highest abundances of Fe_2O_3(total iron), MgO, Sr, Fe^{3+} and second highest values of S, Mn, Zn, pyrite and smectite, as shown in Tables (4.1A & 4.1B). These associations suggest that As in these sediments is very strongly related to Fe_2O_3(total iron) and Fe^{3+}, and a strong relationship exists with S, Ni, Zn, pyrite and smectite. Sample WBK-19 illustrates very well the strong relationship of As with chalcophile elements and sulphide mineral (pyrite). This sample contains the highest abundance of As (27 p.p.m.) associated with the highest amounts of Zn (1304 p.p.m.), and significantly high concentrations of Pb (63 p.p.m.), total Fe_2O_3 (5·43%), S (1·59%), Mn (538 p.p.m.), Ni (49 p.p.m.), Fe^{3+} (3·24%), pyrite (3%) and smectite (32%). These associations confirm that As of the (W.K.B.) sediments is strongly associated with Fe-Mn oxides/hydroxides, sulphide mineral (pyrite). The association of As with Fe-Mn oxides/hydroxides has been mentioned by CALVERT (1976), GOLDSCHMIDT (1954) and RANKAMA and SAHAMA (1950). GAD et al. (1969) and PRICE (1976) also mentioned association of As with Mo, V, Cu, Zn and C_{org}. The concluded relationship of As in the (W.K.B.) sediments is further confirmed by the results of the multi-variant correlations and factor analysis of the analytical data of the (W.K.B.) sediments.

The correlation coefficient matrix in Appendix (4.1C) shows very strong positive correlation of As with only three elements, e.g. total iron ($r = +0.38$), Mn ($r = +0.35$) and Fe^{3+} ($r = +0{\cdot}39$), all being highly significant at the 0·01% level, confirming that the major amount of As in these sediments is associated with the Fe-Mn oxides/hydroxides, as suggested by GOLDSCHMIDT (op.cit.), RANKAMA and SAHAMA (op.cit.) and CALVERT et al. (op.cit.). The association of As with iron-oxides in the Corallian mud-rocks of the Dorset coast has been mentioned by CHOWDHURY (1980). The same correlation matrix shows weak positive correlations of As with S (r = +0·17), Ni (r = +0·18), Zn (r = +0·21), Fe^{2+} (r = +0·17) and pyrite (r = +0·17), indicating that some amount of As is also associated with the sulphide minerals (pyrite). The relationship of As with S and pyrite has been mentioned by CALVERT (1976), PRICE (1976) and GOLDSCHMIDT (1954). According to PRICE (op.cit.), under reducing conditions As species in sea-water and interstitial waters, $HAsO_4^{-2}$ and $H_2AsO_4^-$ (MURRAY and BREWER, 1977) will be reduced to $HAsO_2$ and AsS_2^-, the reduction depending on the $\bar{HS}$ and pH. AsS_2^- especially is quite insoluble and it will be stabilized within the reducing zone, probably by co-precipitation with pyrite. The concluded associations of As are further confirmed by factor analysis. Factor (F-3) in Chapter Five shows the highest loading of As with Fe_2O_3, Mn, Ni and Fe^{3+}.

In the sediments of the (W.B.), arsenic showed similar trends of association with mineral phases and elements as exhibited in the (W.K.B.) sediments. The highest concentration of As (20 p.p.m.) is shown by the (U.O.C.) sediments in association with the highest abundances of Mg, Ca, V, Mn, Pb, Zn, Ni, Fe^{3+}, as shown in Table (4.2A), suggesting the strong relationship of As with Fe-Mn oxides/hydroxides, as explained earlier. The maximum concentration of As (63 p.p.m.) in sample BR-123 is also associated with the highest abundances of MgO (7·04%) and dolomite (36·80%), and significantly high amounts of pyrite (1·70%), illite (65%), mixed-layer (illite-montmorillonite), total Fe_2O_3 (4·77%), Fe^{3+} (3·51%) and minor elements, e.g. V(190 p.p.m.) Mn (193 p.p.m.), Pb (11 p.p.m.) and Ni (34 p.p.m.). These associations explain the strong relationship of As with Fe-Mn oxides/hydroxides, carbonate minerals and mixed-layer mineral. RANKAMA and SAHAMA (1950) mentioned that As is enriched in oxidate sediments, chiefly by adsorption on ferric hydroxides. The relationship of As with dolomite and mixed-layer mineral may be related to the probable oxic conditions prevailing in the sediments of the Upper Oxford Clay, which is indicated by the highest concentration of ferric oxides (Fe^{3+} = 2%) in these sediments.

The correlation coefficient matrix for the (W.B.)sediments in Appendix (4.2C) shows very strong positive correlations of As with total Fe_2O_3, MgO, V, Pb, Ga, Zn, Cu, Ni, mixed-layer mineral and dolomite, indicating that As is strongly associated with these components. The same Appendix shows medium strong positive correlations of As with Mn, Cr, Nb, Fe^{3+} and pyrite, indicating the association of As with Fe-Mn oxides/hydroxides and sulphide minerals (pyrite). The very strong positive association of As with minor elements, e.g. Pb, Ga, Zn, Cu and Ni, may be due to its very strong adsorbing ability onto the clay minerals and Fe-Mn oxides/hydroxides, in association with these metals, as demonstrated by KRAUSKOPF (1956). Factor analysis of the chemical data of these sediments in Chapter Five, which shows in Factor (F-2) very high loadings of As with minor elements, e.g. Pb, Ga, Zn, Cu and Ni, and in Factor (F-4) its strong loading with Mg, V, Mn, Fe^{3+}, confirms the derived conclusions.

It may be concluded that As in the (W.K.B.) and (W.B.) sediments is very strongly associated with Fe-Mn oxides/hydroxides by adsorption. It is also associated with sulphide minerals(pyrite) as a co-precipitate. There is no relationship between As and organic carbon in these sediments, as reported by CHOWDHURY (1980) in the Corallian mud-rocks of the Dorset coast.

m) Gallium

Table (4.3m)

		(W.B.)
Bulk rock	Range	4 - 27+ p.p.m.
	Average	17 p.p.m.
Carbonate free: Average		24 p.p.m.
Clay fraction: Average		32* p.p.m.
Highest in Bulk rock		18 p.p.m. (L.O.C.)
Lowest " " "		14 p.p.m. (K.F.)

* Average value reported by CHOWDHURY (1980).

+ Samples BR-1676 & 1734 showed highest abundance of Gallium.

Gallium was determined only in the (W.B.) sediments in the bulk rock samples. The average value of the clay fraction in Table (4.3m) is reported from CHOWDHURY (1980). The average values of Ga in the studied sediments show agreement with the reported values of Ga in shales and sedimentary rocks, as shown in Table (4.3).

The highest concentration of Ga is present in the (L.O.C.), and is associated with the highest abundances of elements, e.g. K, Cr, Cu, Ni, Rb and C_{org}, illite in bulk rock and total clays, as shown in Tables (4.2A and 4.2B). The highest concentration of Ga (27 p.p.m.) and second highest (25 p.p.m.) are shown by samples BR-1676 and BR-1734 respectively. Both samples show very high concentrations of Al_2O_3, K_2O, Fe^{3+}, C_{org}, Cu, Ni, Cr, Pb, Rb and minerals, illite and total clays, shown in Appendices (4.2A & 3.2), indicating the strong relationship of Ga with alumino-silicates and elements Cu, Ni and Pb in these samples.

The association of Ga with alumino-silicates has been mentioned by many workers. COSGROVE (1973) mentioned the association of Ga with total clays in Red bed mudstone, GAD et al. (1969) mentioned the strong correlation of Ga with Al and K, and concluded that Ga is detrital in origin and occurs in alumino-silicates, particularly micas. The same authors mentioned that a very small amount of Ga is associated with pyrite. HIRST (1962) mentioned that Ga probably occupies the lattice position in all the three clay minerals, e.g. illite, kaolinite and montmorillonite. The same author stated that the geochemistry of Ga^{3+} (0·62Å) is influenced by the similarity of the ionic radius of Al^{3+}(0·61Å). HIRST (op.cit.) studied the Ga/Al ratios and found that the ratios are consistent, indicating that Ga entered into the basin as structurally bound with clay minerals. NICHOLLS and LORING (1962) reported that the bulk of Ga is in silicate minerals. The same authors stated that Ga in Bersham rocks is associated with illite and kaolinite by replacing Al. NICHOLLS and LORING (op.cit.) studied the Ga/Al ratios and found low values ($1{\cdot}6 \times 10^{-4}$) as compared to the igneous rock ratio ($2{\cdot}36 \times 10^{-4}$) reported by SHAH (1957, p.185), and concluded that Bersham rocks are attributed to the weathering of non-igneous material in the source area. The Ga/Al ratio for the total population of the (W.B.) samples showed a value of ($1{\cdot}315 \times 10^{-4}$), which is very low as compared to the value of the igneous rocks ratio. CHOWDHURY (1980) mentioned the very strong correlation of Ga with Al ($r = +0{\cdot}86$) in the Corallian mud-rocks, and concluded that Ga is mainly located in clays.

The correlation coefficient matrix in Appendix (4.2C) for the total population of the (W.B.) sediments shows very strong positive correlation of Ga with elements, e.g. Pb, As, Zn, Cu and Ni, all being highly significant at the 0·01% level, indicating a very strong association of Ga with these metals. KRAUSKOPF (1979) mentioned that in sphelerite, Ga^{3+} (0·70Å) may substitute for Zn^{2+} (0·83Å), there being close similarity of the ionic radii and electro-negativity of Ga^{3+} (1·6) and Zn^{2+} (1·7). KRAUSKOPF (1956) mentioned that metals, e.g. Cu-Zn-Pb are adsorbed more strongly and consistently onto clays than other metals. It is, therefore, possible that in these sediments probably complex compounds of metals, e.g. Zn, Pb, As, Ni and Cu are present in minor amounts and on a very localized scale, and Ga is associated with these compounds, as the ionic radii of Ni^{2+} (0·77Å), Cu^{2+} (0·81Å), Zn^{2+} (0·83Å) and electro-negativity of Ni^{2+} (1·8), Cu^{2+} (1·9) and Zn^{2+} (1·7) are very similar and may facilitate its substitution for these metals. The same correlation matrix shows positive correlation of Ga with Ti ($r = +0·28$), Al ($r = +0·25$), K_2O ($r = +0·17$), Th ($r = +0·24$), and Rb ($r = +0·23$), and weak positive correlations with illite, kaolinite and total clays ($r = +0·21$), all being significant at the 5% level, indicating that some Ga is also associated with the clay minerals, particularly chlorite, which showed the highest correlation coefficient value ($r = +0·15$). It seems that Ga^{3+} (ionic radius = 0·70Å and electro-negativity = 1·6) in the total population is associated with chlorite by its substitution in the octahedral position either for Al^{3+} (0·61Å) or for Fe^{2+} (0·86Å), Fe^{3+}(0·73Å) and Mg^{2+} (0·80Å), there being a close similarity of the ionic radii, as well as the electro-negativity of Al^{3+} (1·5), Fe^{2+} (1·8), Fe^{3+} (1·9) and Mg^{2+} (1·2). In the same Appendix, Ga showed a weak positive correlation with Fe^{3+} ($r = +0·13$), significant at the 5% level, indicating its association with the adsorbed Zn, Cu, Pb onto iron-oxides. There exists no relationship between Ga, S, Fe^{2+}, pyrite, which is indicated by its negative correlations with these components.

Gallium showed its maximum concentration in the (L.O.C.) sediments. Its correlation with elements and minerals in the (L.O.C.) sediments are examined to see which clay mineral is more strongly associated with it. The correlation coefficient matrix showed a very strong positive correlation of Ga with elements, e.g. Si, Ti, Al,

Fe_2O_3(total iron), V, Cr, Ba, Th, Rb, Y , Nb and minerals, kaolinite and total clays, all highly significant at the 0·01% level. Gallium also showed weak positive correlations with Fe^{3+} (r = +0·23), illite (r = +0·14). These correlation trends confirm that Ga in the (L.O.C.) sediments is most strongly associated with kaolinite, as reported by NICHOLLS and LORING (1962) in their Bersham rocks study.

The Ga/Al_2O_3 ratios for the three divisions of the Oxford Clay and Kellaways Formations are recorded in Table (4.2C), which shows the highest value of this ratio ($1{\cdot}59 \times 10^{-4}$) in the sediments of the (U.O.C.) and the lowest value ($1{\cdot}17 \times 10^{-4}$) in sediments of the (K.F.). The highest value of the Ga/Al_2O_3 ratio in the (U.O.C.) sediments suggests that a higher amount of Ga compared to Al_2O_3 was concentrated in these sediments in another phase, in addition to clay minerals. The distribution pattern of Ga and Al_2O_3 in the (M.O.C.) sediments when compared with the (U.O.C.) sediments indicated that the same amount of Ga (17 p.p.m.) in the (M.O.C.) sediments is associated with the higher amount of Al_2O_3, which is shown in Table (4.2A), and confirms the above conclusions. These observations suggest that an appreciable proportion of Ga contents of the (U.O.C.) sediments is associated with a phase other than clay minerals. After clay minerals in the (U.O.C.) sediments, Fe^{3+} is the only phase which showed its highest abundance in these sediments; therefore it is very possible that a significant proportion of the Ga is associated with iron oxides/hydroxides by adsorption. NICHOLLS and LORING (op.cit.) found a lower value of the Ga/Al_2O_3 ratio ($1{\cdot}6 \times 10^{-4}$), as compared to the igneous rock ratio ($2{\cdot}3 \times 10^{-4}$) reported by SHAH (1957, p.185); they concluded that detritus for the Bersham rocks was supplied by the weathering of non-igneous material in the source area. The highest value of Ga/Al_2O_3 ratios ($1{\cdot}59 \times 10^{-4}$) of the (U.O.C.) sediments is very close to the ($1{\cdot}6 \times 10^{-4}$) value of Bersham rocks, suggesting that detritus for the studied sediments was supplied to the area of deposition from a non-igneous material in the source area. The value of the Ga/Al_2O_3 ratio for the total population of the (W.B.) sediments is also lower ($1{\cdot}315 \times 10^{-4}$) than the value for igneous rocks.

It may be concluded that the Ga in these rocks is mainly associated with the complex compounds of Zn,Cu,Ni,Pb and As, present in minor amounts in these sediments. This conclusion is also confirmed in Chapter Five, where Factor (F-2) shows the very strong association of Ga with Pb, As, Zn, Cu and Ni. Some Ga in the total population is also present in the octahedral position of chlorite by its probable substitution for any of these elements: Al, Fe^{2+}, Fe^{3+} and Mg. A minor amount is associated with iron oxides.

In the (L.O.C.) sediments, Ga showed its preferred association with kaolinite (r = +0·41), by its substitution for Al^{3+} in the lattice structure. Some amount of Ga is also associated with iron-oxides, probably as coats on the clay minerals. The consistency of the Ga/Al$_2$O$_3$ ratios, as suggested by HIRST (1962), indicates that Ga reached the basin of deposition as bound in the lattices of clay minerals and adsorbed onto iron-oxides, and is of detrital origin.

n) Niobium and Zirconium

Table (4.3n)

		(W.K.B.)		(W.B.)	
		Nb*	Zr*	Nb+	Zr+
Bulk rock	Range	5-20 p.p.m.	107-308 p.p.m.	10-37 p.p.m.	46-672 p.p.m.
	Average	13 p.p.m.	157 p.p.m.	18 p.p.m.	191 p.p.m.
Carbonate free:	Average	18 p.p.m.	225 p.p.m.	26 p.p.m.	264 p.p.m.
Clay fraction:	Average	20 p.p.m.	154 p.p.m.	18 p.p.m.	158 p.p.m.
Highest in bulk rock		19 " (K.F.)	182 " (K.F.)	25 " (K.F.)	347 " (K.F.)
Lowest " " "		11 " (U.O.C.)	139 " (L.O.C.)	16 " (L.O.C.)	160 " (U.O.C.)

* Samples WBK-26 and 27 showed the highest amount of Zirconium.
* Samples WBK-63, 64 and 65 " " " " " Niobium.
+ Sample BR-1781 " " " " " Zirconium.
+ Samples BR-115 & Br-1771 " " " " " Niobium.

The abundances of Zr and Nb in the bulk rock and clay fraction ($< 2\mu$) samples of both the boreholes are given in Table (4.3n), which shows that the (W.B.) sediments contain higher values of Zr in both bulk rock and clay fraction. The concentration of Nb in bulk rock in the (W.B.) is slightly higher, but in the clay fraction ($< 2\mu$) the value is lower than the (W.K.B.) sediments, showing a strong association of Nb with clays in the (W.K.B.) sediments. The higher concentration of Zr in the bulk rock samples of the (W.B.) may be associated with the exceptionally high abundances of resistate phases, e.g. quartz (40·7 %) and kaolinite (23·70%) in the (K.F.). The higher value of Nb in the bulk rock samples of the (W.B.) may also be related to the high abundances of resistates mentioned above. The average values of Zr in the sediments of both boreholes are in good agreement with the average values of Zr reported by KRAUSKOPF (1979) and TURIKIAN and WEDEPOHL (1961) in the average shales, but they are much lower than the Zr values reported by COSGROVE (1973) in Red bed mud-stones and CHOWDHURY (1980) in the Corallian mud-rocks from the Dorset coast; all average values of Zr are shown in Table (4.3). The higher contents of Zr in the Red bed mud-stones (COSGROVE, op.cit.) and Corallian mud-rocks (CHOWDHURY, op.cit.) may be due to the presence of heavy minerals, particularly zircon. The average values of Nb in the sediments of both boreholes show agreement with the published values of Nb, shown in Table (4.3).

The highest concentration of Zr in the sediments of both the boreholes is present in the (K.F.), as shown in Table (4.3n), which indicates exceptionally high abundance of Zr in the (K.F.) of the (W.B.) sediments. The highest abundance of Zr (182 p.p.m.) of the (W.K.B.) sediments, in the (K.F.), showed association with the highest values of SiO_2, TiO_2, Al_2O_3, Na_2O, Fe^{3+} and combined SiO_2, along with minor elements, e.g. V, Cr, Ba, La, Ce, Th, Rb, Y and Nb, as shown in Table (4.1A). Zr in these sediments also showed its association with the highest values of total clays (57·47%), chlorite (10·50%) and significantly high amounts of quartz (21%) and kaolinite (12%), shown in Table (4.1B), indicating that the distribution of Zr in these sediments is controlled by clay minerals and resistate phases present in these sediments.

The highest value of Zr (347 p.p.m.) in the (W.B.) sediments is present in the (K.F.), and is associated with the highest values of SiO_2, Na_2O, S, P_2O_5, Ba, Ce, Nb, Mo and Fe^{2+}, as shown in Table (4.2A). Zr in these sediments is also associated with the highest abundances of quartz, kaolinite and illite, as shown in Table (4.2B). These associations suggest that the distribution of Zr in the (W.B.) sediments is controlled by clay minerals and resistate phases present in these sediments.

The lowest concentration of Zr (139 p.p.m.) is shown by the (L.O.C.) of the (W.K.B.) sediments, and (160 p.p.m.) by the (U.O.C.) of the (W.B.) sediments. The sediments of the (L.O.C.) of the (W.K.B.) contain comparatively lower amounts of SiO_2 (37·6%) and quartz (17·75%), and the sediments of the (U.O.C.) of the (W.B.) showed, in Tables (4.2B and 4.2A) respectively, the lowest amounts of kaolinite (7·7%), SiO_2 (39·09%), TiO_2 (0·61%), Al_2O_3 (10·7%), Na_2 (0·30%) and combined SiO_2 (18·68%), indicating the role played by these components in the concentration of Zr in these sediments.

The highest value of Zr (308 p.p.m.) in sample WBK-27, in the (W.K.B.) sediments, showed significantly high values of SiO_2 (40·9%), TiO_2 (0·6%), Al_2O_3 (13·31%), Na_2O (0·56%), K_2O (2·42%), total clays (52·6%) and quartz (20%), indicating a strong association of Zr with clays and resistate minerals. Similarly, sample BR-1781 of the (W.B.) sediments showed the highest concentration of Zr (672 p.p.m.) with very high values of SiO_2 (78·53%), quartz (62%), kaolinite (21%) and illite (63%), indicating the strong relationship of Zr with these components.

The association of Zr with quartz, resistate minerals and clay minerals has been studied by many workers. NICHOLLS and LORING (1962) reported high Zr with abundant quartz in the British Carboniferous sediments. GAD et al. (1969) mentioned that most of the Zr occurs as detrital grains in the Whitbian (Upper Lias) sediments, because Zr showed positive correlation at a significant level (5%) with Si only. MOHR (1959b),in the study of Lower Cambrian shales, mentioned that Zr is distributed between clay minerals and detrital zircon. DEGENHARDT (1957) mentioned that Zr may proxy for Al in the structure of clay minerals. KRAUSKOPF (1967, p.593) stated that Zr^{4+} substitutes for Mg^{2+} in montmorillonite. The same author (1979, p.479) mentioned that cations with smaller radii and higher charges (U, Th, B, Be, Mo, Nb, Sn and Zr) are concentrated in felsic end of the series only due to their size and charge. COSGROVE (1973) reported enrichment of Zr in Triassic mud-stones and attributed this to adsorption of Zr by clay minerals; the intense chemical weathering in the source area contributed Zr from zircon. CHOWDHURY (1980) mentioned that Zr is less likely to occur as a structural element in clays, in the study of Corallian mud-rocks, both on grounds of valency and large radius (0·80Å) of this cation.

The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows very strong positive correlations of Zr with Si, Ti, Al, Mg, K, V, Cr, Ba, Ce, Rb, Nb, Fe^{3+} and total clays; all correlations are significant at the 0·01% level. Zr also showed weak positive correlations with Na, illite and kaolinite, but a medium strong positive correlation with chlorite (r = +0·31), significant at the 0·02% level. The same correlation matrix shows very strong negative correlations of Zr with S, P_2O_5, Pb, Zn, Fe^{2+} and pyrite. These correlation trends suggest that the concentration of Zr in these sediments is controlled by alumino-silicates (clays) and resistate minerals; some Zr probably is also associated with iron oxide coatings on the surfaces of clay minerals. The positive correlation of Zr with illite (r = +0·18), kaolinite (r = +0·17) and chlorite (r = +0·31), on the basis of levels of correlation, suggests that comparatively larger amount of Zr^{4+} (0·80Å) is associated with chlorite by its possible substitution for Mg^{2+} (0·80Å), Fe^{3+} (0·73Å), Al^{3+} (0·61Å) in the octahedral layer. The substitution of Zr for Al and Mg has been mentioned by DEGENHARDT (1957) and KRAUSKOPF (1967). The positive correlation of Zr with Na_2O (r = +0·28) suggests either the presence of albite feldspar, as mentioned by COSGROVE (1973) or simply its relationship with clays. Conclusions regarding the concentration of Zr in the (W.K.B.) sediments agree with the results of factor analysis in Chapter Five. Factor analysis shows a strong positive loading of Zr with lithophile elements in Factor (F.1) representing 'total clays', and a stronger loading of Zr with Si, Nb and Ce in Factor (F-2) representing the 'resistate phases'. The very strong positive correlation of Zr with total clays (r = +0·47) is shown in Figure (4.20b), showing an intercept of a value of +104·88 p.p.m., indicating the amount of Zr not related to clays; this may be associated with resistate minerals. The average amount of Zr associated with clays will be 52 p.p.m. (i.e. 157-104·88 p.p.m. = 52 p.p.m.). This amount represents only 33·12% of the total Zr, indicating that the larger amount of Zr (66·88%) is associated as zircon with the resistate phases, e.g. quartz, kaolinite and probably feldspars, present in these sediments.

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) shows very strong positive correlations of Zr with depth. SiO_2, TiO_2, Na_2O, Ba, Nb, kaolinite and quartz, all being significant at the 0·01% level. The same Appendix shows strong to

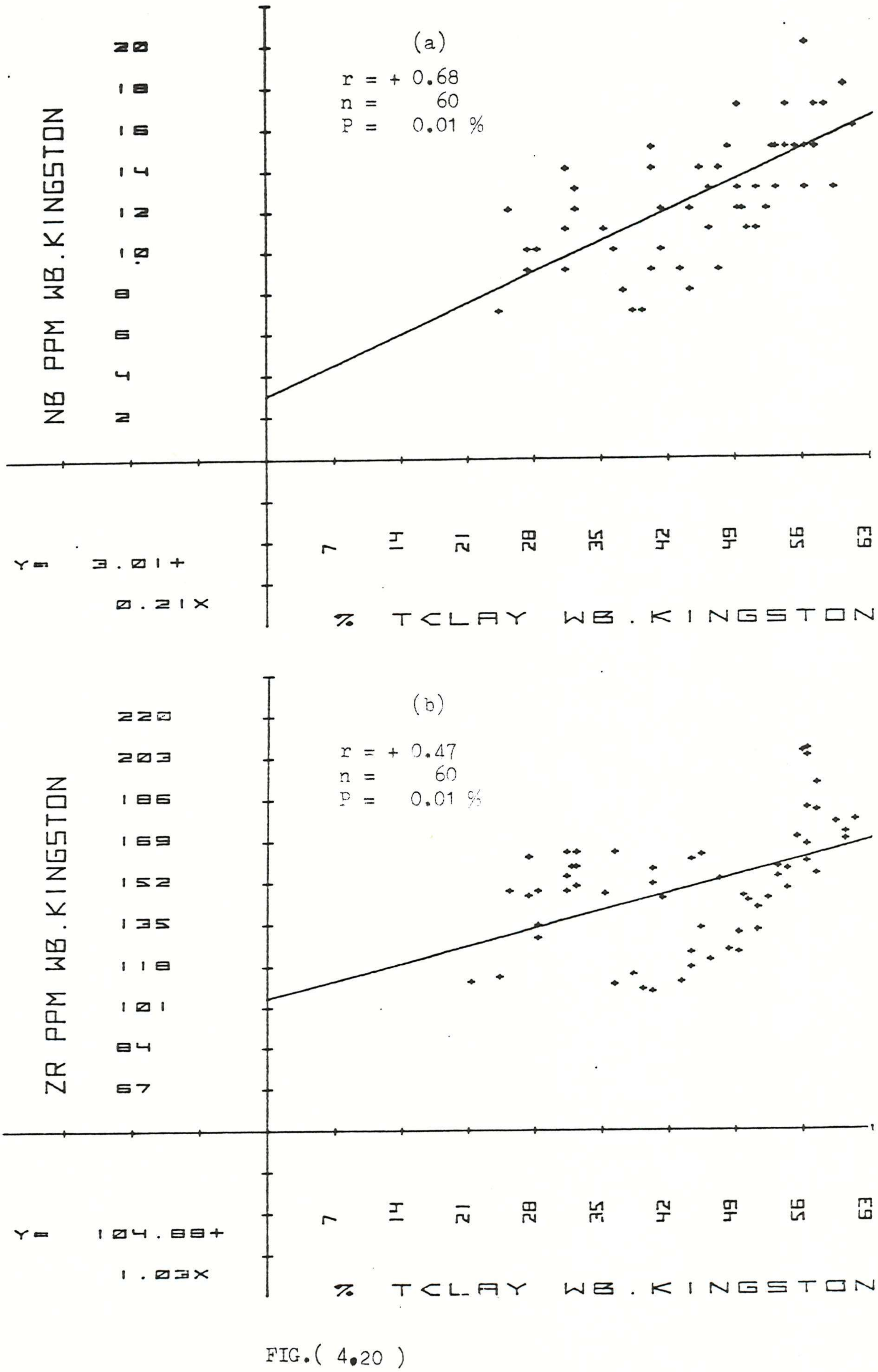
(a)
r = + 0.68
n = 60
P = 0.01 %
NB PPM WB.KINGSTON
2
4
6
8
10
12
14
16
18
20
Y= 3.01+ 0.21X
7
14
21
28
35
42
49
56
63
% TCLAY WB.KINGSTON
(b)
r = + 0.47
n = 60
P = 0.01 %
ZR PPM WB.KINGSTON
67
84
101
118
135
152
169
186
203
220
Y= 104.88+ 1.03X
7
14
21
28
35
42
49
56
63
% TCLAY WB.KINGSTON

FIG.(4.20)

medium negative correlations of Zr with Fe_2O_3, MgO, V, Rb, Mn, H_2O, Fe^{3+}, illite, mixed-layer (illite-montmorillonite) clay minerals and total clays. These correlation trends strongly indicate that Zr in the (W.B.) sediments is only associated with resistate phases e.g. quartz, kaolinite and albite feldspar. The relationship of Zr with kaolinite may be due either to the detrital nature of zircon and kaolinite, or it may be associated in the structure of kaolinite by proxying for Al, as suggested by DEGENHARDT (op.cit.). The very strong correlations between Zr and quartz ($r = +0{\cdot}85$) gave the regression equation $\left((\text{Zr p.p.m.})\ Y = 5{\cdot}23 + 8{\cdot}44\ X\ (\%\ \text{quartz}) \right)$.

This regression equation gives an intercept of +5·23, indicating the amount of Zr not associated with the resistate phase, i.e. quartz. The average amount of Zr associated with quartz will be 186 p.p.m. (i.e. 191 - 5·23 = 186 p.p.m.). This amount represents approximately 97·4% of the total Zr, indicating that almost all Zr is present in the resistate phases. This conclusion is further confirmed by the factor analysis results described in Chapter Five, where Factor (F-5) is the only factor which contains exceptionally high loadings of Zr, Si, Na, Nb and Ba; this factor represents the resistate minerals, e.g. quartz, zirconium, albite feldspar, etc., in these sediments.

Niobium in the sediments of both the boreholes shows its highest concentration in the (K.F.), as shown in Table (4.3n). The clay fraction ($< 2\mu$) samples of the (W.K.B.) showed a comparatively higher amount of Nb (20 p.p.m.), indicating a stronger relationship between Nb and clay minerals of this borehole, as compared to the sediments of the (W.B.). Niobium, like Zr, in the sediments of both boreholes showed its highest concentrations in the (K.F.). It showed similar trends of relationships with elements and minerals in the (K.F.) of both the boreholes, as has been described for Zr. The highest abundance of Nb (20 p.p.m.) is shown by samples WBK-63, 64 and 65. These samples contain the highest or significantly high amounts of SiO_2, TiO_2, Al_2O_3, K_2O, V, Cr, Ba, Ce, illite, kaolinite, quartz and total clays, suggesting the strong relationship of Nb with clay minerals and resistate phases. Similarly, in the sediments of the (W.B.), the samples BR-115 and BR-1771 showed the highest abundance of Nb (37 ppm). Sample BR-1771 also contains the highest abundances of Al_2O_3 (20·81%) Fe_2O_3 (4·60%), Na_2O (0·5%) and total clays (75·98%); illite (49·4%)

and kaolinite (11·40%), both in bulk rock. The same sample also contains significantly high values of SiO_2 (52·7%), TiO_2 (0·9%), K_2O (3·63%) and quartz (14%), suggesting that Nb is associated with clays and resistate minerals.

The correlation coefficient matrix for the (W.K.B.) sediments in Appendix (4.1C) shows very strong positive correlations of Nb with depth, Si, Ti, Al, Mg, Na, K, V, Cr, Ba, Ce, Th, Rb, Y, Zr, H_2O, illite, chlorite, kaolinite and total clays, all being significant at the 0·01% level. The same Appendix shows very strong negative correlations of Nb with Mn (r = -0·53) and smectite (r = -0·44). These correlations suggest a strong relationship of Nb with clay minerals and resistate phases. COSGROVE (1973) mentioned association of Nb with total clays and resistates in the study of Red bed mud-stones. GOLDSCHMIDT (1954) and RANKAMA and SAHAMA (1950) mentioned that Nb^{5+} (0·72Å) commonly substitutes for Zr^{4+} (0·80Å) and Ti^{3+} (0·75Å) in sediments; Nb^{5+} (0·72Å) can easily substitute for Mg^{2+} (0·80Å) and Al^{3+} (0·61A), **there** being close similarity of the ionic radii of these elements. CHOWDHURY (1980) reported significant positive correlation of Nb with Zr and TiO_2, in the study of Corallian mud-rocks, and concluded that appreciable amounts of Nb are present in isomorphous substitution in Zr and Ti minerals. The same author reported greater clay-held Nb from the Dorset coast samples. The present author found a similar concentration of Nb in the clay fraction, in the (W.K.B.) sediments from the Dorset area.

The very strong positive correlation of Nb with total clays (illite, chlorite and kaolinite), significant at the 0·01% level, in the (W.K.B.) sediments suggests that substitution of Nb^{5+} (0·72Å) probably took place for Mg^{2+} (0·80Å) and Al^{3+} (0·61Å) in the lattice structure of the mentioned clay minerals. Its very strong positive correlation with Zr and Ti, significant at the 0·01% level, also suggests possible substitution of Nb^{5+} (0·72Å) for Zr^{4+} (0·80Å) and Ti^{3+} (0·75Å) in clay minerals, as mentioned by GOLDSCHMIDT (op.cit.) and RANKAMA and SAHAMA (op.cit.). The strong association of Nb with total clays in the (W.K.B.) sediments is shown in Figure (4.20a), which shows an intercept of +3·01 p.p.m., indicating the amount of Nb not associated with total clays. The average amount of Nb associated with total clays is thus 10 p.p.m. (i.e. 13 - 3 p.p.m.), which represents 77% of total Nb in the sediments. This result agrees with the results of factor analysis described in Chapter Five. Factor (F-1), which represents the 'total clays', contains the highest loading of Nb and Factor (F-2), which represents the 'resistate minerals' phase, contains a comparatively lower loading value of Nb, confirming that most of the Nb is associated with clay minerals and some with resistates.

Niobium in the sediments of the (W.B.) shows very strong positive correlation, shown in Appendix (4.2C), with elements, e.g. Si, Na, Cr, Th, Zr, significant at the 0·01% level, and weak positive correlations with Ti, Al, Fe_2O_3(total iron), K, Ba, Ce, Rb, H_2O, Fe^{2+}, kaolinite, mixed-layer (illite-montmorillonite) clay mineral, quartz and total clays, being significant at the 5% level. These correlation trends of Nb suggest stronger association of Nb with minerals of the resistate phase (quartz, kaolinite, zircon) and clay minerals. The relationship of Nb with clay minerals may be of similar nature to that already described for the (W.K.B.) sediments.

The above conclusions agree with the results of the factor analysis, described in Chapter Five. Factor analysis shows the highest loading of Nb in Factor (F-5) in association with Si, Na, Zr and Ba, representing the 'resistate phases' of these sediments. Factor (F-4), representing mixed-layer (illite-montmorillonite) and Fe-Mn oxides/hydroxides, also contains a high loading of Nb, indicating its relationship with mixed-layer (illite-montmorillonite) clay minerals.

To summarize, the Zr in the sediments of the (W.K.B.) is associated with clay minerals, particularly in the lattices of chlorite and also with resistate minerals, e.g. quartz, kaolinite, anatase, rutile, etc. The sediments of the (W.B.) contain Zr, largely associated with resistate phase minerals, e.g. quartz, kaolinite, albite and anatase.

Niobium in the (W.K.B.) sediments is associated with clay minerals in their structures and with resistate minerals, e.g. quartz, kaolinite, zircon and anatase, etc. In the (W.B.) sediments Nb is associated with clay minerals, particularly mixed-layer mineral in its structure and also with resistate minerals, e.g. quartz, kaolinite, albite, etc.

o) Thorium

Table (4.3.o)

		(W.K.B.)	(W.B.)
Bulk rock	Range	0 - $\overset{*}{26}$ p.p.m.	0 - $\overset{+}{18}$ p.p.m.
	Average	10 p.p.m.	10 p.p.m.
Carbonate free: Average		14 p.p.m.	15 p.p.m.
Clay fraction: Average		16 p.p.m.	13 p.p.m.
Highest in Bulk rock		14 p.p.m. (K.F.)	13 p.p.m. (L.O.C.)
Lowest " " "		7 p.p.m.(U.O.C.)	9 p.p.m. (U.O.C.)

* Sample WBK-56 from the (K.F.) showed the highest amount of Thorium.
\+ Sample BR-1750 from the (L.O.C.) " " " " " "

The abundances of Th in the sediments of both the boreholes are shown in Table (4.3.o), which shows the same average values of Th in the bulk rock samples of both the boreholes, but slightly higher Th value in the clay fraction ($< 2\mu$) of the (W.K.B.) sediments, which may be related to the comparatively higher average values of kaolinite and chlorite of the (W.K.B.) sediments. The average values of minerals in the sediments of both the boreholes are shown in Appendices (4.1B and 4.2B) respectively. The clay fraction samples of the (W.K.B.) also showed comparatively higher values of Zr (158 p.p.m.), K_2O (4·10%), Al_2O_3 (23·61%) and TiO_2 (0·88%), as compared to the (W.B.) clay fraction samples, which showed lower values of Zr (154 p.p.m.), Al_2O_3 (22·62%), TiO_2 (0·84%), suggesting that for the higher value of Th, these components are responsible.

The highest concentration of Th (14 p.p.m.) of the (W.K.B.) sediments is present in the (K.F.) and is associated with the highest abundances of SiO_2, TiO_2, Al_2O_3, Na_2O, K_2O, combined SiO_2, V, Cr, Ba, La Ce, Rb, Y, Zr, Nb, as shown in Table (4.1A). These sediments also contain the highest abundances of total clays, illite and chlorite in bulk rock, which are shown in Table (4.1B). The maximum concentration of Th (26 p.p.m.) in sample WBK-56 of the (W.K.B.) sediments shows association with the highest abundance of total clays (60·6%), and significantly very high amounts of illite (64%), chlorite (11%), kaolinite (19%), quartz (19%), and elements, e.g. Al (7·83%), K (2·22%), Ti (0·42%), Cr (149 p.p.m.), V (118 p.p.m.), Ni (61 p.p.m.), Ba (294 p.p.m.), and the highest abundance of Rb (149 p.p.m.) These associations suggest that Th in the (W.K.B.) sediments in general is related to the clays.

The correlation coefficient matrix in Appendix (4.1C) shows a very strong positive correlation of Th with depth, Si, Ti, Al, Fe, Mg, Na, K, V, Cr, Ni, Ba, Ce, Cu, Rb, Y, Nb, H_2O, illite, kaolinite, chlorite and total clays, all correlations being significant at the 0·01% level; confirming the very strong relationship of Th with clay minerals, with the exception of smectite (r = -0·62), which showed a very strong negative correlation. The same correlation coefficient matrix shows a very strong negative correlation of Th with Ca, P, Mn, Sr, CO_2 and calcite, confirming that Th is of detrital origin and is only associated with clays. The positive correlation of Th with K_2O (r = +0·68), TiO_2 (r = +0·67), Al_2O_3 (r = +0·66) is much stronger than its correlation with Zr (r = +0·21),indicating its close association with clays rather than with resistates.

The highest abundance of Th (13 p.p.m.) in the (W.B.) sediments is present in the (L.O.C.) and is associated with the highest abundances of TiO_2, Al_2O_3, K_2O, combined SiO_2, Cr, La, Cu, Ni, Rb, Y, Ga, and the second highest concentration of SiO_2, as shown in Table (4.2A). It also showed association with the highest abundances of total clays, illite and chlorite in the bulk rock and the second highest value of kaolinite, all shown in Table (4.2B). The highest concentration of Th (18 p.p.m.) in the (W.B.) sediments is shown by sample BR-1750 from the (L.O.C.), which also contains significantly high amounts of Al_2O_3 (17·74%), TiO_2 (0·8%), K_2O (3·25%), Rb (179 p.p.m.), V (106 p.p.m.), Ni (41 p.p.m.), Ba (321 p.p.m.), and minerals, e.g. illite (62%), chlorite (5%), quartz (29%) and total clays (60·35%). These associations confirm that Th in these sediments in general is also associated with clays.

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) shows a very strong positive correlation of Th with depth, Si, Ti, Al, Fe, Na, K, V, Cr, La, Ce, Rb, Y, Nb, H_2O and total clays, all being significant at the 0·01% level; confirming the strong relationship of Th with clay minerals, with the exception of mixed layer mineral, which showed a very strong negative correlation (r= -0·35), significant at the 0·01% level. The other positive correlations of Th are with P_2O_5, Ba, Ga, Pb, Cu, Zr and are significant at the

0·1 - 5% level, suggesting its lesser association with these components, including the sedimentary phosphate minerals. RANKAMA and SAHAMA (1950) mentioned that, in monazite, Th^{4+} is captured by the trivalent lanthanides and simultaneously $(SiO_4)^{4-}$ substitutes for $(PO_4)^{3-}$. Monazite is the most important mineral of the Rare Earth Elements (REE) and is concentrated in the resistates present in the sediments.

RANKAMA and SAHAMA (1950) described the geochemical behaviour of Th in great detail, and its strong relationship with Zr and its minerals. They stated that mineral thorite ($Th(SiO_4)$) is isomorphic with zircon ($Zr(SiO_4)$), and a large part of the Th in the upper lithosphere is incorporated in the zircon structure due to similar ionic sizes of Th^{4+} (1·10kX) and Zr^{4+} (0·87kX); where Th replaces Zr diadochically. The same authors mentioned that, due to the similarity of the ionic radius of Th with that of the rare earth metals, Th is captured in the structure of lanthanide minerals. HUTTON (1947) mentioned that zircon in some granites is not radio-active, whereas monazite and xenotime are strongly radio-active. Consequently, the available Th and U, owing to their ionic dimensions, seem to prefer the 'REE' minerals; whereas zircon structure allows a very limited degree of substitution. According to RANKAMA and SAHAMA (1950), monazite and allanite, as a rule, contain a considerable quantity of Th (5-10% ThO_2 in monazite). The same authors also mentioned that part of Th is brought into solution during weathering, which is easily hydrolysed and accumulated in the hydrolyzates which contain notably higher contents of Th.

SULAIMAN (1972), in the study of Namurian argillite from Ireland, mentioned the highest contents of Th (14 p.p.m.) with the highest contents of Zr, Nb, Y and Ti in the near-shore sediments. He studied the Al/Th, Zr/Th, Th/Al and Th/K ratios to find out whether Th is strongly associated with clays or with resistate minerals. He noticed that the Al/Th ratio is more consistent than the Zr/Th ratio, indicating a stronger association with clays. SULAIMAN (op.cit.) also mentioned that Th either is substituting for Zr and Nb in their minerals, or Th has formed its own minerals, which are dispersed either only in a kaolinite matrix or a clay matrix. SULAIMAN (op.cit.) noticed a lesser degree of correlation of Th with Zr as compared to Al, and attributed it to its lesser association with resistate minerals.

ROGER and ADAMS (1967) noticed a linear relationship between Th and K; a similar relationship is also reported by SULAIMAN (op.cit.). COSGROVE (1973) reported very strong positive correlation of Th with lithophile elements and total clays, and concluded that Th is related to clays.

The Th/Al, Th/K, Zr/Th, Al/Th ratios for the sediments of the two boreholes were determined, and are shown in Tables (4.1C and 4.2C); the intention was to see whether Th is associated with clays only, or also with resistates. The highest values of Th/Al ratio(1·86) and Th/K ratio (6·51) exist in the sediments of the (K.F.) of the (W.K.B.), indicating a strong linear relationship of Al and K with Th and reflecting a strong association of Th with clay minerals, rather than resistates. The Zr/Th ratio showed its highest value (21·71) in the (U.O.C.) of the (W.K.B.) sediments, which also contain the highest abundance of quartz (23·67%), suggesting that Th is associated with the resistate minerals only in the (U.O.C.) sediments. The very strong positive correlation of Th with TiO_2 ($r = +0{\cdot}67$), Al_2O_3 ($r = +0{\cdot}66$), K_2O ($r = +0{\cdot}68$), Rb ($r = +0{\cdot}67$), illite ($r = +0{\cdot}63$), kaolinite ($r = +0{\cdot}56$), and total clays ($r = +0{\cdot}72$) on the one hand, and its weak positive correlation with Zr ($r = +0{\cdot}21$) on the other hand, in the total population, confirms its very strong association with clays only. The Al/Th ratio of the (W.K.B.) sediments in Table (4.1C) shows its highest value (618·64) in the (L.O.C.) sediments, which also contain the highest amount of kaolinite (21·77%). This relationship may be explained, as mentioned by SULAIMAN (op.cit.), by the possibility that either the leaching processes which are responsible for the concentration of Zr, Ti and Nb are responsible, or that Th is dispersed in the form of Th-bearing minerals in the kaolinite matrix.

The Th/Al, Th/K, Zr/Th and Al/Th ratios for the (W.B.) sediments in Table (4.2C) show the highest value of Th/Al ($1{\cdot}74 \times 10^4$) and and Zr/Al (31·54) in the (K.F.) sediments, which contain the highest amounts of quartz (40·70%), kaolinite (23·70%), SiO_2 (61·82%), Zr (347 p.p.m.) and Nb (25 p.p.m.), indicating that Th in these sediments is related to kaolinite and resistate minerals, as described earlier. The Th/K ratio showed its highest value ($6{\cdot}14 \times 10^4$) in the (L.O.C.) sediments, which contain the highest amounts of illite (35·60%), chlorite (3·23%) in bulk rock and also total clays (54·43%), indicating

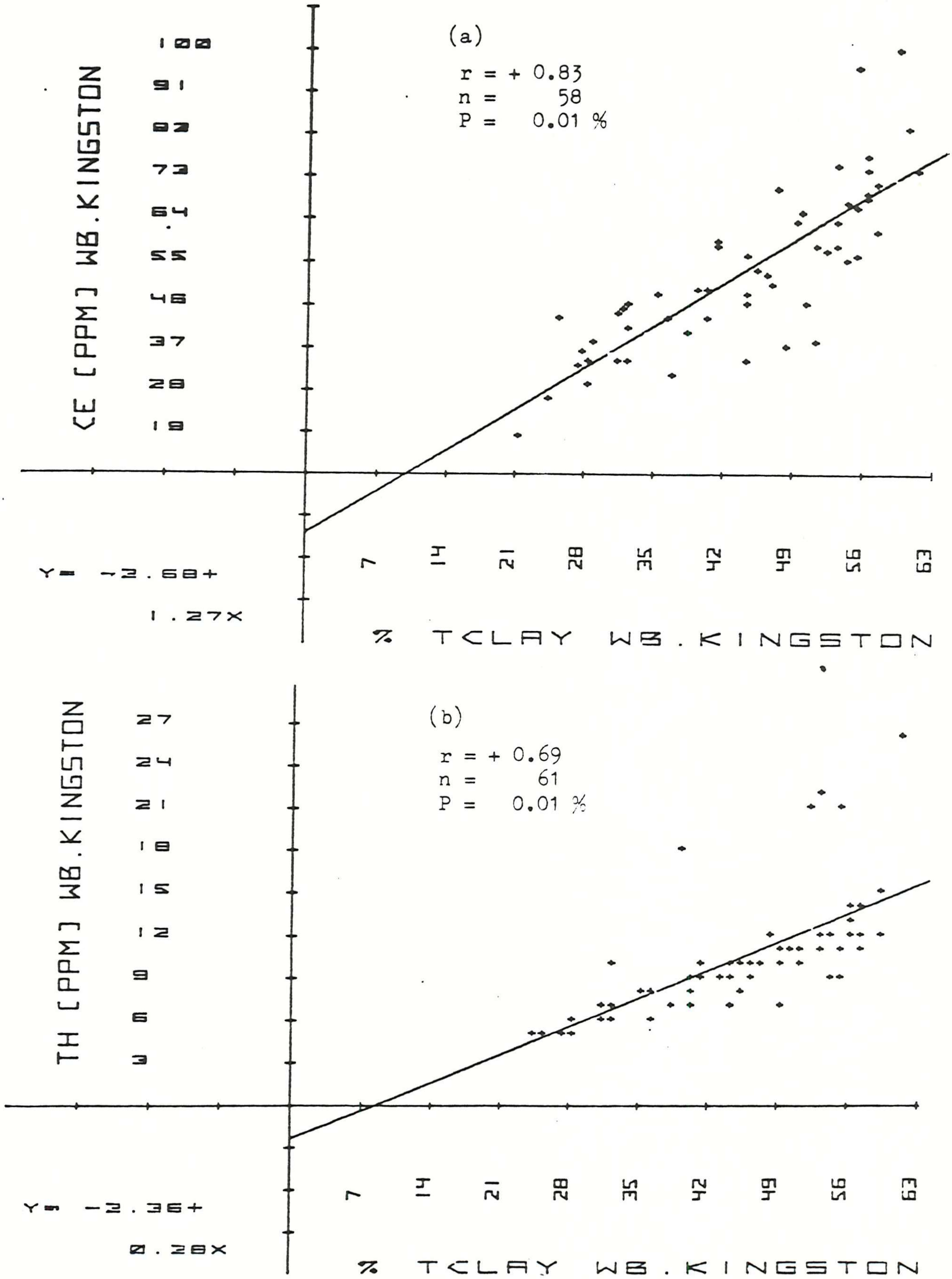

(a)
r = + 0.83
n = 58
P = 0.01 %
CE [PPM] WB.KINGSTON
100
91
82
73
64
55
46
37
28
19
Y= -2.68+
1.27X
7
14
21
28
35
42
49
56
63
% TCLAY WB.KINGSTON
(b)
r = + 0.69
n = 61
P = 0.01 %
TH [PPM] WB.KINGSTON
27
24
21
18
15
12
9
6
3
Y= -2.36+
0.28X
7
14
21
28
35
42
49
56
63
% TCLAY WB.KINGSTON

FIG.(4.21)

that Th is strongly associated with clays. Like in the (W.K.B.) sediments, Th in the total population of the (W.B.) samples showed very strong positive correlations with Al, Ti, K and Rb and as compared with its weak positive correlation with Zr ($r = +0{\cdot}27$) and Nb ($r = +0{\cdot}35$), confirming that in the total population Th is more strongly associated with clays.

To summarize, Th in the (W.K.B.) sediments and the (W.B.) sediments, on the whole, is more strongly associated with detrital clay minerals. Factor analysis results in Chapter Five confirm this conclusion. The strong relationship between Th and total clays in the (W.K.B.) sediments is shown in Figure (4.21b).

4.4 Rare Earth Elements

The lanthanide or rare earth elements consist of 15 elements: 14 occur in nature and one (Pm) was artificially prepared by nuclear reactions (KRAUSKOPF, 1979). The group of 'REE' occupies the 6 period and IIIB group of the transitional metals in the periodic classification of elements (KRAUSKOPF, 1979). According to RANKAMA and SAHAMA (1950), these metals can be divided into two sub-groups: one group is called the Cerium earth metal group and consists of elements from La to Eu; the other is called the Yttrium earth metal group and consists of elements from Gd to Y (see RANKAMA and SAHAMA, 1950, p.517). The same authors mentioned that 'REE' metals are all strongly lithophile and their lithophile character increases with the increase of the ionic radius ($La^{3+} = 1{\cdot}13Å$; $Ce^{3+} = 1{\cdot}09Å$; and $Y^{3+} = 0{\cdot}98Å$). Most of the workers have studied the geochemical characters of the rare earth metals as a group. RONOV et al. (1967) mentioned that, for a better understanding, it is advisable to study the 'REE' metals in groups. In the present study two rare earth elements, i.e. La and Ce were determined in the sediments of both the boreholes. Yttrium, being closely similar to the 'REE' is also included. In the present study the mean values of the Cerium earth metals, i.e. $\leq Ce/2 = \left(\frac{Ce + La}{2}\right)$ and $\Sigma Ce = (Ce + La)$ are used in the determination of $\frac{Ce}{Y}$ ratios shown in Table (4.4C), to study the relationship of the rare earth metals to Y and other elements. SULAIMAN (1972) and CHOWDHURY (1980) also used such mean values.

The average values of Y, Ce and La in the bulk rock and clay

RARE EARTH ELEMENTS

Table (4.4a)

		(W.K.B.)			(W.B.)	
	La *	Ce *	Y *	La +	Ce +	Y +
Bulk rock: Range	0-66 p.p.m.	0-100 p.p.m.	17-38 p.p.m.	3-82 p.p.m.	39-105 p.p.m.	9-67 p.p.m.
Bulk rock: Average	29 p.p.m.	50 p.p.m.	28 p.p.m.	45 p.p.m.	72 p.p.m.	35 p.p.m.
Carbonate free: Average	40 p.p.m.	70 p.p.m.	40 p.p.m.	65 p.p.m.	104 p.p.m.	49 p.p.m.
Clay fraction: Average	65 p.p.m.	98 p.p.m.	32 p.p.m.	40 p.p.m.	73 p.p.m.	27 p.p.m.
Highest in Bulk rock	43 " (K.F.)	74 " (K.F.)	40 " (K.F.)	55 " (L.O.C.)	77 " (K.F.)	43 " (L.O.C.)
Lowest " " "	16 "(U.O.C.)	41 " (U.O.C.)	22 " (U.O.C)	39 " (U.O.C.)	66 " (U.O.C.)	28 " (U.O.C.)

* Sample WBK-42 showed the highest amount of La.
* Sample WBK-58 " " " " " Ce.
* Sample WBK-61 " " " " " Y.
\+ Sample BR-1721 " " " " " La.
\+ Sample BR-1757 " " " " " Ce.
\+ Sample BR-1757 " " " " " Y.

fraction ($< 2\mu$) samples of both the boreholes are shown in Table (4.4a). This Table indicates relatively higher values of all the three elements in the bulk rock samples of the (W.B.) sediments; in the clay fraction the higher values are in the samples of the (W.K.B.) sediments, reflecting that comparatively larger amounts of 'REE' are present in these sediments as structurally bound in the lattices of clay minerals. The enrichment of these elements in the bulk rock of the (W.B.) sediments may be related to comparatively higher abundances of total clays (45·51%) and illite (66·53%) in the (W.B.) sediments as compared to the abundances of total clays (44·18%) and illite (53·34%) in the (W.K.B.) sediments. Many workers, including HIRST (1974), COSGROVE (1973), STEPHENS et al. (1975) and GOLDSCHMIDT (1937), have mentioned the strong association of the 'REE' with clays. BRUNFELT and DYPVIK (1976) mentioned a very strong relationship of 'REE' with illite. CHOWDHURY (1980), in the study of Corallian mud-rocks from the Dorset coast, mentioned a strong positive correlation of Ce, La and Y with Al (significant at the 0·1% level), and attributed it to the fact that the bulk of these elements is associated with clay minerals. The same author found higher contents of these elements associated with the higher abundances of illite and P_2O_5 in the Dorset coast samples. The present author also noticed similar trends and relationships of the Ce, La and Y with clays and P_2O_5 in the (W.B.) sediments.

The highest concentration of Ce, La and Y in the (W.K.B.) is present in the (K.F.) sediments, which also contain the highest average abundances of Si, Ti, Al, Na, K, combined SiO_2, Zr, V, Cr, Ba, Th, Rb, Nb, and the second highest value of iron-oxide (Fe^{3+}); all these values are shown in Tables (4.4a & 4.1A) respectively. The sediments of the (K.F.) also contain the highest abundances of total clays, illite, kaolinite and chlorite, and the second highest amounts of quartz and C_{org}, which are shown in Table (4.1B). These associations strongly suggest that, in general, the 'REE' in these sediments are concentrated in clays, resistate minerals and organic carbon. The lowest concentration of Ce, La and Y in the (W.K.B.) is shown by the (U.O.C.) sediments in association with the lowest abundances of the components described above.

The highest concentration of La and Y in the (W.B.) is shown by the (L.O.C.) sediments, and that of Ce by the (K.F.) sediments. The sediments of the (L.O.C.) also contain the highest abundances of Ti, Al, K, combined SiO_2, Cr, Th, Cu, Ni, Rb, Ga, and the second highest values of iron-oxide (Fe^{3+}), which are shown in Table (4.2A). These sediments also contain the highest amounts of total clays, illite, chlorite, C_{org}, and the second highest values of mixed-layer (illite-montmorillonite) clay minerals, as shown in Table (4.2B), suggesting a very strong relationship of La and Y with these components. Cerium (Ce) showed its maximum abundance in the (K.F.) sediments in association with the highest amounts of Si, Fe_2O_3(total iron), Na, S, P_2O_5, Ba, Zr, Nb, Mo, Fe^{2+}, which are shown in Table (4.2A); and the highest amounts of minerals quartz and kaolinite, as shown in Table (4.2B). The lowest abundances of illite, chlorite, mixed-layer minerals, K, Sr, Rb, Zn, V and Fe^{3+} in the (K.F.) sediments confirm that Ce in these sediments is not concentrated in these clay minerals but, largely, is associated with the resistate minerals. The lowest concentration of the 'REE' in the (W.B.) sediments is shown by the (U.O.C.) sediments, and follow similar trends to those exhibited by the (U.O.C.) sediments of the (W.K.B.). The lower concentration of the 'REE' in the (U.O.C.) sediments of both the boreholes may be related to the depleted amounts of illite, total clays and enriched abundances of smectite (montmorillonite-illite) in the (W.K.B.) and mixed-layer (illite-montmorillonite) in the (W.B.) sediments. CHOWDHURY (1980) reported depleted amounts of the 'REE' in the montmorillonite rich samples in the Corallian mud-rocks from the Dorset Coast.

The maximum contents of the 'REE' in the samples of both the borehole sediments have been checked, along with other chemical and mineralogical components, to observe the possible relationships between them. CALVERT (1976) stated that, in marine sediments, the 'REE' usually concentrate in association with phosphorus and iron oxide coatings on the surfaces of clay minerals. BRUNFELT and DYPVIK (1976) mentioned a strong association of 'REE' and illite in sediments. CHOWDHURY (1980) found significant positive correlation of Ce, La and Y with C_{org} and sulphur, and suggested that phosphorus is the main host of 'REE'. RANKAMA and SAHAMA (1950) stated that apatite is the only common mineral which may contain notable amounts of Y and lanthanides. The same authors further mentioned that apatite of the basic rocks (gabbropegmatite) is richer in 'REE' than the apatite found in granites. The partial chemical and

Table (4.4b)

(W.K.B.)				(W.B.)		
Data	WBK-42	WBK-58	WBK-61	Data	BR-1721	BR-1757
	La=66 p.p.m.*	Ce=100 p.p.m.*	Y=38 p.p.m.*		La=82 p.p.m.^{x}	Ce=105 p.p.m.^{x} Y = 67 p.p.m.^{x}
TiO_2	0·51%	0·63%	0·64%*	TiO_2	0·58%	0·68% ^{x}
Na_2O	0·47%	0·74%*	0·48%	Na_2O	0·28%	0·39% ^{x}
K_2O	2·00%	2·69%*	2·53%	K_2O	2·35%	2·74% ^{x}
Al_2O_3	11·45%	14·45%*	13·91%	Al_2O_3	12·83%	14·35% ^{x}
ΣFe_2O_3	6·62%*	5·04%	5·41%	ΣFe_2O_3	3·59%^{x}	3·42%
Fe^{3+}	3·00%	2·85%	3·43%*	Fe^{3+}	0·48%	2·35% ^{x}
Fe^{2+}	2·27%*	1·37%	1·24%	Fe^{2+}	1·95%^{x}	0·67%
P_2O_5	0·19%*	0·13%	0·13%	P_2O_5	0·34%	0·35% ^{x}
illite	56%	61%	65%*	illite	65%	67%^{x}
kaolinite	19%	24%*	23%	kaolinite	17%	18%^{x}
chlorite	12%*	10%	12%*	chlorite	1%	6%^{x}
C_{org}	4·3%*	2·23%	3·15%	C_{org}	11·35%^{x}	2·08%
Total clays	48·8%	58·7%*	52·35%	Total clays	48·43%	54·38% ^{x}

* Highest in (W.K.B.) samples.

x Highest in (W.B.) samples.

Σ Total iron.

mineralogical analysis of the respective samples is tabulated in Table (4.4b).

Taking into consideration the details given in Table (4.4b), it may be interpreted that Ce in the (W.K.B.) sample seems to be controlled by clay minerals, particularly illite and kaolinite, and probably in feldspar (albite), while in the (W.B.) sample, it seems to be concentrated in the total clays (illite and kaolinite), iron-oxides/hydroxides, Ti-bearing minerals, feldspar (albite) and phosphorus. Yttrium in the (W.K.B.) sample indicated an association with total clays (illite and chlorite), iron-oxides/hydroxides, and Ti-bearing minerals, while in the (W.B.) sample it seems to be concentrated with total clays (illite, kaolinite and chlorite), iron-oxides/hydroxides, feldspar, phosphorus and Ti-bearing minerals. La in the (W.K.B.) sample seems to be concentrated in iron-oxides/hydroxides, phosphorus, C_{org} and clays, while in the (W.B.) sample its concentration seems to be controlled by C_{org}, phosphorus and clays. These assumptions are purely on the basis of the sympathetic relations of the respective 'REE' with the mentioned components, as shown in Table (4.4b).

The correlation coefficient matrix for the (W.K.B.) samples in Appendix (4.1C) shows very strong positive correlations of Y with depth, total clays, Ti, Al, K, Rb, Th, Nb, all being significant at the 0·01% level, suggesting a very strong relationship of Y with alumino-silicates. The same Appendix shows medium strong positive correlations of Y with Si, Mg, Na, V, Cr, Ni, Ba, H_2O, illite, kaolinite and chlorite, indicating its weak association with these components. Illite, amongst all the clay minerals, showed the strongest correlation ($r = +0{\cdot}26$); this implies that a notable amount of Y^{3+}(0·98Å) is associated with illite, either as substituted for Mg^{2+}, Fe^{2+} or for La^{3+} or Th^{4+}, there being close similarity of the ionic radii of these elements (Mg^{2+} = 0·80Å; Fe^{2+} = 0·86Å; La^{3+} = 1·13Å; Th^{4+} = 1·08Å), or as adsorbed onto iron-oxides/hydroxides coatings on the surfaces of clay minerals. The same correlation coefficient matrix shows very strong positive correlations of Ce with depth, total clays, illite, kaolinite, chlorite, iron-oxides (Fe^{3+}), Ti, Al, K, Rb, Zr, Na, Si, Mg, V, Cr, Ba, La, Th, Nb, H_2O, all being significant at the 0·01% level, suggesting a very strong relationship of Ce with these components. The positive correlation of Ce with illite, kaolinite and chlorite is much stronger than their correlation with Y in these sediments; it indicates that Ce is more dominantly associated with clay minerals than Y. It is possible that Ce^{3+} (1·09Å), on the grounds of ionic similarity with Na^{+} (1·10Å), K^{+} (1·46Å), Th^{4+} (1·08Å) and La^{3+} (1·13Å), may be substituted for any of these in the octahedral/interlayer positions of illite and chlorite. The same Appendix shows very strong positive correlations of La with depth, total clays, illite, kaolinite, chlorite, C_{org}, Ti, Al, K, Rb, Mg, V, Cr, Ni, Ba, Ce, Cu, H_2O, all being significant at the 0·01% level, suggesting that La is strongly associated with these components. According to RANKAMA and SAHAMA (1950), the lithophile character of 'REE' increases with the increase of ionic radius. The ionic radius of La^{3+} (1·13Å) amongst the 'REE' is the largest, and this explains its strong relationship with the lithophile elements and clays in the present study.

The correlation coefficient matrix for the (W.B.) sediments in Appendix (4.2C) shows a very strong positive correlation of Y with depth, Si, Ti, Al, Na, K, P_2O_5, Cr, Ba, La, Ce, Th, Rb, Zr, Mo, C_{org}, H_2O, kaolinite and total clays, all significant at the 0·01% level, suggesting that Y is very strongly associated with these components. The other positive correlations of lesser significance level (1 - 5%) of Y, in these sediments, are shown with Fe_2O_3(total iron), S, Ga, Cu, Nb, Fe^{2+}, illite, chlorite and pyrite, suggesting weak association of Y with these components. The strong negative correlations of Y with Mg, Ca, Mn, As, CO_2, mixed-layer minerals, dolomite, calcite, indicate its detrital origin, and that it has no relationship with these components.

The same Appendix shows very strong positive correlations of La with depth. Ti, Al, Na, K, P, V, Ce, Th, Rb, Y, C_{org}, H_2O, total clays, suggesting a very strong relationship between La and these components. Lanthanum, in the same Appendix, shows weak positive correlations with Fe_2O_3(total iron), S, Cr, Ba, Cu, Nb, Mo, Fe^{2+}, kaolinite, chlorite and pyrite, significant at the 5% level, indicating a weak association of La with these components. The strong negative correlations of La with Ca, Mn, CO_2 and calcite suggest its detrital origin.

Cerium in the same Appendix shows very strong positive correlations with depth, Ti, Al, Fe_2O_3(total iron), Na, K, S, P, La, Th, Rb, Y, Nb, H_2O, Fe^{2+}, pyrite and total clays, all being significant at the 0·01% level, strongly suggesting that Ce is closely related with these components. The other positive correlations which Ce exhibited with Si, V, Cr, Ba, Mo, C_{org}, chlorite, are of a lesser degree of correlation (5% level), and indicate a weaker relationship of Ce with these components. The same Appendix shows a strong negative correlation of Ce with Ca, CO_2, mixed-layer minerals, dolomite and calcite, indicating its detrital origin and no relationship with these components.

SULAIMAN (1972), in the study of Namurian argillites from Ireland, reported higher abundances of Y, La, Ce in the near-shore sediments. The highest values of Y, La and Ce in the (W.K.B.) are found in the (K.F.) sediments, which contain higher average values of detrital components, e.g. quartz (20·8%), kaolinite (21·08%) and Zr (182 p.p.m.), as compared to the average values of quartz (20%), kaolinite (15·95%) and Zr (151 p.p.m.) in the whole Oxford Clay Formation, suggesting a great similarity of the (K.F.) sediments with the near-shore sediments described by SULAIMAN (*op.cit.*). The same author reported the highest values of the $\frac{\Sigma Ce/2}{Y}$ ratio (2·13) and $\frac{\Sigma Ce}{Y}$ ratio (4·26) in the near-shore sediments. The present author also determined the $\frac{\Sigma Ce/2}{Y}$ and $\frac{\Sigma Ce}{Y}$ ratios for the sediments of the two boreholes and compared these ratios with the values reported by other workers in Table (4.4c). This Table shows that $\frac{\Sigma Ce}{Y}$ and $\frac{\Sigma Ce/2}{Y}$ ratios of the total population of the (W.B.) samples are in good agreement with the values determined for the average shale (KRAUSKOPF, 1979), and Corallian mud-rocks of the Dorset coast (CHOWDHURY, 1980). The clay fraction samples of both the boreholes showed comparatively higher values of these ratios as compared to the bulk rock samples in Table (4.4c), but these values show good agreement with the values of these ratios determined for the average shales (WEDEPOHL *et al.*, 1961). The sediments of the (W.K.B.) showed lower values of these ratios in the bulk rock samples, as compared to the (W.B.) bulk rock values, but agree with the values reported by SULAIMAN (1972) for the Namurian argillites, indicating a great similarity between the two sediments. The Namurian argillites, according to SULAIMAN (*op.cit.*) were deposited under strong reducing environments.

CALVERT (1976) and PAPAVASILIOU (1979) determined the Ce/La atomic ratios to identify the provenance of sediments. In the present study the Ce/La atomic ratios for the sediments of both the boreholes, lithogenous clays (PIPER, 1974) and basalt and granite (KRAUSKOPF, 1979) are determined and shown in Table (4.4c). The Ce/La atomic ratio for basalt is the highest (2·97). The value of the Ce/La atomic ratio of

Table (4.4c)

	Y ppm	La ppm	Ce ppm	$\frac{\Sigma Ce}{Y}$	$\frac{\Sigma Ce/2}{Y}$	Ce/La At.ratio
Av.shales, KRAUSKOPF (1979)	35	40	70	3·14	1·57	1·73
Av.shales, TURIKIAN <u>et al</u>. (1961)	26	92	59	5·81	2·90	0·636
Red bed mud-rocks, COSGROVE (1973)	33	52	82	4·06	2·03	1·56
Corallian mud-rocks, CHOWDHURY (1980)	31	38	76	3·68	1·84	1·98
Namurian argillite, SULAIMAN (1972)	40	42	58	2·50	1·25	1·37
Namurian argillite, near-shore sediments, SULAIMAN (1972)	34	64	81	4·26	2·13	1·25
38, Russian near-shore marine clays, BALASHOV <u>et al</u>. (1964)	65	58	118	2·71	1·355	2·02
<u>Present work</u>						
1. (W.K.B.) bulk rock	28	29	50	2·82	1·41	1·71
" clay fraction	32	65	98	5·09	2·55	1·49
(W.K.B.) only (K.F.) sediments	40	43	74	2·92	1·46	1·706
" only (O.C.F.) sediments	26·33	28·33	46	2·82	1·41	1·609
2. (W.B.) bulk rock	35	45	72	3·34	1·67	1·57
" clay fraction	27	40	73	4·18	2·09	1·81
(W.B.) only (K.F.) sediments	42	47	77	2·95	1·476	1·62
" only (O.C.F.) sediments	35·33	46·33	72·33	3·36	1·68	1·55
Lithogenous clays, PIPER (1974)		45·5	101			1·62
Basalt, KRAUSKOPF (1979)		10	30			2·97
Granite, KRAUSKOPF(1979)		55	90			1·62

Note: (O.C.F.) = Oxford Clay Formation. At.ratio = Atomic ratio.

the (W.K.B.) bulk rock samples showed very good agreement with the value determined for the average shales (KRAUSKOPF, 1979). The value of the Ce/La ratio for the (W.B.) bulk rock samples is lower than the value of the (W.K.B.) sediments, but it is very near to the value determined for the lithogenous clays (PIPER, 1974). It suggests that sediments of the (W.K.B.) are similar to the average shales (KRAUSKOPF, 1979), and those of the (W.B.) to the lithogenous clays (PIPER, 1974). It may be suggested that different provenances contributed detritus to the sediments of the two boreholes at the time of deposition.

The reason for the lower values of the $\frac{\Sigma Ce}{Y}$ and $\frac{\Sigma Ce/2}{Y}$ ratios of the (W.K.B.) sediments may be related to the concentration of lower amounts of 'REE', clays and the lesser association of 'REE' with phosphorus, C_{org} and iron-oxides/hydroxides in the (W.K.B.) sediments, as compared to the (W.B.) sediments. The values of the $\frac{\Sigma Ce}{Y}$ and $\frac{\Sigma Ce/2}{Y}$ ratios in the (K.F.) of the (W.K.B.) sediments are higher as compared to the values of these ratios in the sediments of the Oxford Clay Formation; all values of the ratios are shown in Table (4.4c). The concentration of 'REE' and their ratios in the (K.F.) follow a similar trend to those mentioned for the near-shore sediments of the Namurian argillite by SULAIMAN (op.cit.), suggesting that the 'REE' in these sediments are concentrated by the detrital components, e.g. quartz, kaolinite and Zr and other detrital clays. The higher values of the $\frac{\Sigma Ce}{Y}$ and $\frac{\Sigma Ce/2}{Y}$ ratios in the (W.B.) are shown by the (L.O.C.) sediments, suggesting that the concentration of 'REE' in the (W.B.) sediments is related to clays, organic carbon, phosphorus and iron-oxides/hydroxides. These components showed their maximum values in the (L.O.C.) sediments as well as in the total population of the Oxford Clay Formation, as compared to the (K.F.) of the Warlingham Borehole sediments.

To summarize, the 'REE', i.e. La, Ce and Y in the (W.K.B.) sediments, in general, are associated with clays (particularly illite, kaolinite and chlorite), iron-oxides, C_{org}, and resistate minerals. Factor analysis results in Chapter Five show loadings of La, Ce and Y in Factor (F.1), which represents total clays, and loading of Ce with Zr, Si, Nb in Factor (F-2), representing resistates, confirming the above conclusions. The strong relationship of Ce with total clays in the (W.K.B.) sediments is shown in Figure (4.21a).

The concentration of Ce, La and Y in the (W.B.) sediments is controlled by total clays (particularly kaolinite and chlorite), C_{org}, phosphorus and resistates. Factor analysis results show, in Factor (F-1), high loadings of Ce, La and Y in association with the lithophile elements, and in Factor (F-4) loadings of Y with P_2O_5, Mo, C_{org}, confirming the above conclusions.

CHAPTER FIVE

R-MODE FACTOR ANALYSIS OF BULK ROCK CHEMICAL DATA

R-Mode Factor Analysis

Introduction

Factor analysis was first developed to study and solve the psychological problems, but in more recent years it has been found to be very useful to the applied scientists, particularly when observations are multiple and a very large data matrix is to be interpreted. CATTELL (1965a & b) and JÖRESKOG et al. (1976) have contributed to the theoretical background of the applications of factor analysis. LANDERGREN (1964) stated that, in the use of multiple correlations and regression analysis, sometimes negative or positive correlations between the variables are completely masked by the strong positive or negative correlations between the pairs of variables. Factor analysis tackles such problems satisfactorily. According to SPENCER (1966), factor analysis affords a way of locating the coherent groups of elements and measures the influence of the whole group at any particular locality. SPENCER et al. (1968) mentioned that, with the help of factor analysis, we are able to study simultaneously the relationship between many variables.

The first application of factor analysis in geological sciences was done by STRAHI (1958), in the investigations of the mineralogy and petrology of U-bearing shales. In later years many workers, including IMBRIE et al. (1964), SPENCER (1966), KLOVAN (1966), SPENCER et al. (1968), HIRST and KAYE (1971), COSGROVE (1973), SULAIMAN (1972), COOK (1974), HIRST (1974), CALVERT (1976), PAPAVASILIOU (1979) and CHOWDHURY (1980) have used factor analysis successfully for the geochemical and mineralogical interpretations of the multivariant data of both sediments and sedimentary rocks. Mineralogical data, being semi-quantitative and relatively imprecise, has not been included with the chemical data in the factor analysis, either by other workers or in the present study.

In the present study the factor analysis programme used was written by MATHER (1970). It gives primary factors, varimax factors and promax factors. The promax solution was run with K_{min} = 3-6, but it was noticed that runs with $K_{min} > 4$ did not produce better results. Therefore K_{min} = 3 and 4 was chosen as the routine value in the present study. Factor loadings higher than 0·25 are arbitrarily represented (SULAIMAN, 1972: HIRST and KAYE, 1971; HIRST, 1974). A correlation matrix between the various factors was also obtained in the oblique promax solutions, which is of great help in the interpretation of the factors, which otherwise might be difficult to interpret.

5.1 Factor Analysis of the Bulk Rock Chemical Data of Winterborne Kingston Borehole Sediments

Chemical data of 63 bulk rock samples of the Oxford Clay and Kellaways Formations from the Winterborne Kingston Borehole were used in the factor analysis. Three factors were extracted, which explained 71·06% of the total variance. The selection of three factors was done after inspecting factor analysis matrices containing up to eight factors, which showed that beyond three factors the remaining factors are not meaningful; their loadings being repetitions of the same elements more coherently grouped in Factors 1-3. The promax oblique factor pattern matrix; the promax factor correlations, and scores of the promax factors of the 63 samples of the Winterborne Kingston Borehole sediments, as obtained from the computer, are presented in Tables (5.1.1, 5.1.2 and 5.1.3) respectively. Each factor is interpreted and described in detail as follows:

Factor (F-1):

This is the most important factor, as it explains 44·26% of the total variance. Table (5.1.1) shows that Factor (F-1) has captured loadings of 29 out of 36 components, which include all the major elements except Fe(total) Among the minor elements, very high positive loadings are exhibited by the typical lithophile elements V, Cr, Ni, Ba, Ce, Th, Cu, Rb, Nb, and among other components with very high positive loadings are depth, C_{org} and H_2O. The elements of moderate to low loadings include La, Y, Zr and Fe^{3+}. The negative phase of this factor shows very strong loadings of Ca, Mn, CO_2 and moderate to low loadings are shown by P_2O_5, Sr and Pb.

The very strong positive loadings of major elements, including particularly Al and K, coupled with very high loadings of typically lithophile minor elements, e.g. Rb, Cr, V, Ba, Ce, Th, Ni, Nb, Cu and C_{org}, indicate that this factor represents the phases of clay minerals (total clays). HIRST (1974), COSGROVE (1973), PAPAVASILIOU (1979), TABLE (5.1.1) Promax Factor loadings with $K_{min} = 3$ and correlations between Promax Factors for $K_{min} = 3$ for the 63 samples of the Oxford Clay and Kellaways Formations, Winterborne Kingston Borehole samples.

Components	F1	F2	F3
Depth	0·866	0·278	
Si	0·822	-0·459	
Ti	0·975		
Al	0·971		
Fe	0·260	0·755	0·554
Mg	0·823		0·295
Ca	-0·972		
Na	0·657		
K	0·974		
S		0·914	
P	-0·465	0·659	
V	0·892		
Cr	0·885		
Mn	-0·821		0·456
Ni	0·709	0·509	0·256
Ba	0·909		
Ce	0·694	-0·466	
La	0·481		
Th	0·685		
Pb	-0·292	0·696	
As			0·786
Zn		0·703	
Cu	0·631	0·538	
Rb	0·964		
Sr	-0·367		
Y	0·374		
Zr	0·494	-0·607	
Nb	0·705	-0·330	
Mo		0·646	-0·434
C_{org}	0·560	0·484	-0·369

/contd.over

TABLE (5.1.1) contd.

Components	F1	F2	F3
CO2	-0·962		
H_2O^+	0·802	0·306	
Fe^{2+}		0·929	
Fe^{3+}	0·252	-0·339	0·707
Percentage of total explanation	44·26	19·52	7·28

Correlations between Promax Factors for $K_{min} = 3$

F1	1·0000		
F2	0·1246	1·0000	
F3	0·0689	0·1372	1·0000
	F1	F2	F3

Note: (i) Cumulative explanation = 71·06%

(ii) Factor loadings $<$ 0·25 were omitted.

(iii) The values of loadings represent values of correlation coefficients for the 5% and 1% levels of confidence. For 60 degrees of freedom these are:

5% level $\geqslant$ 0·25

1% level $\geqslant$ 0·325

SULAIMAN (1972), HIRST and KAYE (1971) and CHOWDHURY (1980), have all reported the presence of a clay minerals (total clays) factor, having similar high loadings of similar elements in the sediments studied by them. The very strong positive loading shown by depth in this factor is of significant importance; it provides confirmation that this factor really represents the clay phase, as they show a very strong sympathetic relationship between their abundance and depth (see Appendix 3.1).

There are some components, including Fe(total), Mg, P_2O_5, Mn Ni, Cu, Pb, Ce, Zr, Nb, C_{org}, Fe^{3+} and H_2O, which show loadings in more than one factor, indicating their multiple geochemical behaviour. Such behaviour of some of the elements, particularly Fe(total), Mg, Pb, Cu, Mn and Ni, associated with such phases as carbonate minerals, pyrite, C_{org}, Fe-Mn oxides/hydroxides, have been proved by the acid-reducing agent leaching study of these sediments (CHESTER and HUGHES, 1967), described in Chapter Six. Thus, it has been clearly demonstrated that these elements are shared, either by co-precipitation or substitution, in the authigenically produced phases, e.g. carbonate minerals, pyrite and C_{org}. Further, they may be adsorbed, either individually or in association with Fe-oxides/hydroxides, onto the surfaces of clay minerals and also on resistate minerals.

The positive loading pattern of this factor, as previously mentioned, relates to the clays, but the strong influence of such elements as Si, Ti, Zr, Nb, V, Cr and Ni with Al and K strongly suggests a detrital origin for the clay minerals. This indicates illite, kaolinite and chlorite, which are of detrital origin and contribute 75·54% of the total clay population. Major elements such as Al, Mg, Fe(total) and K, and minor elements, e.g. Cr, Cu and Ni, have demonstrated a very strong association with the lattice-held (lithogenous) fraction of the studied sediments, as demonstrated by the leaching study. These elements usually reside in the lattice structures of the clay minerals, which form the sediments of the (W.K.B.); this means the lattices of illite, kaolinite and chlorite (see Chapter Four, regarding the details about the residence of major and minor elements in clay mineral lattices).

The association of C_{org} and Fe^{3+} in the positive phase of Factor (F-1) may be explained easily. Both components show loadings in all three factors. C_{org} shows its strongest loadings in (F-1) and Fe^{3+} in the positive phase of (F-3). The relationship of C_{org} with clays is a well established fact as both components may be of detrital origin; C_{org}, being terrestrial, may accompany the detritus during transportation, and both are generally deposited in the deepest part of the basin. The association of C_{org} here indicates that some amount of C_{org} present in these clays is of terrestrial origin; a conclusion also drawn in Chapter Four. The strong positive correlation of Factor (F-1) with Factor (F-2) (Table 5.1.1), which represents the 'sulphide + C_{org} + phosphate' phases typical of the reducing environments, further clarifies the association of C_{org} with clays, indicating that C_{org} is generally of marine origin. The loading of Fe^{3+} in this phase, being the weakest loading, suggests that, on the whole, a very small amount of Fe^{3+} is present, being adsorbed onto the surfaces of the clay minerals in the studied sediments.

The very high loadings of Si, Ti, Ba, Nb and Na associated with the moderate loading of Zr, as shown in Table (5.1.1), suggest the presence of very fine grains of resistate minerals, e.g. quartz, zircon, feldspar, anatase, and probably other heavy minerals which may be present in minor amounts in these sediments. SPENCER (1966) mentioned the association of Ti and Zr as an indication of the presence of heavy minerals in the sediments of a Silurian graptolite band. He further stated that it is likely that Ti and Zr occur as minute crystalline grains of Ti-bearing minerals and zircon in the sediments studied by him. The sediments of the (W.K.B.) contain significantly high abundances of detrital components, including quartz, which showed a range of distribution from 16-54%, and Zr which also showed the significantly high value of 225 p.p.m., which is not very far removed from the average abundances of Zr (245 p.p.m. and 214 p.p.m.) reported by COSGROVE (1973) in Red bed mudstones, and CHOWDHURY (1980) in the Corallian mud-rocks from the Dorset coast,respectively; both sediments contain heavy minerals, including zircon. It is very difficult to separate the very fine grains of quartz and zircon etc. completely from the clays, and that is the reason why some of the clay fraction ($< 2\mu$) samples of these sediments showed peaks of quartz, feldspar and anatase on the X-ray diffractograms.

A summary of the mineral phases and their correlations with elements is presented in Table (5.1.3B). The detrital clay minerals phase represented by illite, kaolinite and chlorite shows a strong positive correlation, significant at the 1% and 5% levels, with the typical lithophile elements, which also have shown strong positive loadings in Factor (F-1). This is clear confirmation of the determined clays and their relationships with major and minor elements.

As a final check on the validity of Factor (F-1) as a clay factor, the abundances of total clays determined semi-quantitatively are plotted against the factor scores. The abundances of total clays are given in Appendix (3.1) and factor scores in Table (5.1.2). This plot shows a very strong positive correlation in Figure (5.1.1a) between the factor scores and abundances of total clays ($r = +0{\cdot}92$; $r^2 = +0{\cdot}85$), significant at the 0•01% level, confirming the conclusions derived earlier.

The total clays in Table (5.1.3B) show a very strong negative correlation, significant at the 1% level, with elements Ca, P, Mn, Sr, CO_2, and minerals such as smectite and calcite. This correlation is to be expected because these components are of non-detrital origin and should show an antipathetic relationship with detrital clays.

The negative phase (Ca, CO_2, Mn, P_2O_5 and Sr) are typical of the carbonate minerals, as reported by many workers, including COOK (1974), COSGROVE (1973), SULAIMAN (1972), PAPAVASILIOU (1979). These loadings demonstrate the obvious antipathetic relationship of carbonates with the total clays, which is illustrated in Figures (5.1.1a and b). The abundances of calcite tabulated in the Appendix (3.1) and the factor scores shown in Table (5.1.2) are plotted in Figure (5.1.1b), which shows a very strong negative correlation between the factor scores and abundances of calcite ($r = -0{\cdot}93$; $r^2 = -0{\cdot}86$).

The negative phase of Factor (F-1) representing the carbonate mineral phases also shows an association of the loadings of P_2O_5, Mn Sr and Pb with Ca and CO_2, although P_2O_5 shows a much stronger loading in the positive phase of Factor (F-2). The nature of the loadings of P_2O_5 in (F-1) and (F-2) suggests that probably a sedimentary apatite (hydroxy apatite ?) was precipitated as a primary phosphate in the 'sulphide + C_{org}' phase (F-2). In the negative phase of (F-1) a substitution of PO_4 groups for CO_3 groups in carbonate minerals most probably took place, as suggested by KRAUSKOPF (1979) and DEGENS (1965, p.220), and thus produced a phosphate probably of second generation.

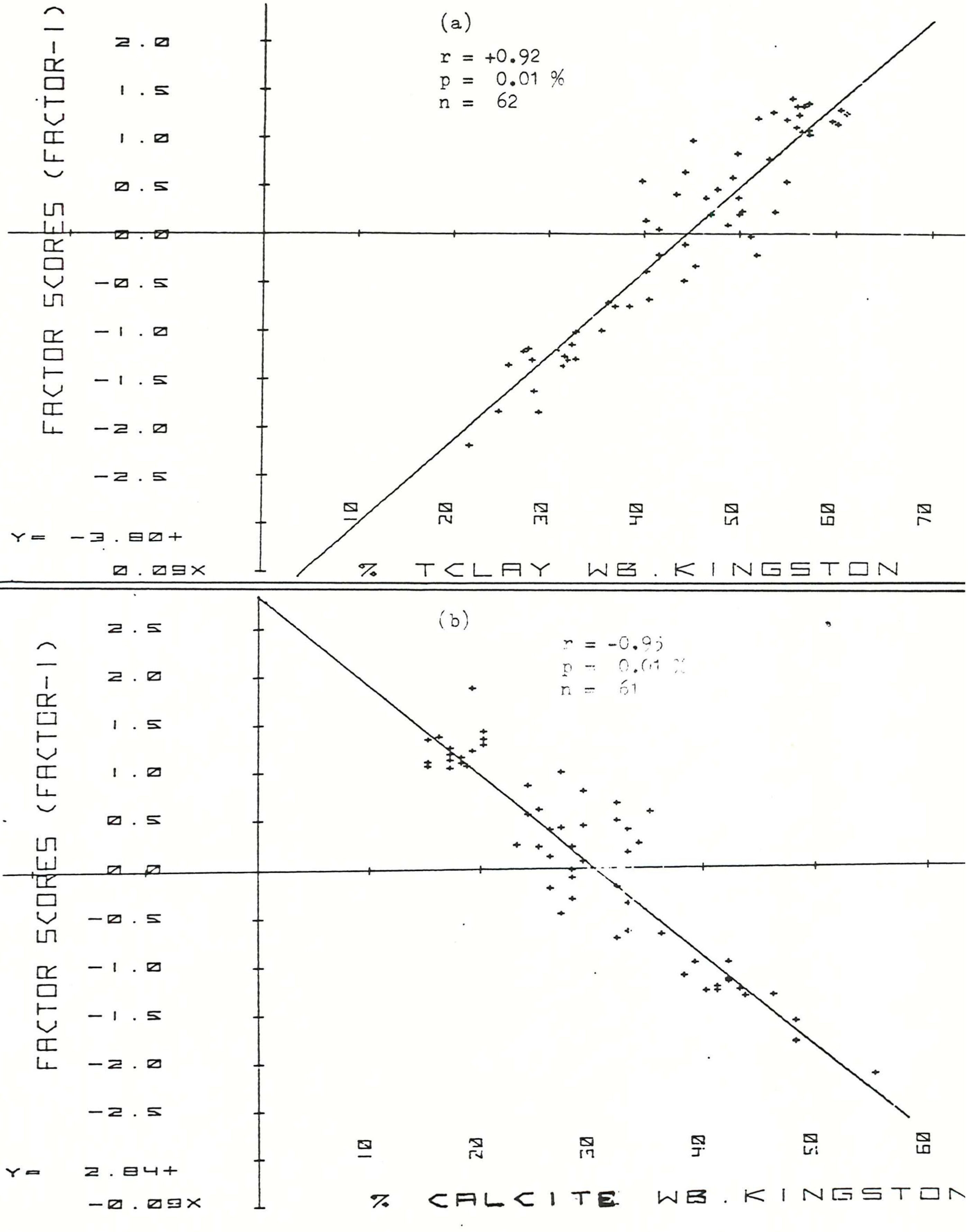
(a)
r = +0.92
p = 0.01 %
n = 62
FACTOR SCORES (FACTOR-1)
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
10
20
30
40
50
60
70
Y= -3.80+
0.09X
% TCLAY WB.KINGSTON
(b)
r = -0.95
p = 0.01 %
n = 61
FACTOR SCORES (FACTOR-1)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
10
20
30
40
50
60
Y= 2.84+
-0.09X
% CALCITE WB.KINGSTON

FIG.(5.1.1)

<u>TABLE (5.1.2)</u>: Scores on Promax Factors

(F-1)	(F-2)	(F-3)
-1·350	-1·040	-1·279
-1·246	-1·202	-1·406
-1·284	-1·053	-1·263
-1·295	-1·168	-0·812
-1·833	-0·767	-1·165
-1·175	-0·997	-0·500
-1·184	-1·096	-0·276
-1·609	-0·830	-0·568
-2·172	-0·216	-0·795
-1·197	-0·749	-0·769
-0·704	-0·911	-0·114
-1·340	-0·338	-0·207
-1·134	-0·279	-0·332
-1·290	-0·269	-0·604
-0·380	-0·647	0·475
-1·003	-0·883	-0·255
-1·822	1·390	0·795
-0·995	-0·532	0·663
-0·668	-0·040	0·987
-0·333	-0·492	0·918
-0·112	-0·535	1·228
-0·208	-0·464	0·459
-0·744	0·973	0·757
-0·737	0·690	0·457
0·372	-0·987	1·333
0·775	-1·160	0·866
0·835	-1·243	1·259
0·200	0·005	1·508
0·047	0·025	0·753
0·465	-0·764	1·115
-0·476	0·682	0·832
0·233	-0·411	1·278
0·199	-0·278	1·016
0·393	0·240	0·992

/contd.over

TABLE (5.1.2) contd.

(F-1)	(F-2)	(F-3)
-0.225	1.083	1.776
0.638	-0.831	1.629
0.530	-0.361	1.472
-0.789	2.878	1.627
0.550	-0.596	1.427
0.222	2.319	-0.431
0.581	1.328	-0.415
0.374	1.424	-1.152
-0.034	2.471	-1.553
0.139	2.498	-1.311
0.407	1.561	-1.655
0.095	1.678	-1.660
0.967	0.915	-1.027
1.045	0.556	-0.835
1.231	0.346	-0.836
1.019	0.620	-1.032
1.185	0.552	-0.985
1.258	-0.124	-0.647
1.070	0.178	-0.575
1.401	-0.589	0.152
1.243	0.031	-0.628
1.279	-0.225	-0.452
1.131	-0.218	-0.022
1.104	-0.255	0.185
1.160	-0.295	0.066
1.316	-0.473	0.207
1.354	-0.435	0.039
1.320	-0.236	-0.402
1.200	-0.456	-0.309

The sediments of the (W.K.B.) (Appendix 4.1C) show a very strong positive correlation of P_2O_5 with Ca (r = +0·42), significant at the 0·01% level, suggesting the occurrence of a carbonate apatite. The proposed phosphate, being in minor amounts or cryptocrystalline (DEGENS, 1965, p.143), escaped detection on X.R.D. DEGENS (op.cit.) used the term 'collophane' for such sedimentary precipitated phosphate. The association of phosphorus with anoxic sediments is also mentioned by CALVERT (1976). In the study of the Silurian graptolite band sediments, SPENCER (1966) found an association of Ca-P, and explained that it is due entirely to the preservation of an hydroxy apatite phase, produced initially by the planktonic and nectonic organisms, rather than to a carbonate replacement process, as suggested by DEGENS (1965, p.220). It is therefore concluded that, in the (W.K.B.) sediments, sedimentary phosphate of two generations is present, which through its low abundance escaped detection by X.R.D.

The association of Sr may be explained, according to KRAUSKOPF (1979), by the fact that $SrCO_3$ and $CaCO_3$, both near to saturation in sea-water, are co-precipitated. This relationship may be due to possible substitution of Sr^{2+} for Ca^{2+}, the ionic radius of Sr^{2+}(1·12Å) and Ca^{2+}(0·99Å) being similar. DEER et al. (1962) mentioned that a small amount of Sr commonly substitutes for Ca in calcite.

The association of Mn may be explained, according to GOLDSCHMIDT (1954),by the fact that under anaerobic conditions Mn will be liable to solution and leaching; under aerobic conditions it will be liable to precipitate. According to the same author, the divalent Mn, under non-oxidizing (anaerobic) conditions, forms soluble manganese bicarbonate $Mn(HCO_3)_2$, and under oxidizing (aerobic) conditions,it forms very insoluble manganese dioxides. In the present study, the Mn association is better explained as being due to the replacement of Ca^{2+}(1·08Å) by Mn^{2+}(0·91Å), which is also suggested by RANKAMA and SAHAMA (1950).

The association of Pb in the phase represented by carbonates is very weak, as indicated by its very low loading, suggesting a very distant relationship with the mineral phases. From the correlation coefficient matrix shown in Appendix (4.1C), it becomes clear that Pb shows a much stronger correlation with P_2O_5(r = +0·41), significant at the 0·01% level, as compared with Ca (r = +0·16) and calcite (r = +0·16).

These correlations strongly suggest that Pb displays a preferred association with phosphate rather than with calcite. The relationship of Pb with sedimentary phosphate or calcite has been described in Chapter Four. This relationship may be purely on genetic grounds; due to co-precipitation of Pb with either of the two phases, there being a common source of organisms for Pb and Ca. BOSTRÖM et al. (1974) suggest that diatoms and plankton are enriched in Pb relative to shales, and BATURIAN (1969) reported 0•8% P_2O_5 in diatoms.

Factor (F-2)

This factor explains 19•5% of the total variance, and is thus the second most important factor in the present study. It shows, in its positive phase, very strong loadings of elements Fe(total), S, P, Pb, Zn, Mo, Ni, Cu and Fe^{2+}, and moderate to low loadings of C_{org} and depth respectively. The negative phase of this factor shows a very strong loading of Zr and moderate to low loadings of Ce, Si, Nb and Fe^{3+} respectively; all loadings are shown in Table (5.1.1).

The components loaded in the positive phase of Factor (F-2) may be grouped as follows:

1. Fe(total), S, Mo, Pb, Zn, Cu, Ni and Fe^{3+}
2. C_{org}
3. P.

The elements of Group One are typical of the chalcophile group (GOLDSCHMIDT, 1954; BRUNLOW, 1979), with a strong affinity for sulphur. The abundances of sulphur and pyrite in the sediments of the (W.K.B.) vary between 0•7 to 3•66% and 1•5 to 6•8% respectively, which are significantly high values as compared with the contents of these components in average shales reported by KRAUSKOPF (1979), but show good agreement with the values reported by GAD et al. (1969) in the Whitbian shales of reducing environments, as shown in Table (4.3). CALVERT (1976) and PRICE (1976) both associated a strong relationship between the reducing environments and elements such as S, Mo, As, Pb, Zn, Ni and P.

Considering the total population in the positive phase, it can be safely suggested that sulphide minerals play a major role in the control of these elements and, on this basis, this factor may be called the 'sulphide factor'. However, taking into consideration the significantly high loadings of P_2O_5 and C_{org} in this phase, it appears that these components also hold some control over the elements associated in Factor (F-2).

The correlation coefficients shown by pyrite and C_{org} with the elements are summarized in Table (5.1.3B), which shows that all the components loaded in the positive phase of (F-2) are very strongly positively correlated with pyrite and C_{org} at the 1% level. Pb is the only element which showed strong positive correlation with pyrite and no correlation with C_{org}, suggesting its association only with sulphides. Phosphorus showed a very strong positive correlation, significant at the 1% level, with a group of elements, i.e. S, Pb, Zn, Mo, Fe^{2+}, and a correlation of a lesser degree with Fe(total) and C_{org}, significant at the 5% level, indicating a much stronger relationship with S, Pb, Zn, Mo and Fe^{2+}. The correlation trends of pyrite and C_{org} suggest that both phases played a significant role in the control of elements, with a minor amount of the variance controlled by phosphorus, probably hydroxy apatite (collophane ?). KRAUSKOPF (1956, p.25) mentioned that elements such as Zn, Cu, Pb possess a very strong adsorptive ability on sedimentary apatite. The very strong positive correlation of P_2O_5 with Zu, Cu and Pb in the studied sediments is shown in Appendix (4.1C), which suggests that such a relationship with apatite as mentioned by KRAUSKOPF (op.cit.) exists here. Thus it seems reasonable to re-designate this factor as the 'Pyrite + C_{org} + Phosphate' factor, representing the authigenically produced phases; opposed by the detrital components loaded in the negative phase. There exists a good agreement between the correlation coefficients of pyrite and C_{org} with these elements, which is shown in Table (5.1.3B), and the levels of correlations of loadings of (F-2) shown in Table (5.1.3A), confirming that the conclusions drawn are reasonably satisfactory. CHOWDHURY (1980) mentioned the association of S, Mo, P, Cu, Pb, Ni, Zn, As, Ce, La, Y and C_{org} in the study of the Corallian mud-rocks from the Dorset coast, and interpreted this association as 'C_{org} + sulphide' factor.

The association of S, P. Mo, Pb, Cu, Ni and Zn in the positive phase of (F-2) suggests that these elements were available either in

TABLE (5.1.3A): Summary showing the levels of significance of the loaded components in the respective factors of the (W.K.B.) sediments.

Confidence Levels		FACTOR (F-1)	FACTOR (F-2)	FACTOR (F-3)
+ve	5%	Fe_2 (total iron)	NONE	Mg, Ni
	1%	Depth, Si, Ti, Al, Mg, Na, K, V, Cr, Ni, Ba, Ce, La, Th, Cu, Rb, Y, Zr, Nb, C_{org}, H_2O, Fe^{3+}	Depth, Fe_2(total iron), S, P, Ni, Pb, Zn, Cu, Mo, C_{org}, H_2O, Fe^{2+}	Fe(total iron), Mn, As, Fe^{3+}
-ve	1%	Ca, P, Mn, Sr, CO_2	Si, Ce, Zr, Nb, Fe^{3+}	Mo, C_{org}
	5%	Pb	NONE	
Percentage variance		44·26	19·52	7·28

(i) Cumulative Percentage = 71·06

(ii) The values of factor loadings represent correlation coefficients for the 5% and 1% levels of significance. For 60 degrees of freedom these are:

5% $\geq$ 0·25
1% $\geq$ 0·32.

TABLE (5.1.3B): Correlation Coefficients for 5% and 1% levels of significance shown by the mineral phases and chemical elements of the 63 bulk rock samples of the Winterborne Kingston Borehole sediments.

Confidence levels		Total Clays	Quartz	Calcite	Pyrite	Organic Carbon	Fe^{3+}(iron oxides)
+ve	5%	Mo, Fe^{3+}	Mn	NONE	NONE	Na, Th, Fe^{3+}	Ti,Al,Cr,Mn, Ce,As,Rb, CHLR,TClays
	1%	Depth,Si,Ti,Al, Fe(total),Mg,Na, K,V,Cr,Ni,Ba,Ce, La,Th,Cu,Rb,Y,Zr Nb,C_{org},H_2O^+,ILL, KAOL,CHLR	Ca,CO_2,SMECT, CAL	Ca,P,Mn,Sr,CO_2 SMECT,QTZ	Depth,Fe(total) S,P,Ni,Pb,Zn, Cu,Mo,C_{org}, H_2O^+,Fe^{2+} ILL, KAOL.	Depth,Ti,Al, Fe(total),Mg,K,S, V,Cr,Ni,Ba,La,Zn, Cu,Rb,Mo,H_2O, Fe^{2+},ILL,KAOL, CHLR,Pyt,TClays	Si,Mg,K,V, Zr
-ve	1%	Ca,P,Mn,Sr,CO_2, SMECT,QTZ,CAL.	Depth,Ti,Al, Fe(total), Mg, K,S,V,Ni,Ba, La,Th,Cu,Rb, Mo,C_{org},H_2O Fe^{2+},ILL,KAOL, CHLR,Pyt, TClays	Depth,Si,Ti,Al, Fe(total), Mg, Na,K,V,Cr,Ni, Ba,Ce,La,Th,Cu, Rb,Y,Zr,Nb, C_{org},H_2O, ILL, KAOL,CHLR, TClays	Zr,Fe^{3+}, SMECT,QTZ	Ca,Mn,CO_2,SMECT, QTZ,CAL.	P, Mo, Pyt.
	5%	NONE	Na,Cr,Zn	Mo,Fe^{3+}	Si		Ca,S,C_{org}, Fe^{2+}, CAL.

(Note: ILL = Illite; KAOL = Kaolinite; CHLR = Chlorite; SMECT = Smectite; QTZ = Quartz; CAL = Calcite; Pyt = Pyrite; TClays = Total Clays)

For 60 degrees of freedom these levels are: 5% level $\geqslant$ 0·25 No.of samples = 63.

1% level $\geqslant$ 0·325.

solution from which they co-precipitated or some (e.g. Zn, Cu, Pn and Ni) were present adsorbed onto the surfaces of clay minerals, C_{org} and sedimentary phosphates (hydroxy apatite/collophane), as suggested by KRAUSKOPF (1956, p.25). The positive correlation shown by Factor (F-2) with Factor (F-1) in Table (5.1.1) provides strong evidence regarding the availability of the prospective adsorbent, i.e. total clays and C_{org}. The association of metals such as Cu, Ni, Pb, Zn and Mo with C_{org} in this factor may be due to the presence of complexes of these metals with C_{org}, as suggested by TOURTELOT (1964), HIRST (1962a&b), KONONOVA(1966), PRICE (1976). According to SCHNITZER and SKINNER (1965), DROZDOVA (1968) and ZUNINO et al. (1972), it is well established that organic matter reacts with metals and produces 'organo-metal' complexes of reasonably stable nature.

The association of depth in (F-2) suggests that abundances of C_{org}, pyrite and the associated elements increase with depth. This is true; the sediments of the (L.O.C.) in Table (4.1A) show the highest concentrations of these components. According to CALVERT (1976) and PRICE (1976), the association of P, V, Cu, Pb, Zn, Mo and As is typical of reducing environments. CALVERT (1976, p.256) has quoted that values of the elements in the 'oxic' and 'anoxic' sediments reported by DOFF (1969), showing enriched values of S, Fe^{2+}, Mo, Pb, Zn, Cu, Ni in the 'anoxic' (reducing) sediments, as compared to the oxic sediments. Similar enrichment has been observed in the sediments of the (L.O.C.), which confirms that reducing conditions existed at the time of deposition of these sediments, or immediately after burial.

The presence of pyrite and C_{org} in sediments is usually considered as an indication of reducing conditions in the sediments. Both components have shown their presence in the complete sequence and demonstrated their highest concentrations in the sediments of the (L.O.C.), as shown in Table (4.1B). The depositional conditions of the (L.O.C.) sediments of Woodham in Buckinghamshire have been studied by HUDSON and PALFRAMAN (1969). These authors, on the basis of the studies of ecology and preservation of the fauna in the Lower Oxford Clay, have mentioned the existence of 'oxic' and 'anoxic' conditions prevailing in these sediments at the time of deposition. They noticed the presence and absence of certain species of fauna, e.g. epifaunal, infaunal, suspension feeders, benthonic and burrowing animals, and on that basis decided that the bottom conditions of these sediments during the deposition time were never stagnant. They found fossils of the shallow infaunal animals in the surface layers of the sediments, and concluded that toxic conditions did not exist. According to these authors, the rarity of 'deep-burrowers' in these sediments suggests that the lower layers of the sediments may be anaerobic (anoxic). DUFF (1975), in his palaeoecological studies of the Lower Oxford Clay of Central England, mentioned the presence of pyrite, C_{org}, benthic fossils and benthonic burrows in the sediments of the Lower Oxford Clay studied by him. DUFF (1975) also established that bottom conditions of the (L.O.C.) in Central England were less anaerobic on the basis of faunal studies. Regarding pyrite, he stated that it is a post-depositional preservative change, which suggests the existence of 'micro-environments' of reducing conditions (anoxic), probably created within the freshly deposited sediments. KAPLAN et al. (1963) reported the presence of pyrite in the samples of the oxidising environments from the basin of South California. He further mentioned that, for the formation of pyrite, it is not essential that reducing conditions should always persist in the sediments throughout. The occurrence of macroscopic pyrite, below 10 cms at all depths, in the oxidising sediments of the 'San Diego Trough' suggests that the formation of pyrite took place below 10 cms depth, where reducing conditions were created in association with sulphur, iron, etc. BERNER (1970) mentioned that pyritization is almost completed within the top 5 cms of the newly deposited sediments, because at this depth H_2S in solution is so depleted that no further reaction can take place.

The distribution of Fe^{2+} and Fe^{3+} iron in the different parts of the Oxford Clay and Kellaways Formations in Table (4.1A) shows higher values of Fe^{3+} as compared to Fe^{2+}, which does not mean that sediments of the Oxford Clay and Kellaways Formations were deposited under oxidising environments throughout. It shows that iron was being supplied to the basin of deposition as Fe^{3+}, either bound in the structures of clay minerals, particularly chlorite, or adsorbed as Fe-oxides/hydroxides onto the surfaces of clay minerals, as suggested by KAPLAN et al. (1963), MACKENZIE and GARRELS (1966). After the deposition of sediments at a depth of 5 to 10 cms, as mentioned by BERNER (op.cit.), the processes of pyritization within these sediments

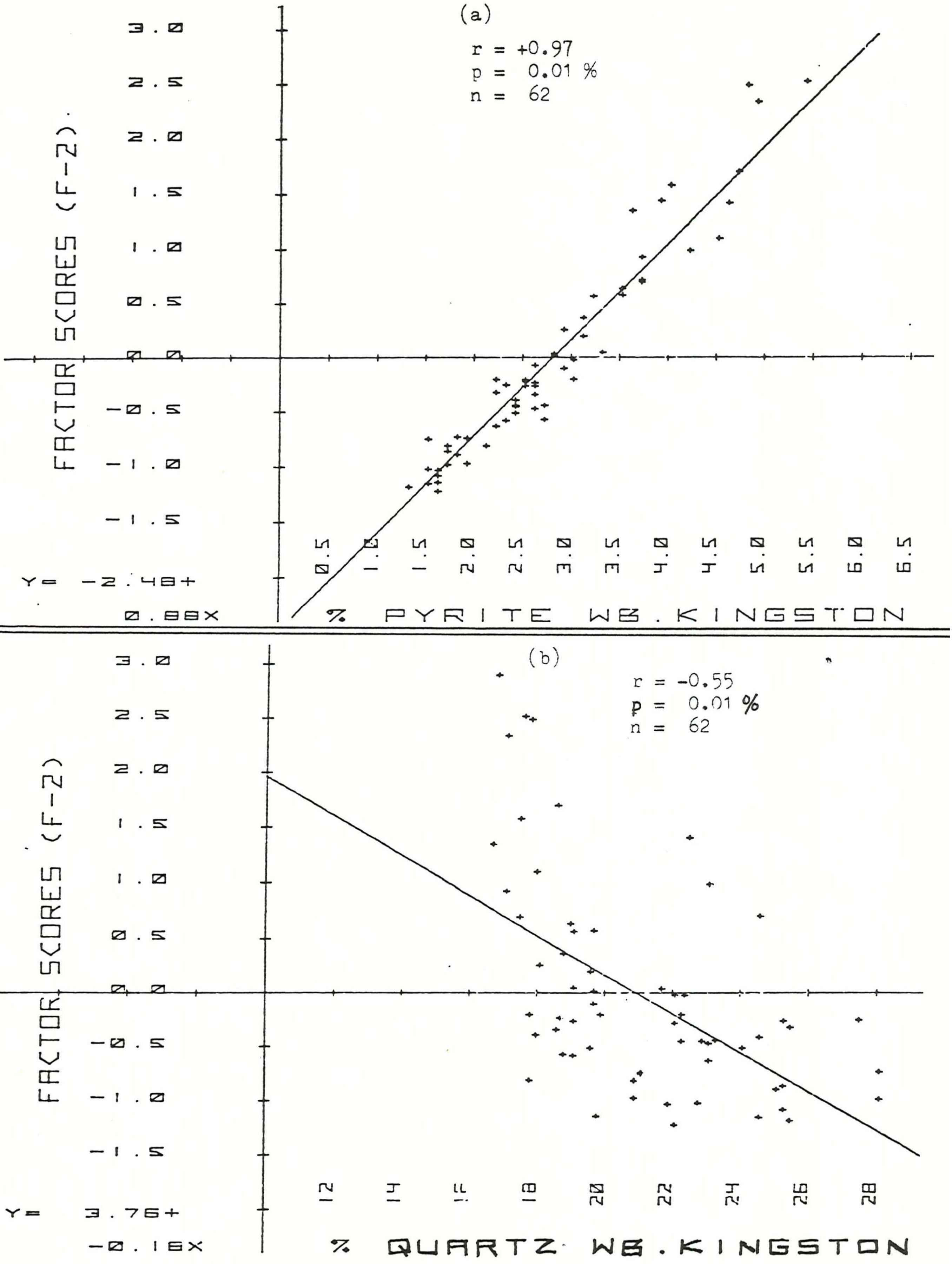

(a)
r = +0.97
p = 0.01 %
n = 62
FACTOR SCORES (F-2)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
Y= -2.48+
0.88X
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
% PYRITE WB.KINGSTON
(b)
r = -0.55
p = 0.01 %
n = 62
FACTOR SCORES (F-2)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
Y= 3.76+
-0.16X
12
14
16
18
20
22
24
26
28
% QUARTZ WB.KINGSTON

FIG.(5.1.2)

was completed. For the formation of pyrite, all the necessary components, i.e. iron, sulphur and reducing bacteria, were available at all times. HUDSON and PALFRAMAN (1969) proposed three possible sources for the sulphide ion in these sediments, for the formation of pyrite, which are as follows:

i) sulphide from the decomposition of the proteins in the trapped organic matter of fossils;

ii) reduction of sulphate in the sea-water by sulphate-reducing bacteria;

iii) reduction of sulphate by bacteria, from the overlying sea-water, taking place at the interface or within diffusional contact with it.

Sulphur, in the present sediments, seems to be largely contributed by the reduction of sulphate in sea-water, as suggested by KAPLAN _et al_. (_op.cit_.) and HUDSON et al. (_op.cit_.); some amount was probably also contributed by the organic matter, as suggested by KUMMEL (1948).

The negative phase of (F-2) shows a very strong loading of Zr and moderate to low loadings of Ce, Si,Fe^{3+} and Nb. This association represents a typical resistate group of minerals, e.g. quartz, zircon and probably a Ce-bearing member of the epidote group of rock forming minerals called 'orthite or allanite' (see READ and RUTLEY, 1947, p.316). Factor scores of (F-2) shown in Table (5.1.2) are plotted against the abundances of quartz in Figure (5.1.2b), which shows a good negative correlation between the two variables ($r = -0{\cdot}55$) significant at the 0·01% level; but in the scatter, many points are away from the regression line, indicating that quartz is not the only resistate mineral representing this phase; other resistates such as zircon and probably Ce-bearing silicates are also present. The association of Ce and Fe^{3+} suggests that Ce is associated with iron oxides, coating onto the surfaces of the resistate minerals. The association of Nb may be due to isomorphous substitution of Nb^{5+}(0·72Å) for Zr^{4+}(0·80Å), suggested by GOLDSCHMIDT (1954).

It may be summarized that Factor (F-2) represents the authigenically produced phases of pyrite + C_{org} + phosphate, which are opposed by detrital components such as quartz, zircon and probably Ce-bearing silicate. The strong relationship of the factor scores of (F-2) with pyrite is shown in Figure (5.1.2a), showing a strong positive correlation ($r = +0{\cdot}97$; $r^2 = 0{\cdot}94$), highly significant at the 0·01% level. The value of r^2 indicates the very close nature of the association of the two variables. The remaining variance may be controlled by C_{org} and phosphate.

Factor (F-3)

This factor explains only 7·3% of the total variance, which indicates the subordinate role of the phases represented by this factor in the (W.K.B.) sediments. The positive phase of this factor shows strong loadings of As, Fe^{3+} and Fe_2O_3(total), with As being the highest. Other elements, e.g. Mn, Mg and Ni show moderate to low loadings, indicating their less active participation, their dominant roles being in (F-1) or (F-2). The negative phase of Factor (F-3) shows loadings of only two components, i.e. Mo and C_{org}.

The association in the positive phase of this factor strongly suggests that it represents the 'oxic conditions' in the sediments, while the associations in the negative phase, being typical of anoxic (reducing) conditions, suggest that it represents the 'anoxic conditions' (reducing conditions) in the sediments. The occurrences of oxic and anoxic conditions in the sediments of the Lower Oxford Clay have been established by HUDSON (1978), HUDSON and PALFRAMAN (1969) and DUFF (1975). It seems reasonable that, taking into consideration the associations of both the phases of Factor (F-3), it may be designated on the whole as a 'Redox' factor. This factor also represents the iron-rich, arsenic-rich and smectite-rich sediments of the lowermost part of the Upper Oxford Clay and the entire population of the Middle Oxford Clay. These sediments have shown significantly high abundances of Fe^{3+}, Fe_2O_3(total iron), As and smectite, which are shown in Tables (4.1A and 4.1B), and also the highest positive values of the factor scores on the samples of these sediments, which are shown in Table (5.1.2).

Factor (F-3) in Table (5.1.1) shows a strong negative correlation with Factor (F-2), which has already been described as the factor representing the authigenically produced phases of sulphide + C_{org} + phosphates (positive loadings), having an antipathetic relationship with the phases of detrital components such as quartz, zircon and probably Ce-bearing silicates (negative loadings). The positive phase of Factor (F-3) has been recognised as the phase representing the 'oxic conditions' in the sediments, and the correlated negative phase of (F-2) as the phase of the detrital components. The correlation between these two phases may be explained according to CHESTER and MESSIHA-HANNA (1970) and CALVERT and ASTON (1976). These authors mentioned that detrital material could contain phases like hydrous Mn or Fe oxides which formed at the site of weathering and then became detrital particles.

The relationship of the negative phase of (F-3) representing the typical association of reducing conditions, with the positive phase of (F-2), representing the phases of sulphides + C_{org} + phosphates, is self-explanatory. SPENCER et al. (1968, p.981) reported similar associations in the factor recognised as 'iron - manganese - hydroxide' factor, in the studies of sediments from the Gulf of Paria. CHOWDHURY (1980) also reported the association of Fe, Mg, Mn, Ni, Zn and As in the study of the Corallian sediments from the Dorset coast, and recognised this association as an Fe-bearing phases factor.

The associations of the components in the positive phase of (F-3), particularly As, deserve a detailed comment. This phase shows the only and the highest loading of As, indicating that, in the (W.K.B.) sediments, As is related only with the phases represented by this factor. The usual association of As in sediments and sedimentary rocks has been reported by CALVERT (1976), PRICE (1976), GAD et al. (1969) and PAPAVASILIOU (1979) with sulphur and organic matter, although the association of As with clay minerals, detrital components and Fe-Mn oxides/hydroxides is also well documented (GOLDSCHMIDT, 1954; CALVERT, 1974). CHOWDHURY (1980) reported a higher concentration of As in the 'Upper Calcareous Grit' group in the study of the Corallian rocks, and attributed this concentration to the adsorption of As onto Fe-Mn oxides/hydroxides.

In the present study, As showed no relationship with C_{org}, and a very weak correlation with S ($r = +0 \cdot 17$) and pyrite ($r = +0 \cdot 16$), indicating its lesser association with sulphide phase minerals. According to TOURTELOT (1964), the shales of the deepest part of the basin contain the highest amount of As. The highest amount of As in the present sediments is shown by the sediments of the Middle Oxford Clay (formed in a comparatively less deep environment than the Lower Oxford

Clay), which also contain the highest abundances of Fe^{3+} and Fe_2O_3(total), and second highest amount of Mn, as shown in Table (4.1A). The arsenic showed strong positive correlations with Fe_2O_3(total), Fe^{3+} and Mn in Appendix (4.1C), indicating that As, in general in these sediments, is strongly related to Fe-Mn oxides/hydroxides and not with sulphides.

RANKAMA and SAHAMA (1950) stated that arsenic, antimony and bismuth are all enriched in the oxidate sediments, chiefly by adsorption on ferric oxides. The same authors further mentioned that iron-rich oxidate sediments contain a higher abundance of As as compared to the manganese-rich oxic sediments. The highest concentration of As in association with the highest abundance of Fe^{3+} is present in the Middle Oxford Clay sediments, while a lower amount of As, associated with the highest abundance of Mn, is present in the sediments of the Upper Oxford Clay, as shown in Table (4.1A). The sediments of the Upper/Middle Oxford Clay also show the higher concentrations of smectite, as shown in Table (4.1B). The relationship of As with smectite becomes more clear by examining the correlation coefficient matrix of the clay fraction ($< 2\mu$) chemistry of the representative samples of the (W.K.B.) sediments, which is given in Chapter Seven. It shows strong positive correlations of As with SiO_2, MgO and smectite, all being highly significant at the 0·02% level, and another positive correlation with Fe_2O_3(total) and Mn, significant only at the 0·1% level. As showed a very strong negative correlation with illite, kaolinite and chlorite in the same matrix. These correlation trends clearly indicate that there exists a very strong relationship between As and smectite. The octahedral positions of the montmorillonitic component of smectite can easily accept As^{3+}(0·60Å) for Al^{3+}(0·61Å), Fe^{3+}(0·73Å) or Mg^{2+}(0·80Å), there being close similarity of the ionic radii. This substitution can take place either at the time of formation of smectite or during its transportation with detritus. The sediments at present under study contain smectite in significant amounts; it is non-detrital and is believed to be the product of the alteration of volcanic/volcanogenic material. RANKAMA and SAHAMA (1950) mentioned that sedimentary rocks of marine origin should contain higher amounts of As than the igneous rocks, because much arsenic has evidently been introduced directly into the exogenic cycle by volcanic activity. The association of As with smectite in the (W.K.B.) sediments may be explained in the light of the suggestion by RANKAMA and SAHAMA (op.cit.). The major amount of As in these sediments is associated with the Fe-Mn oxides/hydroxides, as mentioned earlier. The associations of the As, Fe^{3+} and smectite in the Middle Oxford Clay suggest that, at the time of their deposition at the Winterborne Kingston site, the weathering conditions in the source area were favourable for the abundant supply of iron as ferric oxides, which accompanied the detritus as colloidal material adsorbed onto the clays and detrital components. Some of the Fe^{3+} went into solution, probably due to low Eh conditions, as suggested by GARRELS and CHRIST (1965), and after its reduction to Fe^{2+} was associated with sulphides (DREVER, 1971). The highest abundance of Fe^{3+} in the Middle Oxford Clay sediments also suggests that the rate of desolution of iron hydroxides at that time was probably slow. SPENCER et al. (1968) and CALVERT (1976) have reported, in recent marine sediments accumulating in reducing environments, the presence of Fe-Mn hydroxides, precipitated in the minerals in the source region from weathering solutions and during transportation. The association of As, particularly in the Middle Oxford Clay, with smectite probably suggests that some As from the volcanic/volcanogenic material, during the transportation of the detritus, was directly added, as suggested by RANKAMA and SAHAMA (op.cit.).

The association of Mg in the positive phase of (F-3) suggests that Fe^{2+}(0·86Å) has been replaced by some amount of Mg^{2+}(0·80Å), due to close similarity of the ionic radii. The association of Ni may be explained, according to SPENCER et al. (1968, p.981), by the fact that precipitated ferric and manganese hydroxides possess a strong scavenging ability for the covariant elements.

The occurrence of iron-oxides in the sediments of the Oxford Clay is not uncommon. It has been mentioned by JACKSON (1972) during his study of the Lower Oxford Clay sediments. According to JACKSON(op.cit.), the presence of ferric oxides in the Oxford Clay sediments was suspected from the red stains in the samples in hand specimens. It was not confirmed by X-ray analysis, probably because of their poor crystalline nature, being very small in amount, and possibly being adsorbed by the CuKα X-rays of the X.R.D. DEGENS (1965) also stated the cryptocrystalline nature of iron oxides (goethite, etc.) The detection of iron oxides on X.R.D. firstly is difficult due to their cryptocrystalline nature (DEGENS, op.cit.), and secondly due to the peak positions of goethite, which are masked by other minerals. The strongest peaks of goethite on the X.R.D. are at 4·18Å and 2·69Å, which may be easily masked by a strong peak of quartz at 4·26Å and a strong peak of pyrite at 2·71Å respectively. The sediments of the Oxford Clay in general, and those of the (W.K.B.) in particular, contain significantly high abundances of quartz and pyrite; therefore peaks of these two minerals can easily mask the peaks of goethite. JACKSON (1972) also reported association of organic matter with pyrite and its partially oxidised form, limonite (iron oxide), in the sediments of the Lower Oxford Clay. It has already been mentioned in the description of Factor (F-2) that, on the whole, complete anoxic conditions (reducing) never persisted in the sediments of the Oxford Clay, which implies that during sedimentation these sediments enjoyed oxygenated conditions too.

It may be summarized that Factor (F-3), on the whole, represents the 'Redox' conditions of the sediments of the (W.K.B.). The positive phase represents the oxic conditions or Fe-Mn oxides/hydroxides phase. The scores of Factor (F-3) are plotted against the abundances of Fe^{3+} shown in Appendix (4.1A). Figure (5.1.3) shows a very strong positive correlation of this plot ($r = +0{\cdot}72$), highly significant at the 0·01% level.

Summary

It is concluded that factor analysis not only confirmed the inferences regarding the distribution of elements in the studied sediments, based on the multivariate correlations and regression analysis, but also enabled the present author to interpret the overall geochemical environments of the sediments of the Oxford Clay and Kellaways Formations. It has enlightened the role of some of the elements, particularly As, P, Pb, Mn, Ce and C_{org}, which were not clear in the bivariate correlations.

Three factors were extracted, which explained 71·06% of the total variance satisfactorily. Factor (F-1) is interpreted as the 'clays factor', representing detrital clay minerals antipathetically related to the authigenically produced carbonates. Factor (F-2) has been recognised as the 'sulphides + C_{org} + phosphates' factor, being opposed by a resistates phase. Factor (F-3) has been identified as the 'Redox' factor.

This study provided insight regarding the physico-chemical conditions of the studied sediments. The conclusions drawn here show

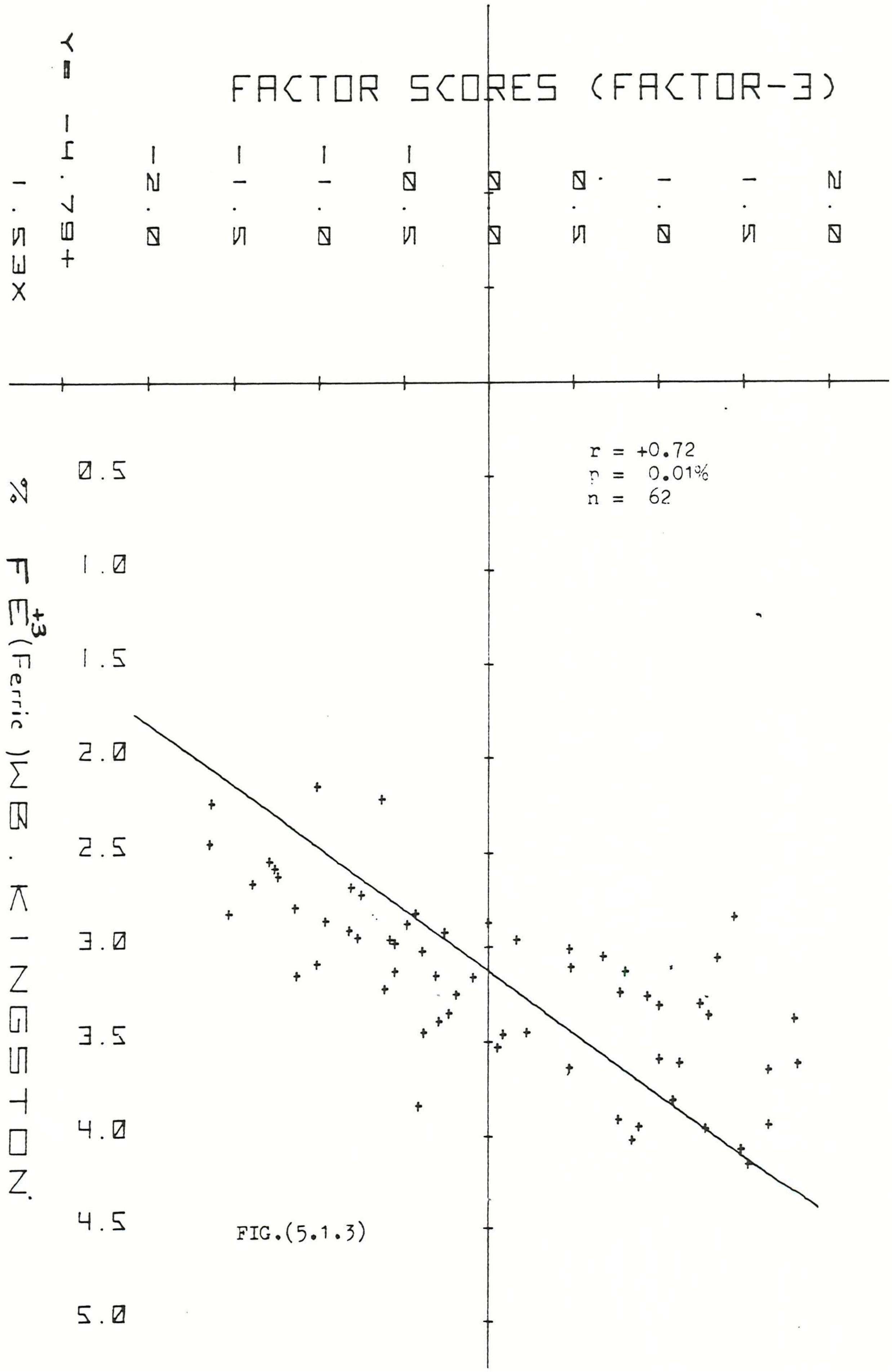
FACTOR SCORES (FACTOR-3)
Y= -1.79+1.53X
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
r = +0.72
p = 0.01%
n = 62
% FE^{+3}(Ferric) WB. KINGSTON.
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

FIG.(5.1.3)

good agreement with the views expressed by HUDSON (1978), HUDSON and PALFRAMAN (1969), regarding the depositional environments based on isotopic studies and the preservation and ecology of the fauna in these sediments and also with the conclusions of DUFF (1975).

5.2 R-Mode Factor Analysis of the Bulk Rock Chemical Data of Warlingham Borehole Sediments

Chemical data of 78 bulk rock samples of the Oxford Clay and Kellaways Formations were used in the R-mode factor analysis. Four factors were extracted which explained 67·04% of the total variance. The selection of four factors was made on the same basis as described earlier in the factor analysis of the (W.K.B.) sediments. The promax oblique factor matrix; the promax factors correlation and scores of the promax factors as obtained from the computer, are tabulated in Tables (5.2.1 & 5.2.2) respectively. The detailed study and interpretation of each factor is as follows.

Factor (F-1):

This is the most important factor, explaining 30·05% of the total variance. This factor shows loadings of 22 variables out of 35 (Table 5.2.1). The positive phase of this factor shows strong to very strong loadings of 14 components, including TiO_2, Al_2O_3, Na_2O, K_2O, V, Cr, La, Ce, Th, Rb, Y, Fe^{3+} and H_2O^+, and medium to low loadings of 6 components, i.e. depth, SiO_2, Fe(total), Ba, Nb and C_{org}. The negative phase shows very strong loadings of CaO and CO_2 and a very low loading of As. The positive phase does not show loadings of Mg, Ni, Cu and Zr, although these elements are strongly loaded in Factor (F-1) of the (W.K.B.) sediments. The negative phase of Factor (F-1) likewise does not show the loadings of P_2O_5, Mn and Sr seen in Factor (F-1) of the (W.K.B.) sediments.

Taking into consideration that TiO_2, Na_2O, V, Cr, La, Ce, Th, Rb, Y, Fe^{3+} and H_2O^+ (strong loadings) and Fe(total), Ba, Nb, SiO_2 and C_{org} (medium loadings) are all lithophile elements, together with the strong association of Al and K, it suggests that the positive phase of (F-1) represents the clay minerals present in the studied sediments. This conclusion is confirmed by the summary of correlation coefficients of the elements with mineral phases in the (W.B.) sediments

TABLE (5.2.1): Promax Factor loadings with K_{min} = 3 and correlation between the Promax Factors for K_{min} = 3 for 78 Bulk rock samples of the Oxford Clay and Kellaways Formations, Warlingham Borehole sediments.

COMPONENTS LOADED	(F-1)	(F-2)	(F-3)	(F-4)
Depth	0·32		0·30	0·52
SiO_2	0·28			0·81
TiO_2	0·82			
Al_2O_3	0·86			
Fe_2O_3(total)	0·33		0·59	-0·43
MgO				-0·72
CaO	-0·65			-0·49
Na_2O	0·565			0·40
K_2O	0·80			
S			0·91	
P_2O_5			0·64	
V	0·68			-0·49
Cr	0·42		0·34	
Mn			-0·27	-0·60
Ba	0·37			0·48
La	0·40			
Ce	0·525		0·30	
Th	0·73			
Pb		0·95		
As	-0·25	0·75		-0·25
Ga		0·925		
Zn		0·66		
Cu		0·87		
Ni		0·90		
Rb	0·93			
Sr				-0·57
Y	0·546		0·266	0·26
Zr				0·87
Nb	0·31			
Mo			0·88	
C_{org}	0·27		0·60	

/contd.over

TABLE (5.2.1) contd.

COMPONENTS LOADED	(F-1)	(F-2)	(F-3)	(F-4)
CO_2	-0·60			-0·55
H_2O^+	0·61		0·51	
Fe^{2+}			0·91	
Fe^{3+}	0·465		-0·48	-0·556
Per cent of total explanation	30·05	14·11	13·13	9·75

Cumulative explanation = 67·04

Correlations between Promax Factors for $K_{min} = 3$

F-1	1·0000			
F-2	0·1764	1·0000		
F-3	0·1670	0·0496	1·0000	
F-4	0·2353	-0·0740	0·1708	1·0000
	F-1	F-2	F-3	F-4

Note: Factor loadings $< 0·25$ were omitted.

and shown in Table (5.2.3B). The relationships of the loaded components with illite and chlorite shown in Table (5.2.3B) strongly supports that this phase represents clay minerals of detrital origin. The positive loading of depth in this factor reflects its sympathetic relationship with total clays and the antipathetic relationship with calcite, as shown in Appendix (3.2).

The antipathetically related phase of Factor (F-1) shows association of CaO, CO_2 and As, typical of carbonate minerals, representing the phase of calcite only,in the studied sediments. The loadings of CaO, CO_2 and As associated with Fe(total), Mg, Mn, Sr and ferric oxides in Factor (F-4) are shown in Table (5.2.1), and indicate their association in a second carbonates phase. The sediments at present under study contain two carbonate minerals, i.e. calcite and dolomite; both show higher abundances in the Upper Oxford Clay sediments. The factor scores of (F-1) in Table (5.2.2) indicate high negative values of factor scores on those samples which contain higher abundances of calcite, and similarly high positive values on the samples containing high abundances of total clays, and therefore confirming the identification of both phases of (F-1). The abundances of calcite and total clays are shown in Appendix (3.2).

The complete absence of elements such as Mg, Ni, Cu and Zr in the positive phase of Factor (F-1) in the (W.B.) sediments and their significant loadings in the positive phase (F-1) of the (W.K.B.) sediments is of special interest. It gives a vital clue as to the provenance of sediments of both the boreholes. According to KRAUSKOPF (1979, pp.544 & 545), the highest abundances of Si and Zr are in granite, and that of Mg, Ni and Cu in basalts, as compared with the shales. The same author also mentioned the highest concentration of Cr and V in basalt, while Ba and Ce occur more in granite as compared with the sedimentary rocks and shales. The stronger association of Si, Mg, Ni, Cu and Zr in Factor (F-1) of the (W.K.B.) sediments and their complete absence in the positive phase of (F-1) of the (W.B.) sediments (both representing clay minerals), strongly suggests that detritus of the (W.K.B.) sediments was derived from an area with a significant proportion of freshly weathered granitic and basaltic materials, while that of the (W.B.) sediments was dominated by recycled sedimentary material. The grain size of quartz in particular, and the sediments in general, of the (W.B.) is very fine as compared with the grain size of these components in the (W.K.B.) sediments, indicating the recycled nature of the detritus of the (W.B.) sediments. Illite in these sediments, being degraded, also supports a predominantly sedimentary provenance for these sediments. The elements such as Cr, Ba and V are loaded in the Factors (F-1) of both the boreholes, but their comparatively higher loadings are shown in Factor (F-1) of the (W.K.B.) sediments, which also supports the idea of the presence of igneous components in the detritus of the (W.K.B.) sediments.

The components such as depth, CaO, Na_2O, V, Cr, Ba, Ce, As, Y, C_{org}, CO_2, H_2O^+ and Fe^{3+} show loadings in other factors, in addition to Factor (F-1). Fe^{3+} showed the strongest loading in Factor (F-4); its loading in Factor (F-1) indicates the lattice-held iron present in clay minerals, particularly chlorite and mixed-layer (illite-montmorillonite). The leaching study of representative bulk rock samples of the (W.B.) sediments, by the acid reducing agents (CHESTER and HUGHES, 1967) indicated that most of the elements mentioned above are associated with either soluble or non-soluble (lithogenous) fractions (see Chapter Six). Therefore, it follows that these elements are related to phases such as carbonates, sulphides, C_{org}, ferric oxides and resistate minerals, in addition to clay minerals.

The components loaded antipathetically in Factor (F-1) include CaO, CO_2 and As; these components also show loadings of a varying nature in other factors, as shown in Table (5.2.1). As, shows its strongest loading in Factor (F-2) and a very low loading in Factor (F-4), indicating its preferred association in Factor (F-2). Similarly, CaO, CO_2 showed loadings in the negative phase of (F-4), indicating their participation with the phases of (F-4). The factor (F-1) shows in Table (5.2.1) positive correlations of varying levels of significance with the remaining factors. The correlation with (F-4) being strongest ($r = +0{\cdot}23$) suggests very close association of the detrital clays with the phases represented by positive loadings of (F-4). The levels of significance of loadings of CaO, CO_2 and As, shown in Table (5.2.3A) explain the geochemical role of the respective elements in the respective factors.

As, showed its strongest loading in Factor (F-2), indicating its preferred association with rare metals. The loadings of As in

TABLE (5.2.2): Scores on Promax Factors

F-1	F-2	F-3	F-4
-0.712	0.202	-0.294	-1.628
-0.494	0.079	-0.301	-1.490
-2.919	-0.541	-0.681	-1.725
-2.003	-0.442	-0.680	-1.292
-2.445	-0.385	-0.554	-1.093
-2.054	-0.496	-0.589	-1.199
-0.552	-0.193	-0.161	-0.550
-0.683	-0.243	-0.049	-0.342
-1.500	-0.304	-0.392	-1.004
0.335	0.193	-0.377	-0.058
-1.355	0.199	0.939	-0.952
-0.961	-0.375	-0.562	-0.600
-1.216	-0.417	-0.719	-0.257
-1.297	-0.433	-0.524	-0.430
-0.014	-0.263	-0.637	0.149
0.272	0.048	-0.442	-0.089
0.326	-0.064	-0.546	-0.270
-0.733	-0.242	-0.732	-0.538
0.286	0.178	-0.638	-1.072
0.643	0.021	-0.660	-0.752
-0.053	-0.059	-0.440	-0.244
0.664	0.010	-0.502	-0.292
0.717	0.231	-0.686	-0.614
0.644	0.052	-0.138	-0.170
0.912	0.109	-0.853	-0.335
0.183	0.046	-0.867	-0.862
0.633	0.054	-0.578	-0.637
0.305	-0.028	-0.617	-0.241
0.106	8.380	-0.739	-0.104
-0.081	-0.266	-0.686	-0.181
0.288	-0.035	-0.723	0.060
-1.813	-0.229	-0.486	-0.938
-2.188	-0.381	-0.773	-0.803
-0.263	0.037	-0.307	-0.616
-0.755	-0.370	-0.496	0.047

/contd.over

TABLE (5.2.2) contd.

F-1	F-2	F-3	F-4
0·086	-0·166	-0·590	-0·178
0·113	-0·214	-0·639	0·195
0·414	0·445	1·478	-0·414
0·348	-0·157	0.005	0·596
-0·524	-0·158	0.104	-0·966
-0·821	-0·236	-0·179	-0·619
0·195	0·043	-0·236	-0·066
0·273	-0·138	-0·120	-0·201
0·913	0·205	-0·060	0·024
0·685	-0·041	-0·144	0·011
0·473	-0·067	0·373	0·046
0·405	-0·267	-0·140	-0·010
0·538	0·043	0·468	-0·155
0·728	0·041	0·504	-0·214
0·617	-0·008	0·337	-0·190
0·167	-0·170	0·074	0·178
-0·485	-0·444	0·149	0·407
-0·331	-0·316	0·061	-0·097
0·154	-0·097	0·186	-0·055
0·041	-0·099	0·029	0·241
0·643	-0·179	0·070	0·541
0·309	-0·031	0·238	0·367
0·600	-0·076	0·493	0·226
0·704	-0·056	0.310	0.039
0·822	-0·049	0·257	0·261
1·202	0·201	0·189	0·603
0·955	0·116	0·437	0.160
0·976	0·095	0·246	-0·024
0·737	0·237	1.080	0.009
1·121	-0·010	0·299	0.076
0·266	0·285	2·690	0.143
2·271	0·355	0·707	0.300
1·454	-0·132	0·273	1·084
0·626	-0·247	0·814	1·386
0·706	-0·329	0·401	1·072

/contd.over

TABLE (5.2.2) contd.

F-1	F-2	F-3	F-4
-0·328	0·407	6·666	0·922
2·389	0·371	0·903	0·611
-0·157	-0·731	-0·180	3·506
-1·838	-0·915	-0·825	1·500
0·161	0·027	0·091	0·588
-0·579	-0·881	-0·712	3·882
-0·006	-0·605	0·135	3·421
0·757	-0·128	1·250	1·916

Factors (F-1 and F-4) are very low, and suggest a very weak association with the present phases. The relationship of As with carbonates seems to be of similar nature, as mentioned by CHOWDHURY (1980) in the 'Upper Calcareous Grit' group of the Corallian sediments. As, in the (W.B.) sediments, shows its maximum concentration in the (U.O.C.) samples associated with the highest abundances of calcite, Fe_2O_3(total), Mn and Fe^{3+}, and the lowest amounts of S, C_{org} and pyrite, as shown in Tables (4.2A & 4.2B). The association of As with calcite and Fe-Mn oxides/hydroxides is a well established fact (GOLDSCHMIDT, 1954; CALVERT, 1976). This relationship has been studied in detail in the (W.K.B.) sediments. A small amount of As may be contributed by plants and animals, such as fishes, molluscs, crustaceans and plankton, as suggested by RANKAMA and SAHAMA (1950). The same authors mentioned that concentration of As in sediments takes place in iron-rich oxidate sediments. The sediments of the (U.O.C.), as already mentioned, contain the highest abundance of As associated with the highest concentration of Fe^{3+} and calcite, suggesting the oxidizing nature of these sediments.

It may be concluded that Factor (F-1) of the (W.B.) sediments represents the phase of detrital clay minerals, e.g. illite, chlorite, etc. antipathetically related to calcite, a carbonate of first generation. The antipathetic relationship of clays and calcite is shown by Figure (5.2.1a & 5.2.1b). The strong positive correlation between the factor scores of (F-1) and abundances of total clays ($r = +0{\cdot}94$) is shown in Figure (5.2.1a), which is highly significant at the 0·01% level. Similarly a strong negative correlation of factor scores with calcite ($r = -0{\cdot}86$), significant at the 0·01% level, is shown in Figure (5.2.1b). The factor scores of (F-1) and abundances of total clays and calcite are tabulated in Table (5.2.2) and Appendix (3.2) respectively.

Factor (F-2):

This factor explains 14·11% of the total variance, and is the second important factor in the present study. This is the only factor that is not bimodal. It shows very strong (positive) loadings of Pb, Ga, Cu, Zn, Ni and As. From this association only As shows loadings in other factors, indicating its multiple geochemical behaviour. The very high loadings of the remaining metals in this

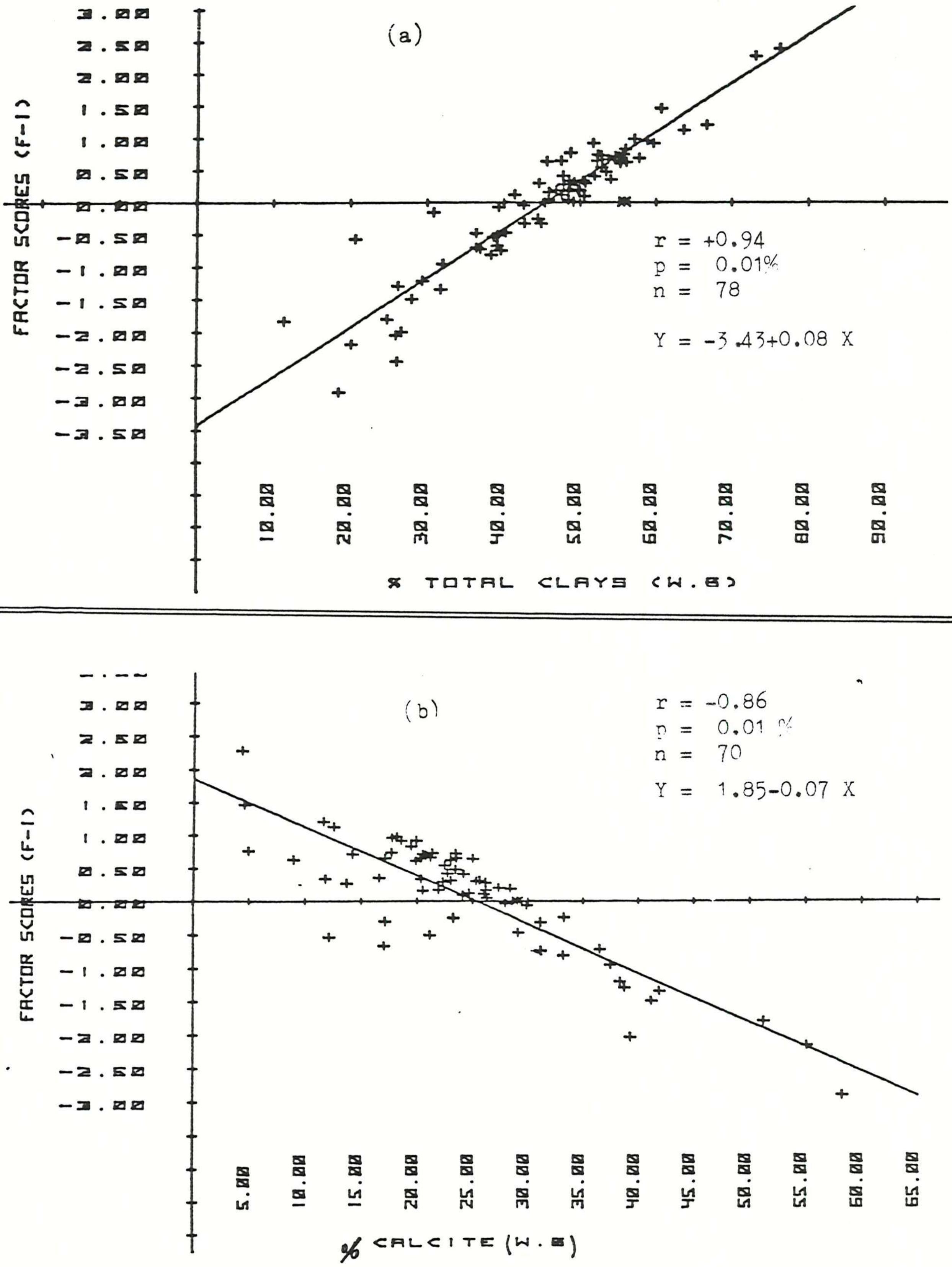

(a)
FACTOR SCORES (F-1)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
% TOTAL CLAYS (W.B)
r = +0.94
p = 0.01%
n = 78
Y = -3.43+0.08 X
(b)
r = -0.86
p = 0.01 %
n = 70
Y = 1.85-0.07 X
FACTOR SCORES (F-1)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
% CALCITE (W.B)

FIG.(5.2.1)

factor may be the result of many similar characters of these metals, such as ionic radii and electro-negativity, as shown in KRAUSKOPF (1979, pp.547-48).

All the metals loaded in Factor (F-2) show their maximum concentrations in the sediments of the (U.O.C.) in association with the highest abundances of carbonates, illite, mixed-layer (illite-montmorillonite) and amongst elements Fe^{3+} and Mn, Tables (4.2A & 4.2B), suggesting a very close relationship between these phases. The association of Factor (F-2) may be explained in various ways. The best approach seems to be according to the suggestions of KRAUSKOPF (1956), which is summarized as follows:

a) The concentration of Pb, Ga, Cu, Zn, Ni and As in the (U.O.C.) with the highest concentration of carbonate minerals may be due to the formation of relatively insoluble compounds which are formed by some of these metals in association with abundantly available anions such as Cl^{-}, SO_4^{--} and CO_3^{--} which are present in the ordinary oxygenated sea-water.

b) These metals may be enriched as a result of the concentration of organisms which are known to contain many of these metals. It is a well-established fact that abundant fauna flourished in the environments under which these sediments were deposited.

c) They may occur as colloidal particles.

d) They may be adsorbed on other colloidal particles. According to KRAUSKOPF (1956), ferric oxide and manganese dioxide adsorb great amounts of these metals; both are present in significant amounts in the studied sediments and show enriched values in the (U.O.C.) sediments.

It is very likely that the element association of Factor (F-2) is due to a combination of several effects described above. Table (5.2.3B) shows the summary of the correlation coefficients between the elements and mineral phases in the (W.B.) sediments. This Table indicates a positive correlation between Cu, Ni and total clays, significant at the 5% level, and that of As with total carbonates, also significant at the 5% level. There exists no correlation between the metals loaded in Factor (F-2) and pyrite and C_{org}, with the exception of a negative correlation shown by As with C_{org}. These

<u>TABLE (5.2.3A)</u>: Summary showing the levels of significance of the loaded components in the respective factors in the (W.B.) sediments.

Confidence levels		FACTOR (F-1)	FACTOR (F-2)	FACTOR (F-3)	FACTOR (F-4)
+ve	5%	C_{org}	NONE	Y	Y
	1%	Depth, SiO_2, TiO_2, Al_2O_3, Fe_2O_{3T}, Na_2O, K_2O, V, Cr, Ba, La, Ce, Th, Rb, Y, Nb, H_2O^+, Fe^{3+}	Pb, As, Ga, Zr, Cu, Ni	Depth, Fe_2O_{3T}, P_2O_5, S, Cr, Ce, Mo, C_{org}, H_2O^+ Fe^{2+}	Depth, SiO_2, Na_2O, Ba, Zr
-ve	1%	CaO, CO_2	NONE	Fe^{3+}	Fe_2O_{3T}, MgO, CaO, V, Mn, Sr, CO_2, Fe^{3+}
	5%	As	NONE	Mn	As
Percentage variance		30·05	14·11	13·13	9·75

Note: i) Cumulative explanation = 67·04%

ii) The values of factor loadings represent correlation coefficient for the 5% to 1% levels of confidence. For 76 degrees of freedom these are:

5% = $\geqslant$ 0·22
1% = $\geqslant$ 0·28

iii) Fe_2O_{3T} = Total iron.

TABLE (5.2.3B): Correlation Coefficient for 5% and 1% levels of significance shown by the mineral phases and chemical elements of 78 samples of the Warlingham Borehole sediments.

Confidence Levels		Total Clays	Pyrite	Carbonates(T)	C_{org}	Quartz	Fe-oxides	Calcite
+ve	5%	SiO_2, Cu, Ni Nb, Fe^{3+}		As	TiO_2, Ba, Ce, KAOL	Depth	Fe_2O_3(total), Rb, CHLR	Fe_2O_3(total)
	1%	Depth, TiO_2, Al_2O_3, Fe_2O_3(total), Na_2O, K_2O, V, Cr, Ba, La, Ce, Th, Rb, Y, C_{org}, H_2O^+, ILL, CHLR	Depth, Fe_2O_3 (total), S, P_2O_5, Cr, Ce, Mo, C_{org}, H_2O^+, Fe^{2+}	MgO, CaO, Mn, Sr, CO_2, LOI, M.L., DOL, CAL	Depth, Al_2O_3, S, P_2O_5, Cr, La, Th, Cu, Rb, Y, Mo, H_2O^+, Fe^{2+}, Pyt, TClay	SiO_2, Na_2O Ba, Zr, KAOL	MgO, K_2O, V Mn, ILL	CaO, Mn, Sr, CO_2, LOI (T)carbonates
-ve	1%	CaO, Mn, CO_2, LOI, M.L, QTZ, DOL, CAL	Mn, CO_2, Fe^{3+}, CAL	Depth, SiO_2, TiO_2, Al_2O_3, Na_2O, K_2O, S, P_2O_5, Cr, Ba, La, Ce, Th, Rb, Y, Zr, Nb, C_{org}, H_2O^+, Fe^{2+}, KAOL, CHLR, QTZ, TClay	CaO, Mn, CO_2, Fe^{3+}, T.DOL+CAL	Fe_2O_3(total) MgO, CaO, V, Mn, Rb, Sr, CO_2, H_2O^+, LOI, ILL, M.L, CAL, TClay, T.DOL+CAL	Depth, S, P_2O_5, Ze, Mo, C_{org}, Fe^{2+}, KAOL	Depth, SiO_2 TiO_2, Al_2O_3, Na_2O, K_2O, V, Cr, Ba, La, Ce, Th, Rb, Y, Zr, Nb, C_{org}, H_2O^+, FeO, KAOL, QTZ, TClay
	5%	As	MgO, CaO, DOL+CAL	Pyt	As, M.L, DOL, CAL	Al_2O_3, Fe^{3+}, DOL	SiO_2, QTZ, Pyt.	S, Pyt.

Number of samples = 78.

For 76 degrees of freedom the levels of significance are: 5% level $\geq 0{\cdot}22$

1% level $\geq 0{\cdot}28$

TABLE (5.2.3B) contd.

Note: i) carbonates(T) = total carbonates
ii) ILL = illite
iii) CHLR = chlorite
iv) DOL = dolomite
v) CAL = calcite
vi) TClay = total clay
vii) QTZ = quartz
viii) M.L = mixed layer
ix) Pyt = pyrite
x) KAOL = kaolinite
xi) LOI = loss on ignition

facts suggest that the concentration of these metals in the sediments of the (U.O.C.) was facilitated by an oxygenated environment.

KRAUSKOPF (1956) carried out experiments to observe the "adsorbability" of rare metals on various phases such as clays, apatite, ferric oxide, manganese dioxide and peat-moss; a summary of KRAUSKOPF's results is reproduced in Table (5.2.4). This table shows that four metals (i.e. Zn, Cu, Pb and Ni) of Factor (F-2) are present. The phases such as clays, ferric oxide, manganese dioxide and sedimentary apatite are also common in the sediments under study. Taking into consideration the results of the adsorption study of KRAUSKOPF (op.cit.), reproduced in Table (5.2.4), and considering the associations of Factor (F-2), it seems reasonable to designate this factor as an 'adsorption' factor.

The 'inter-factor' correlations given in Table (5.2.1) help in understanding the associations of Factor (F-2). This Table shows only strong positive correlation of Factor (F-2) with Factor (F-1), and a negative correlation of a very weak nature with Factor (F-4). The strong positive correlation of (F-2) with (F-1) explains the availability of the phases for the adsorption of the metals, particularly Pb - Zn - Cu, as shown in Table (5.2.4). Factor (F-1) has been explained as a detrital clays factor. The correlations of (F-2) with (F-3) and (F-4) are very low and are probably of no significance.

The association of Ni is due to the strong adsorption of Ni onto hydrated MnO_2 (GOLDBERG, 1954) and hydrated Fe_2O_3. The association of Ga^{3+} (0·70Å) in Factor (F-2) may be explained due to its probable substitution for Zn^{2+} (0·83Å) in sphelerite, which may be present in these sediments in minor amounts, as suggested by KRAUSKOPF (1979). Taking into consideration the close similarity of the ionic radii of Ga^{3+} (0·70Å), Ni^{2+} (0·77Å) and Cu^{2+} (0·81Å), it is suggested that some Ga in the Factor (F-2) might have substituted for any of these elements in their compounds present in these sediments.

Elements such as As, Ga and Pb show their higher concentrations in shale as compared to granite and basalt (KRAUSKOPF, 1979). These elements have shown the highest values of the loadings in Factor (F-2) and therefore suggest a sedimentary origin. It indicates that probably elements As, Ga and Pb reached the site of deposition adsorbed onto the surfaces of clay minerals and Fe-Mn oxides/hydroxides, and the

TABLE (5.2.4): Summary of the Results of Adsorption Experiments, carried out by KRAUSKOPF (1956)

Metal	Hydrated Fe_2O_3	Hydrated MnO_2	Apatite	Clay	Plankton	Peat-moss
Zn	95		86	99	40 (48)	99
Cu	96	96	77	94	54	
Pb	86		96	>96		>96
Ni	33 ($\underline{94}$)	99	8 ($\underline{69}$)	10	8	
Co	35 ($\underline{91}$)	93 (94)	15 ($\underline{82}$)	18	8	
Hg	50 (> 95)		< $\underline{5}$ ($\underline{25}$)	96	98	99
Ag	$\underline{22}$ ($\underline{20}$)	(8)	23 ($\underline{6}$)	20	49 (96)	54
Cr	$\underline{10}$ ($\underline{49}$)	94	12	8	10	
Mo	25 ($\underline{56}$)	50 (74?)	10	35	15	53?
W	80	99	$\underline{5}$		c. 8	
V^{iv}	> 96		$\underline{19}$	27	16	
V^{v}	95	23 (40)	17	33	< 3	

Concentration of adsorbate: 0·6-2·5 p.p.m. for first seven elements, 2-10 p.p.m. for last five. A second number in parentheses is the per cent adsorption for lower concentrations of adsorbate, in the range 0·1-0·7 p.p.m.

Concentrations of adsorbent: for Fe_2O_3,MnO_2, and apatite, 0·02-0·1 gram/litre, except for underlined figures, which have 0·3-0·7 gram/litre; for clay and peat-moss, 7-20 gram/litre; for plankton, not measured.

All values are given as per cent of metal adsorbed. Figures are the same as figures marked with an asterisk in Table 7.

Temperature 18^o-23^oC, pH 7·7-8·2.

(Note: Table 5.2.4 is reproduced from KRAUSKOPF, 1956) remaining elements, such as Cu, Ni and Zn, were present in solution in sea-water, to join the others, possibly in the form of complex compounds of unstable nature, suggested by the leaching study results by acid-reducing agents, shown in the summary given in Table (5.2.6a). This Table shows that some of the samples contain the entire amounts of Pb, Zn, Cu and Ni in the soluble fractions. It implies that in the respective samples either these metals were present as unstable compounds or were associated with the soluble fraction. KRAUSKOPF (1956) quoted the data of BJERRUM (1950), which indicates that a solution of 0·5M Cl^- (like sea-water) should have mostly Cu^{++}, about one-third as much $CuCl^+$, one thirtieth as much $CuCl_2$ and negligible quantities of the negative ions. KRAUSKOPF (op.cit.) mentioned that it is certain that dissolved Cu will be in the form of positive ions and the most abundant ions will be Cu^{++} and $CuCl^+$. Similarly, zinc is present in sea-water as Zn^{++} and $ZnCl^+$ (from the data of SILLEN & LILJEQVIST, 1944). Colloidal manganese dioxide is commonly thought to carry a negative charge and hence will attract cations, and colloidal iron oxide normally carries a positive charge and will therefore attract anions.

It may be summarized that Factor (F-2) represents the adsorptive phase in the present sediments. The metals showing association in this Factor are strongly adsorbed by the phases of clays, Fe^{3+} and Mn oxides/hydroxides present in these sediments. Some of the metals are in an easily removable form, as proved by the leaching study, which shows that the entire amount of Pb is present in the soluble fraction of all the samples.

Factor (F-3):

This factor explains 13·13% of the total variance. It shows strong positive loadings of Fe(total), S, P, Mo, C_{org}, Fe^{2+} and H_2O^+, and moderate to low loadings of Cr, Ce, Y and depth. The negative phase of (F-3) shows a moderate loading of Fe^{3+} and a low loading of Mn. Some of the components loaded in this factor, such as Fe(total), Y, Mn, C_{org}, Fe^{3+} and depth, show loadings in other factors as well, indicating their more complex geochemical roles. There exists a strong sympathetic relationship between the positive factor scores and the abundances of components present in the samples of the (L.O.C.)

and (K.F.) sediments, which explains the association of depth in this factor. This relationship suggests that the positive phase of Factor (F-3) represents the population of the (L.O.C.) and (K.F.), which contains the highest abundances of sulphur, Fe^{2+}, pyrite and C_{org}, as shown in Tables (4.2A & 4.2B).

Factor (F-3) of the (W.B.) sediments shows similar strong loadings of Fe(total), S, P, Mo, C_{org}, Fe^{2+} and H_2O^+, as observed in the study of the factor analysis of the (W.K.B.) sediments, where Factor (F-2) showed these loadings and was identified as the 'sulphide + C_{org} + phosphate' factor showing an antipathetic relationship with the resistate phases. Factor (F-3) of the (W.B.) sediments does not show the association of the metals Pb, Zn, Cu and Ni in its positive phase; these metals being present in Factor (F-2), as described above. The absence of these metals in Factor (F-3) of the (W.B.) sediments suggests that at the time of formation of pyrite in these sediments, these metals were not available in solution, as was possible in the case of the (W.K.B.) sediments. Factor (F-2) of the (W.B.) sediments shows the strongest loadings of the metals Pb, Cu, Zn, Ni and Ga, and has been interpreted as the 'adsorption' factor. It suggests that these metals were strongly adsorbed onto Fe-Mn oxides/hydroxides, or on clay phases, and were thus not available for co-precipitation with sulphides. The absence of these metals in this factor may also be related to their preferred association with the phases of the (U.O.C.), which is indicated by their highest concentration in those sediments. The components loaded in the positive phase of (F-3) may be grouped as follows:

1. Fe(total), S, Mo, Cr, Fe^{2+} and depth.
2. C_{org}, H_2O^+ and depth.
3. P, Ce, Y.

The association of elements of Group One is typically of a chalcophile nature (GOLDSCHMIDT, 1954). This association was also observed in the (W.K.B.) sediments. These elements possess a strong affinity for sulphur. The sediments of the (W.B.), like those of the (W.K.B.), also contain significantly high abundances of sulphur and pyrite in general. However, the sediments of the (K.F.) show the highest concentrations of sulphur, Fe^{2+}, Mo and pyrite (Tables 4.2A

& 4.2B). The association of the positive phase of this factor indicates the occurrence of the reducing (anoxic) conditions, while the negative phase (Fe^{3+} & Mn) exhibits the oxidizing (oxic) conditions prevailing in these sediments at the time of deposition. The occurrence of reducing (anoxic) and oxidizing (oxic) conditions in the sediments of the Oxford Clay is a well established fact, as described by HUDSON (1978), HUDSON and PALFRAMAN (1969) and DUFF (1975). A detailed account of the oxic and anoxic conditions of the Oxford Clay has been given earlier in the study of the (W.K.B.) sediments.

Taking into consideration the nature of components loaded in Factor (F-3), it is suggested that this factor is called the 'Redox' factor, representing the phases of sulphides + C_{org} + phosphates, showing an antipathetic relationship with the phases of Fe-Mn oxides/hydroxides. The correlation coefficients of minerals and elements given in Table (5.2.3B) show a strong positive correlation of all the components, with the exception of Y, with pyrite, significant at the 1% level. The same Table shows strong positive correlations of all the components of the positive phase of (F-3) with C_{org}, significant at the 1% level, with the exception of Ce, which showed correlation of a lesser degree with C_{org}. Y and Ce showed much stronger positive correlation with P_2O_5 ($r = +0{\cdot}66$, $r = +0{\cdot}46$), indicating their preferred association with phosphates rather than C_{org} and pyrite. Phosphorus in the (W.B.) sediments did not show its association with carbonate phases as it does in the case of the (W.K.B.) sediments. This suggests that in these sediments only one generation of phosphate exists. Phosphorus showed much stronger positive correlations with depth, S, Ce, Y, C_{org}, La, Fe^{2+} and pyrite, all being significant at the 0·01% level. It showed a weak positive correlation with Fe(total) and Cu, significant at the 5% level, indicating its stronger relationship with sulphur, C_{org} and 'REE'. The association of P_2O_5 with sulphur and C_{org} may be due to genetic relationship; organic organisms contribute sulphur and phosphorus both to the organic matter and the sediments.

Taking into consideration the trends of correlations described above, it may be suggested that the major part of the population of the positive phase of (F-3) is controlled by sulphides (pyrite) and C_{org}. The variance of Ce and Y, however, is controlled by a sedimentary precipitated phosphate (hydroxy apatite/collophane?). The association of Y and Ce with phosphates is well known, as mentioned by CALVERT (1976) i.e. that 'REE' (in the present case Ce and Y) are usually concentrated with phosphorus and iron oxide coats on the clay minerals. RANKAMA and SAHAMA (1950) also mentioned that apatite is the only mineral which may contain notable amounts of Y and lanthanides. According to KOSTOV (1968, p.444) and HURLBUT, Jr. and KLEIN (1977), monazite is the phosphate which may contain Ce, Y, La and Th in it. The present association of Ce - P - Y strongly suggests the presence of monazite in these sediments which, being in minor amount or cryptocrystalline, escaped detection by X.R.D. Monazite is an accessory mineral in acidic rocks. It is also found as rolled grains in sands, because of its resistance to chemical weathering attack, and also its high specific gravity. Thus monazite in sediments may be present in association with other heavy minerals, such as magnetite, ilmenite, rutile and zircon. The sediments of the (K.F.) of the (W.B.) contain the highest abundances of Zr, SiO_2, P_2O_5, Ce, Y and quartz, which are shown in Tables (4.2A & 4.2B) respectively. These sediments are sandy also; therefore the presence of monazite in them is not unexpected. The interfactor correlations shown in Table (5.2.1) display a much stronger positive correlation of Factor (F-3) with Factor (F-4) ($r = +0{\cdot}1708$), as compared with the positive correlation of (F-3) with Factor (F-1) ($r = +0{\cdot}1670$), indicating a preferred association of monazite with the highly loaded resistate components, i.e. Si and Zr in Factor (F-4).

The association of Cr in the positive phase of (F-3) may be explained due to either the well-known strong relationship of Cr with C_{org}, suggested by many workers including WEDEPOHL (1964) and GAD et al. (1969), or its association with sulphide phases, particularly with pyrite, as suggested by NICHOLLS and LORING (1960) and GAD et al. (op.cit.). The association of Cr in this factor may be related to the reducing conditions that prevailed in these sediments just after their burial. Many workers, including KRAUSKOPF (1956), CALVERT (1976) and BONATTI et al. (1971), stated that under reducing conditions the Cr^{4+} reduces to Cr^{2+} and precipitates as insoluble Cr-hydroxides. It is, therefore, possible that such Cr-hydroxides in minor amounts may be present in these sediments.

The association in the negative phase of this factor shows a much stronger loading of Fe^{3+}, as compared with the loading of Mn.

Further, Fe^{3+} shows a higher loading value in the negative phase of Factor (F-4). The negative phase of Factor (F-3), being antipathetically related to the reducing conditions phases, represents the oxidation (oxic) phase that existed in the studied sediments. This phase represents the samples of the (U.O.C.) of the (W.B.) sediments, which showed the highest concentrations of Fe^{3+}, Mn and carbonate minerals, as shown in Tables (4.2A & 4.2B) respectively. This relationship is further confirmed by the negative factor scores of Factor (F-3) exhibited by the samples of the (U.O.C.) of the (W.B.) sediments. It means that the sediments of the (U.O.C.) of the (W.B.) enjoyed well oxygenated environments.

The Fe^{3+} and Mn association may be explained according to RANKAMA and SAHAMA's (1950) suggestions, described as follows:

i) Hydroxides of ferric iron and manganese form the bulk of the oxidate sediments. These hydroxides are precipitated in lakes, shallow bays and even on the bottom of the open sea.

ii) Natural waters contain iron in many forms, including ferrous bicarbonate $Fe(HCO_3)_2$, ferric fluoride FeF_3, colloidal ferric hydroxides and ferric phosphates. Ferrous bicarbonate is readily soluble but, in the presence of molecular oxygen, it is quickly oxidized and, as a result of this, ferric hydroxide is precipitated.

iii) According to CORRENS (1941), iron and manganese both promote the growth of diatoms, and Mn replaces Ca diadochically in the calcite structure of the shell.

iv) According to RANKAMA and SAHAMA (1950) the most favourable conditions for the non-reversible precipitation of Mn include oxidizing environments (relatively high redox potential), and the presence of small quantities of solid calcium carbonate (relatively low pH).

v) According to the same authors, alkaline solutions and oxidizing conditions are most favourable for the precipitation of iron as ferric hydroxides. Like manganese, iron also preferably precipitated in oxidizing surroundings in the presence of calcareous material.

vi) According to RANKAMA and SAHAMA (1950), iron and manganese are completely separated from each other in oxidate sediments due to the fact that manganese has less affinity for oxygen as compared to iron. Therefore, iron is readily oxidized to the ferric state and subsequently precipitates as ferric hydroxides, whereas manganese remains in solution until the whole bulk of the iron is precipitated.

vii) Ferric hydroxide $Fe(OH)_3$ is weakly basic, whereas manganic hydroxide $Mn(OH)_4$ is weakly acidic in nature; therefore the $Fe(OH)_3$ hydrosol is positively charged and $Mn(OH)_4$ hydrosol is negatively charged. Due to this basic difference in the properties of colloidal ferric and manganic hydroxides, the formation of iron-poor or iron-free manganese deposits or manganese-poor/manganese-free iron deposits is facilitated. The strong positive correlation between Factors (F-3) and (F-4) explains the occurrence of the oxidate sediments phase of the (W.B.) sediments, represented by the negative loadings of the Factor (F-3).

It may be summarized that Factor (F-3) in the (W.B.) sediments represents the 'Redox' conditions that existed in them during deposition and immediately post-burial. These sediments contain a sulphide phase mainly represented by pyrite. A very strong positive correlation ($r = +0{\cdot}92$; significant at the 0·01% level) between the combined abundances of pyrite + C_{org} (shown in the Appendix (3.2) and the factor scores of Factor (F-3) (tabulated in Table 5.2.2) is shown in Figure (5.2.2a). The majority of the C_{org} in these sediments seems to be marine in origin; a minor amount of terrestrial C_{org} is also present, which is indicated by its very low loading in Factor (F-1), where it is mainly associated with the detrital clays. These sediments contain sedimentary phosphate of a first generation. The reducing phase of this factor shows an antipathetic relationship with the oxidate phase mainly represented by the ferric oxides/hydroxides. A minor amount of insoluble manganese dioxide may be present in association with ferric oxides/hydroxides. Figure (5.2.2b) shows the values of Fe^{3+} plotted against the values of factor scores of (F-3), and demonstrates a strong negative correlation ($r = -0{\cdot}424$; significant at the 0·01% level) between the two variables.

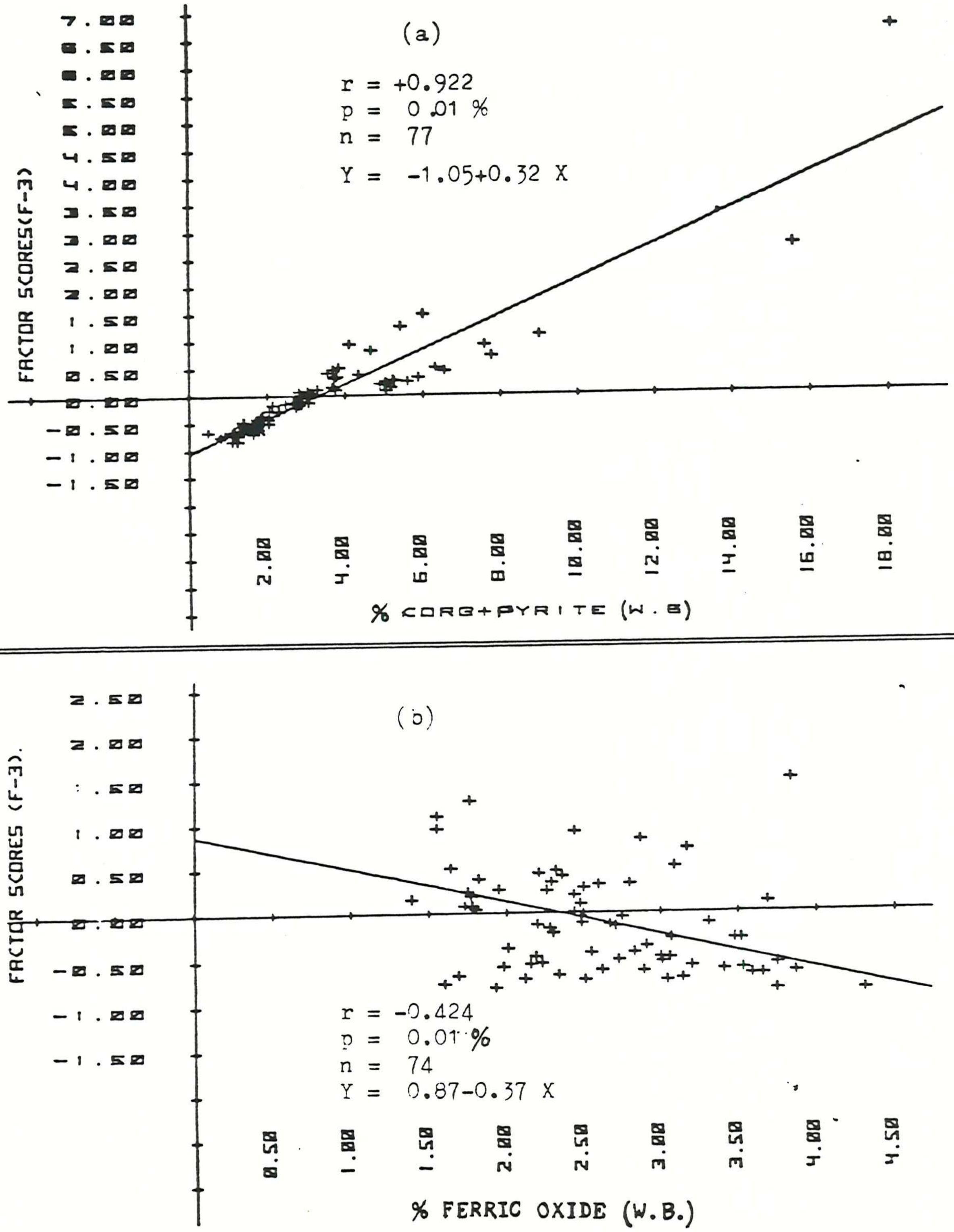

(a)
r = +0.922
p = 0.01 %
n = 77
Y = -1.05+0.32 X
FACTOR SCORES(F-3)
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
% CORG+PYRITE (W.B)
(b)
FACTOR SCORES (F-3)
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
r = -0.424
p = 0.01 %
n = 74
Y = 0.87-0.37 X
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
% FERRIC OXIDE (W.B.)

FIG.(5.2.2)

Factor (F-4):

This factor explains 7·08% of the total variance. It shows very strong positive loadings of typical detrital elements, i.e. Zr and Si, associated with moderate to low loadings of depth, Ba, Na and Y. The negative phase of this factor shows very strong loadings on the elements, i.e. Mg, Mn, Sr, Fe^{3+} and CO_2 and moderate to low loadings on Ca, V, Fe(total) and As. Elements such as Na, Ba and Y show comparatively higher loading values in Factor (F-1), which represents the detrital clays. Zr, Sr and Mg are the only elements which do not show loadings in any factor other than Factor (F-4), thus indicating their independent nature. Fe(total) shows loadings in Factors (F-1, F-3 and F-4), with the strongest loading in Factor (F-3), indicating its dominant association with the sulphide phases, mainly represented by pyrite. The negative loading of Fe(total) in Factor (F-4) indicates its subordinate nature of participation in the phases represented here. Other elements such as Ca, V, As and CO_2 loaded in the negative phase of Factor (F-4) also indicate their subordinate type of participation in this Factor. Elements Mg and Sr show unique loadings in this negative phase.

Factor (F-4) represents, through its positive phase, the population of the (K.F.) sediments, which contain the highest abundances of elements such as Si, Na, Ba, Zr, Y and the minerals quartz and kaolinite. This relationship is confirmed by the strong sympathetic trends between the high positive values of the factor scores of (F-4) shown by the samples of the (K.F.). Similarly the negative phase of Factor (F-4) represents the population of the (U.O.C. and M.O.C.) sediments, which contain the higher abundances of Ca, Mg, Fe(total), Mn, V, As, Fe^{3+} and calcite, dolomite and mixed layer (illite-montmorillonite) clay minerals (Tables 4.2A & 4.2B). Like the positive phase, the relationship between the negative phase and the population of the (U.O.C. and M.O.C.) was confirmed by similar sympathetic relationships.

The positive phase shows the strongest loadings of Zr and Si associated with moderate loadings of depth, Ba, Na and a low loading of Y. The association of Zr with Si, coupled with Nb and Ce, was studied in Factor (F-2) of the (W.K.B.) sediments, which showed an antipathetic relationship with the authigenically produced phases, comprising sulphides, C_{org} and precipitated phosphate, and was interpreted as the phase of detrital/resistate minerals. Factor (F-4) of the present sediments also shows similar antipathetic relationships between detrital elements and non-detrital elements. HIRST (1974), in the geochemical studies of eleven Black Sea core sediments, reported a similar association, which he interpreted as the association of silicates opposed by carbonates. Taking into consideration the strong sympathetic relationships between the factor scores of (F-4) and the abundances of the detrital components such as Zr, Si, Nb, quartz and kaolinite in the respective samples of the (K.F.), and a strong similarity of Factor (F-4) with Factor (F-2) of the (W.K.B.) sediments, this factor is called a 'resistates' factor showing an antipathetic relationship with the authigenically/diagenetically produced phases.

The association in the positive phase of Factor (F-4) is self-explanatory. The strong loading on Si reflects the association of exceptionally high abundance of quartz exhibitied by the (K.F.) sediments, as is shown in Table (4.2B). Zr showed its strongest loading in this phase only, suggesting the occurrence of zircon in minor amounts. A detailed account regarding the possible occurrence of zircon is given in Chapter Four, and also in Factor (F-2) of the (W.K.B.) sediments. A moderate loading on Na suggests the presence of albite feldspar in the studied sediments. The presence of Na-bearing and K-bearing feldspars in the sediments of the Oxford Clay is reported by JACKSON and FOOKES (1974), from various localities in central and southern England, including the Dorset area. The present sediments indicated the presence of feldspars, particularly in the samples from the (K.F.), in minor amounts, by weak peaks for feldspar on the X.R.D. diffractograms. COSGROVE (1973) mentioned the association of Na with Zr in the study of Red bed mudstones and explained it as being due to the presence of albite feldspar and zircon. As mentioned earlier, sediments of the (K.F.) contain minor amounts of both feldspars, i.e. albite and K-feldspar; therefore substitution of Ba^{2+} (1·44Å) for K^{+} (1·46Å), due to close ionic radii, might have taken place in these sediments. The association of Ba in this phase may also be explained, taking into consideration the strong positive correlation of Ba with kaolinite (r = +0·62), significant at the 0·01% level, which is also shown in Appendix (4.2C). SULAIMAN (1972) found correlation between Ba and kaolinite in the study of Namurian argillite and explained that this association is due to possible precipitation of $BaSO_4$(Barite). A detailed account regarding the precipitation of

$BaSO_4$(Barite) in the (W.B.) sediments is given in Chapter Four. Barite crystals in the concretions found in the Oxford Clay have been reported by HUDSON (1978). He stated that precipitation of barite in concretions was the result of the mixing of anoxic pore-waters with sulphate-bearing ground-waters. Low loading of Y shows association of Y with Zr, as already explained in the study of 'REE' in Chapter Four.

The components loaded in the negative phase of Factor (F-4) may be grouped as follows:

1. Mg, Ca, CO_2, Fe(total), Mn.
2. Ca, CO_2, Sr, As, Mn.
3. V.
4. Fe^{3+}.

The components in Group One, particularly Mg, Ca, CO_2, Fe(total) indicate the presence of dolomite (ferroan). According to DEER et al. (1962), in the structure of dolomite, Mn may replace Mg. These authors reported that 3-4% MnO is common in dolomites, while ferroan dolomite may contain up to 1·18% of MnO. The occurrence of dolomite in the sediments of the Oxford Clay has been reported by JACKSON and FOOKES (1974) and SIDDIQUI(1979), from various localities in England. The present sediments show higher abundances of dolomite (ferroan) in the samples from the (U.O.C.) and a decreasing trend of dolomite (ferroan) with the depth in the borehole. Dolomite in sedimentary rocks occurs as a hydrothermal product. A considerable proportion of sedimentary dolomite can be formed from calcite rocks under the influence of Mg from the sea-water, during the processes of diagenesis or through interaction with hydrous magnesian carbonates included in calcareous deposits. According to BISSELL and CHILINGAR (1958), diagenetic dolomites have formed in the past, and the occurrence of numerous mottled dolomites is reported in the literature as cases of "arrested diagenesis". It is therefore possible that, in the present sediments, the dolomite is of diagenetic origin, and is produced by the alteration of unstable carbonate minerals, such as aragonite and magnesium-rich calcite. The occurrence of carbonate minerals, i.e. calcite (pure), calcite (Mg-rich) and dolomite is reported by JACKSON and FOOKES (1974) in the sediments of the Oxford Clay. A brief summary of their data is presented in Table (5.2.5) as follows:

Table (5.2.5)

Locality	% Dolomite	% Calcite (pure)	% Calcite(Mg-rich)
BLETCHLEY	0 - traces	0 - 5	0 - 4
CALVERT	0 - 3	0 - 26	0 - 5
STEWARTBY	0 - 1	2 - 33	0 - 8
WHITTLESEY	0	3 - 40	0
CHICKRELL	0	0 - 9	0 - 4

The presence of aragonite and aragonitic material in the shells of the fossils found in the Oxford Clay sediments has been reported by many workers, including HALL and KENNEDY (1967), GRANDJEAN et al. (1964, p.566), COLLOMAN (1968), and HUDSON and PALFRAMAN (1969). The presence of aragonite in the shells present in the sediments of the Warlingham Borehole sediments is reported by COLLOMAN et al. (1971).

According to BISSELL and CHILINGAR (1958), diagenetic dolomite is particularly effective when the calcium carbonate is metastable, and is in a realm conducive to replacement. The same authors stated that replacement of carbonate ooze containing metastable aragonite and magnesian calcite, by magnesium-bearing solutions during diagenesis possibly occurs in various environments and under varying chemical conditions. BERNER (1966) stated that much of the total Ca-Mg exchange may take place only on the surface of grains of high magnesian calcite and aragonite. According to BISSELL and CHILINGAR (1958), the Mg^{2+} ions are available in solutions, in the crystal structure of calcite in warm sea-water under certain conditions. According to these authors, this metastable condition of carbonates facilitates the diagenetic changes in carbonate minerals. Aragonite, being a metastable carbonate, can change into dolomite, providing the Mg^{2+} ions are available during the diagenesis (BISSELL and CHILINGAR, 1958). The same authors stated that it seems that primary carbonate should be in an environment of sufficient alkalinity $(\Sigma HCO_3^- + CO_3^=)$ to effect dolomitization and certain catalysts, such as somewhat elevated temperature and pressure (yet still in the sedimentary realm), are required.

All the necessary prerequisites for the formation of diagenetic dolomite mentioned above, which include mainly the sources of Mg ions, calcite (Mg-rich), aragonite and sufficient alkalinity, were available in the environments under which the sediments of the (U.O.C.) of the (W.B.) were deposited, in particular. The existence of sufficient alkalinity in the environments of the (U.O.C.) sediments is indicated by the highest concentration of Fe-Mn oxides/hydroxides, as suggested by RANKAMA and SAHAMA (1950). The mixed-layer minerals also show the highest concentration in the (U.O.C.) sediments. It is probable that the mixed-layer (illite-montmorillonite) was initially in the form of the smectite (montmorillonite-illite) found in sediments of the (W.K.B.), and showed the highest concentration in the (U.O.C.) sediments. This smectite, being rich in Mg contents, might have released some Mg for the formation of the present dolomite in the (W.B.) sediments. Other details regarding the origin of dolomite are given in Chapter Three.

The loadings in Group Two include Ca, CO_2, As, Sr and Mn, and represent the presence of calcite, probably of secondary origin. The association of Ca - CO_2 - As has been explained earlier in the study of Factor (F-1) of both the borehole sediments. The association of Sr with calcite is well known. According to DEER et al. (1962), a small amount of Sr commonly substitutes for Ca in calcite, due to the similarity of the ionic radii of Sr^{2+} (1·21Å) and Ca^{2+} (1·08Å). BATHURST (1975) mentioned about 500 p.p.m. Sr associated with the ancient limestone, and 800-4000 ppm of Sr in most of the molluscs. EL-SHAHAT and WEST (in press) mentioned 526 p.p.m. of Sr in early lithified biosparrudites containing 93·3% calcite. OXBURGH et al. (1959) and KOTOV (1968, p.533) mentioned that elements such as Mn, Fe, Sr, Zn, Ba and Pb may substitute for Ca in calcite. The biogenous origin of Sr is mentioned by CHESTER (1965), TUREKIAN (1964), BOSTROM et al. (1974) and PAPAVASILIOU (1979). A detailed account of Sr and its relationship with minerals in the (W.B.) sediments is given in Chapter Four. Table (5.2.6a) shows a summary of the partial abundances of minerals and elements in the lithogenous and clay fractions, and confirms that Sr is strongly associated with calcite in the studied sediments. Table (5.2.6b) shows the correlation coefficients of elements and the mineral phases present in the studied sediments, which help in the understanding of geochemical behaviour of elements and their relations with the minerals.

Group Three of the negative phase of Factor (F-4) contains only one component, i.e. V, which suggests the possible occurrence of vanadates in these sediments. The sediments of the (U.O.C.) show the highest abundance of vanadium associated with the highest abundances of

Ca, Mg, Mn, Fe^{3+}, calcite, dolomite and mixed-layer (illite-montmorillonite) clay minerals. According to RANKAMA and SAHAMA (1950), vanadium in sedimentary rocks produces a number of vanadates. The same authors further mentioned that, for the formation of vanadates in sedimentary rocks, vanadium may be contributed by the ground waters, thermal waters and also by numerous plants and terrestrial animals. According to RANKAMA and SAHAMA (op.cit.), the chief metals found in vanadates include Ca, Mn, Fe^{3+}, U, Pb, Cu and Zn. The present association shows the presence of V - Ca - Mn - Fe^{3+}, and therefore supports the idea of the occurrence of vanadates in minor amounts in the present sediments.

Equally, the V may be associated with the phases of the last group, which shows Fe^{3+}, indicating the presence of ferric oxides/hydroxides. According to RANKAMA and SAHAMA (op.cit.), the ferric oxides are precipitated under alkaline conditions, in sediments. The existence of alkaline conditions in the (U.O.C.) sediments at the time of deposition is indicated by the highest abundances of the carbonate minerals, manganese and mixed-layer (illite-montmorillonite) clay minerals. Figure (5.2.4) is reproduced from BISSELL and CHILINGAR (1958); it explains the genesis of the authigenic minerals and their associations in the negative phase of Factor (F-4) in particular, and the Oxford Clay sediments in general. Taking into consideration the details given earlier, it seems reasonable to call this phase of Factor (F-4) the 'total carbonates phase', representing the carbonate minerals of secondary origin.

To summarize, Factor (F-4) represents the detrital phase through its positive loadings, which is opposed by the phases of secondary origin, particularly carbonates. This Factor represents the populations of the (K.F.) in the positive phase, and that of the (U.O.C.) and (M.O.C.) in the negative phase. The factor scores of Factor (F-4) show high positive values on the samples of the (K.F.) and high negative values on the samples of the (U.O.C.) and (M.O.C.), which is shown in Table (5.2.2). The abundances of total carbonates (calcite + dolomite) shown in Appendix (3.2),and the factor scores of (F-4), are plotted in Figure (5.2.3b), which indicates a strong negative correlation ($r = -0{\cdot}825$; significant at the 0·01% level) between the two variables, and confirms that this phase represents the total carbonates of secondary origin.

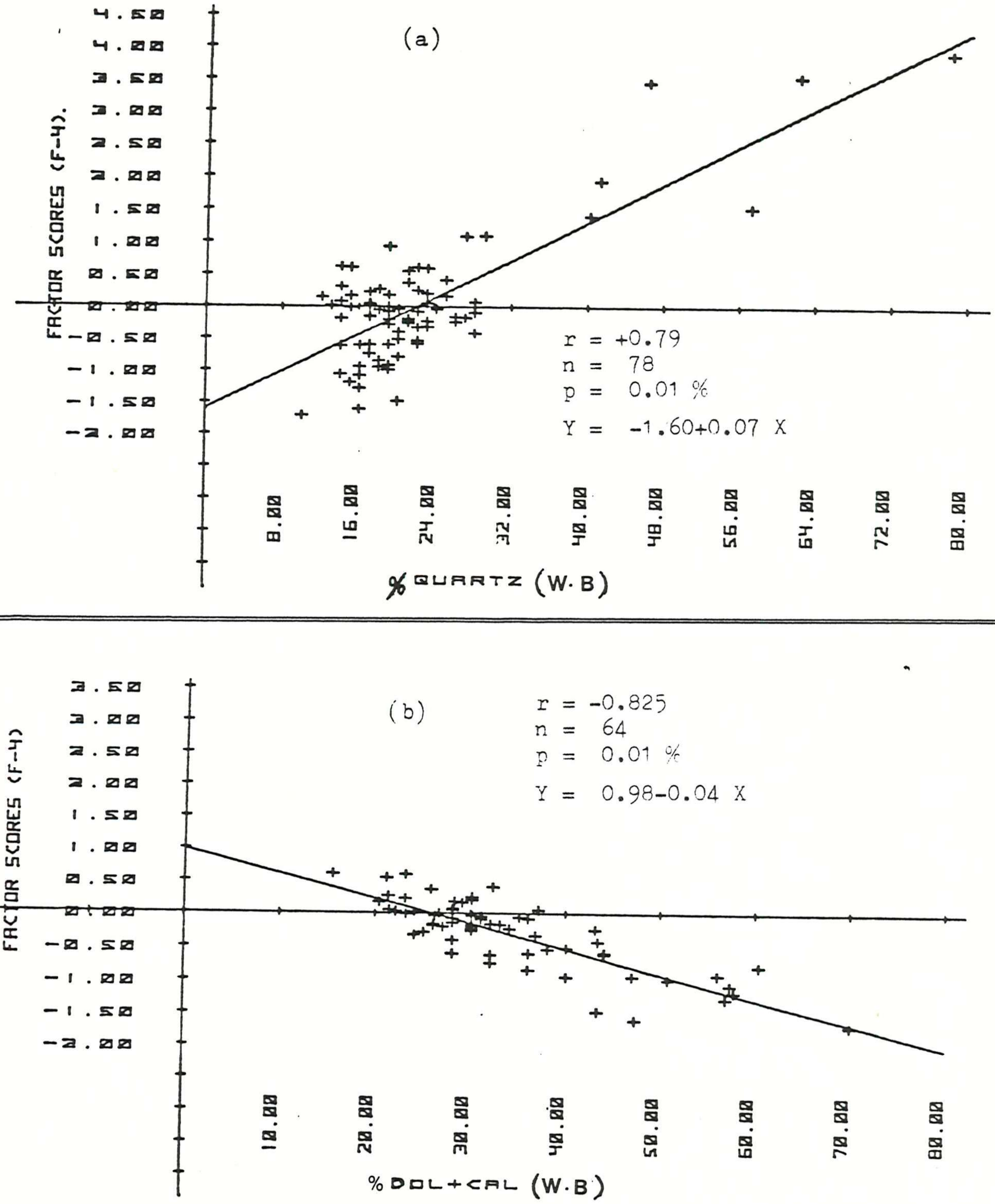
(a)
FACTOR SCORES (F-4).
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
r = +0.79
n = 78
p = 0.01 %
Y = -1.60+0.07 X
8.00
16.00
24.00
32.00
40.00
48.00
56.00
64.00
72.00
80.00
% QUARTZ (W.B)
(b)
r = -0.825
n = 64
p = 0.01 %
Y = 0.98-0.04 X
FACTOR SCORES (F-4)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
% DOL+CAL (W.B)

FIG. [5.2.3]

TABLE (5.2.6a): Summary showing the partial abundances of minerals and elements in the lattice-held and clay fraction ($< 2\mu$) samples of the (W.B.) sediments.

Components	BR-134			BR-278			BR-826			BR-988			BR-1544		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
I. Major Elements in %		%			%			%			%				
MgO	2·26	49	(n.d.)	1·91	70	2·06	2·33	75	2·02	2·90	45	1·81	2·34	(n.d.)	(n.d.)
II. Minor Elements in p.p.m.															
Sr	239	35	(n.d.)	246	40	104	270	0	86	342	54	104	391	(n.d.)	(n.d.)
Mn	192	10		208	0	186	116	42	158	181	0	163	86		
Pb	6	0		9	0	26	16	0	24	19	0	26	18		
Zn	14	0		38	3	94	52	40	94	28	11	75	45		
Cu	9	11		12	63	27	19	74	25	15	67	24	20		
Ni	28	11		25	8	84	32	34	80	25	0	65	45		
III. Bulk rock minerals in per cent															
1. Dolomite ferroan	27			5·40			3·42			18·80			1·94		
2. Calcite pure	30			38·60			33·10			21·00			19·84		
3. Total Clays	26			26·00			44·00			39·00			55·00		
IV. Clay fraction ($< 2\mu$) minerals in per cent															
1. Illite	65			64			64			68			67		
2. Chlorite	1			9			14			7			9		
3. M/Layer	34			17			16			12			10		

Note: (a) Abundances of elements in Bulk rock samples. (b) Percentages of elements in lattice-held fractions.
(c) Abundance of elements in Clay Fraction ($< 2\mu$) in the respective samples.
(n.d.) = Not determined.

TABLE (5.2.6b): Summary showing the average abundances of respective elements in 12 representative samples of the clay fraction (< 2μ), highest concentrations of the elements in the bulk rock samples in the studied sequence and correlation coefficients of the elements with mineral phases in the (W.B.) sediments.

1	2	3	4
MgO	2·92% (U.O.C.)	2·13%	i) 0·01% level with M.L. ii) " " " Dol. iii) None with Cal.
Sr	283 p.p.m. (U.O.C.)	105 p.p.m.	i) 0·01% level with M.L. ii) 5% " " Ch. iii) -ve correl. with Dol.
Mn	203 p.p.m. (U.O.C.)	174 p.p.m.	i) 0·01% level with M.L. ii) " " " Cal. iii) " " " Dol.
Pb	19 p.p.m. (U.O.C.)	25 p.p.m.	i) 10% level with T.C. and Ch.
Zn	84 p.p.m. (U.O.C.)	88 p.p.m.	i) 5% level with Ill. ii) 10% " " T.C. & Ch.
Cu	24 p.p.m. (L.O.C.)	27 p.p.m.	i) 0·01% level with C_{org}. ii) 5% " " T.C. iii) 10% " " Pyt.
Ni	46 p.p.m. (U/L.O.C.)	73 p.p.m.	i) 5% level with T.C.

Explanation of TABLE (5.2.6b)

1. Components studied.
2. Highest concentration of elements in bulk rock.
3. Average abundance of elements in Clay fraction (< 2μ).
4. Levels of significance of correlation coefficients.

M.L = Mixed-layer; Dol = Dolomite; Ch = Chlorite; T.C. = Total clays; Pyt = Pyrite.

Figure (5.2.3a) shows a very strong positive correlation ($r = +0{\cdot}79$; significant at the 0·01% level) between the abundance of quartz shown in Appendix (3.2) and the factor scores of Factor (F-4).

Summary

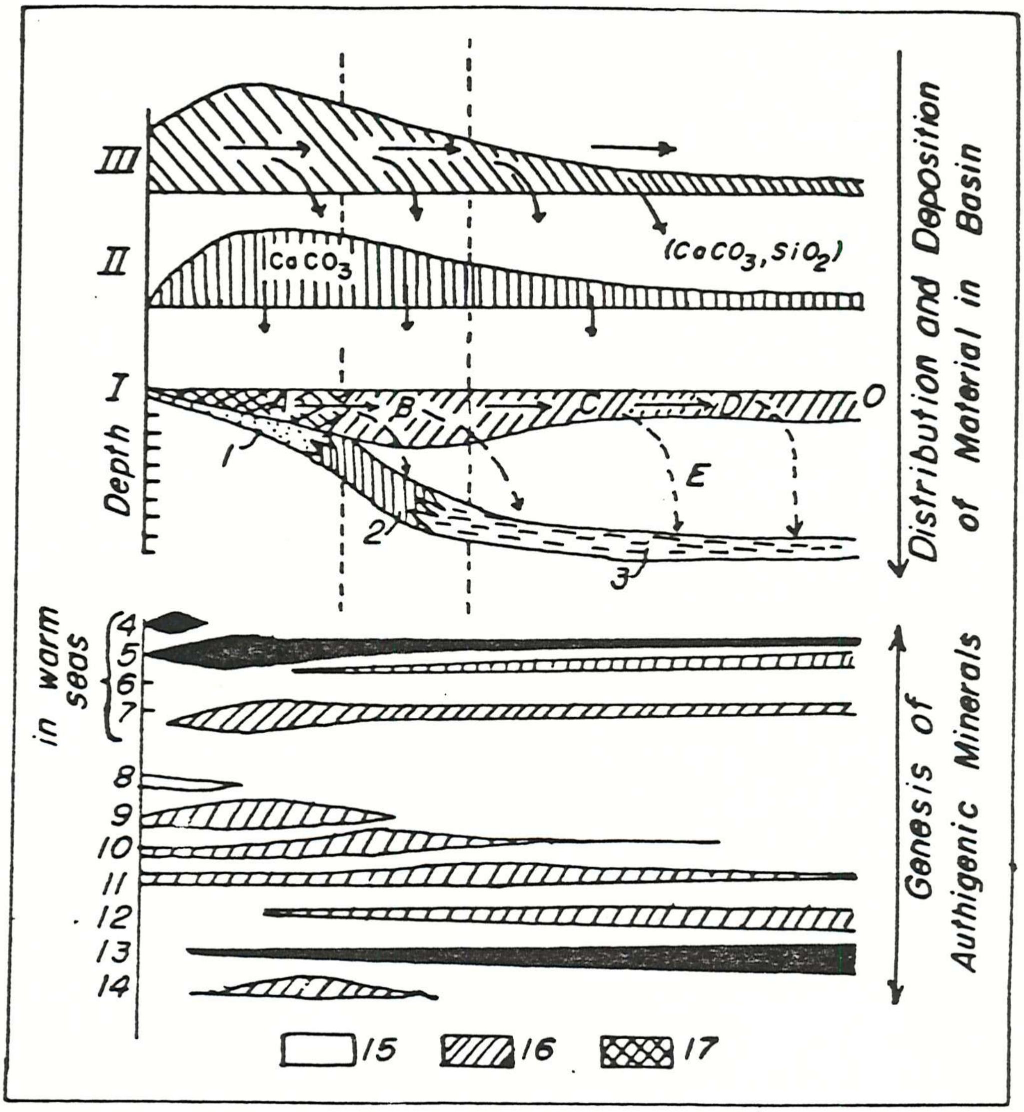
It is concluded that the factor analysis of the chemical data of the (W.B.) sediments confirms the conclusions drawn earlier regarding the distribution of the major and minor elements in the studied sediments, as described in Chapter Four. Four factors were extracted which explained 67·04% of the total variance satisfactorily. Factor (F-1) is interpreted as the clay factor representing the abundances of detrital clay minerals; this factor, in its negative phase, reflects the presence of calcite, most probably authigenic in origin. Factor (F-1), as detrital clay phase, controls the major variance of Ti, Al, K, La, Th, Rb and Nb, and a significant amount of variance of components such as Fe(total), Na, V, Cr, Ba, Ce, Y, H_2O^+, Fe^{3+}, and a minor amount of variance of Si, and C_{org}, indicating the nature of association of these components with detrital clays. The negative phase controls significant variances of Ca and CO_2, and a minor amount of As.

Factor (F-2) is interpreted as the 'adsorption factor'. It is an independent factor and shows that it controls the major variance of metals such as Pb, Ga, Zn, Cu and Ni, and a significantly high amount of the variance of As. These metals in the sediments of the (W.B.) have shown a totally different distribution from their distribution in the (W.K.B.) sediments, where they are associated with clay minerals and sulphide phases.

Factor (F-3) has been identified as the 'Redox' factor, showing that high variances of S, Mo, Fe^{2+} and a significant amount of the variance of Fe(total) and Cr is controlled mainly by sulphide minerals (pyrite). Organic carbon showed its strongest loading in Factor (F-3), reflecting the presence of marine organic matter. Some C_{org} of detrital origin,(terrestrial), plants, is also present in the detrital clays. Phosphorus showed its unique loading in Factor (F-3), suggesting that phosphate of primary origin (hydroxy apatite/collophane?) is present in these sediments. The negative phase of (F-3) reflects the presence of the Fe-Mn oxides/hydroxides, which is not unusual. Oxidate sediments generally facilitate the precipitation of Fe-Mn oxides/hydroxides.

Factor (F-4) is interpreted as the 'resistates' factor, showing an antipathetic relationship with the diagenetically produced minerals of secondary origin. The positive phase of (F-4) showed that major amounts of the variance of Si and Zr are associated with the resistate minerals. It also shows that a significant part of the variance of Na and Ba is controlled by feldspars. The negative phase of Factor (F-4) showed the major variance of Mg,in association with significant variance of Fe(total), Ca, Mn and CO_2, is controlled by dolomite (ferroan). A significant proportion of the variance of Ca, Mn, CO_2 and the major variance of Sr is controlled by calcite,probably of secondary origin, produced during an early diagenetic phase by the alteration of Mg-rich calcite and aragonite of these sediments. The association of V in the negative phase suggests the presence of secondary vanadates, or V associated with Fe^{3+} oxides/hydroxides. Table (5.2.6a) summarizes the results of the partial abundances of minerals and elements in the lattice-held and clay fractions of the studied sediments, and confirms the lattice-held and non-lattice-held characters of the elements, particularly of Sr, Mn, Mg and the rarer metals.

Factor analysis, as with the (W.B.K.) sediments, helped in understanding the physico-chemical conditions which prevailed during the deposition and after the burial of the sediments. It enabled the distinction to be made between the generations of the minerals present in these sediments. It further helped to understand the multiple nature of geochemical behaviour of many major and minor elements. It also clarified the singular nature of participation of many major and minor elements, such as Ti, Al, K, Rb, La, Th in detrital clays. Elements Mg and Sr showed associations with dolomite, calcite and Fe^{3+} respectively. Zirconium does not show any association with clays; it is mainly present as zircon in the detrital phase. Figure (5.2.4) illustrates the genesis and associations of the mineral phases present in the studied sediments. Tables (5.2.6a & b) demonstrate the lattice-held and non-lattice-held characters of major and minor elements in the studied sediments, as well as the correlation coefficients between the elements and mineral phases of the studied sediments.



I—Progress of mechanical deposition of clastic material;
II—Progress of biologic deposition of components;
III—Progress of chemical precipitation of components;
A—turbid zone of fine-grained material, and its carrying out from near-shore zone into more central parts of the basin; B—areas of currents usually of circulatory type; C–D—surface zone of agitation and wind currents in central parts of basins; E—deep, quiet (with very slight movements of water) horizons of pelagic part of basins. Arrows show carrying out of fine material from the zone of turbidity to the more central parts of the basin; dashed arrows—hypothetical trajectories of particles falling to the bottom.
1—sands; 2—siltstones; 3—pelites; 4—$CaCO_3$, oölites;
5—biogenous and chemically precipitated $CaCO_3$; 6—diagenetic $CaCO_3$ (bacterial); 7—various forms of diagenetic dolomite; 8—Fe_2O_3, oxides of Mn, Al_2O_3; 9—leptochlorites;
10—glauconite; 11—carbonates of Fe and Mn (in muds without $CaCO_3$ or having very small $CaCO_3$ content); 12—sulfides of Fe, Mn (Cu, etc.) in muds with high $CaCO_3$ content;
13—biogenically formed SiO_2; 14—primary and diagenetic phosphorites; 15—minerals forming through direct precipitation from water; 16—diagenetic minerals;
17—partly primary, partly diagenetic minerals.

Fig.(5.2.4),has been reproduced from Fig.1,BISSELL and CHILLINGAR (1958)

CHAPTER SIX

PARTITIONING GEOCHEMISTRY OF MAIN MAJOR AND MINOR ELEMENTS IN THE BULK ROCK SAMPLES

Introduction

Geochemical partitioning study of the major and minor elements in sediments and sedimentary rocks helps in understanding the distribution and partitioning patterns of elements in the different fractions of the components present in the sediments. CHESTER and HUGHES (1967) stated that it is possible to distinguish between the elements incorporated in the sediments from the sea-water and the elements occurring in the pre-existing mineral lattices, in a variety of marine sediments, with the application of an ideal chemical separation technique. According to the same authors, for interpreting the complex geochemistry of pelagic sediments, it would be of great help if each of the components is considered individually. This would lead to a knowledge of partitioning of trace elements among sedimentary components and ultimately to an understanding of the processes by which they have been incorporated into the sediments.

Several authors, including HIRST and NICHOLLS (1958), CHESTER (1965a), GOLDBERG and ARRHENIUS (1958), ARRHENIUS and KORKISH (1959), LYNN and BONATTI (1965), CHESTER and HUGHES (1967), CHESTER and MESSIHA-HANNA (1970) and CHESTER et al. (1976) have used different chemical methods for the separation of detrital and non-detrital fractions of the sediments, and studied the partitioning trends of the chemical elements in sediments. Published data on the partitioning of the elements in sediments mostly pertain to deep-sea sediments; data on ancient marine sediments is scarce. CHESTER et al. (1976) described the partitioning characters of Ni, Co, Cu, Cr, Zn and Pb in the Upper Cretaceous and pre-Upper Cretaceous sediments, during the geochemical studies of a D.S.D.P. core of sediments from the north-eastern flank of the Burmuda Rise.

The present study was undertaken with the aim of observing the lattice-held and non lattice-held characters of the main major and minor elements in the studied sediments. Having this aim in mind, Al, Ti, Mg, Na, K, S, P, Pb, Zn, Cu, Ni, Cr, Mn and Sr were studied in 12 selected samples from each borehole, representing all divisions of the Oxford Clay and Kellaways Formations.

The selected samples were subjected to an acid-reducing agent (1M-hydroxylamine hydrochloride/25% ($^{v}/v$) acetic acid solution), a leaching technique proposed by CHESTER and HUGHES (1967). According to these authors, sediments after receiving this leaching treatment leave an unattacked residue, comprising silicates, alumino-silicates, sulphates, sulphides and metals tightly bound with organic material. PAPAVASILIOU (1979), during the X-ray diffraction examination of some of the unattacked residues of the studied sediments, noticed that dolomite was also leached to a significant degree and chlorite was partially attacked. The details of the method used and the chemical calculations done are described fully in Chapter Two (p.68-70); a list of the studied samples is also given.

The results of the partitioning studies of the (W.K.B.) and (W.B.) sediments, consisting of the abundances of the non lattice-held elements and the lithogenous (lattice-held) phases present, were subjected to a series of statistical analyses, which included correlation studies of the elements and mineral phases and R-mode factor analysis of the lattice-held chemical data of each borehole; R-mode factor analysis confirmed the results derived from the correlations. The terms 'lithogenous', 'biogenous', hydrogenous' and 'cosmogenous' were proposed by GOLDBERG (1954) for deep-sea sediments. These terms, however, may be used for near-shore marine and ancient sediments, as these sediments also contain, as principal components, many of the components found in the deep-sea environment, as indicated in Table (6.1). Details of the study regarding the partitioning of elements in each borehole's sediments are as follows:

6.1 Partitioning Geochemistry of Main Major and Minor Elements in the (W.K.B.) Sediments

a) Results

All results pertaining to the leaching study are tabulated in Tables (6.1A, 6.1B and 6.3) and Appendices (6.1A, 6.1B and 6.1C). A summary of the percentages of lattice-held elements and the abundances of minerals etc. present in the bulk rock samples is given in Table (6.1B). The average values of the lattice-held chemistry and the components present in the (W.K.B.) sediments and (W.B.) sediments are compared in Table (6.3). This Table shows distinguishing characters of some of the elements, which are explained in forthcoming pages. Table (6.5) shows the comparison of the chemistry of the lithogenous fractions of the (W.K.B.) and (W.B.) sediments, determined in residue, carbonate-free sediments and clay fractions, with the chemistry of detrital sediments reported by other workers.

The main results exhibiting the characteristic lattice-held

TABLE (6.1) : The principal minerals in the various components of deep sea sediments

Lithogenous Components	Hydrogenous Components		Biogenous Components	Cosmogenous Components
	Primary	Secondary		
Clay Minerals	Ferro-manganese nodules	Montmorillonite (inc.nontronite)	Carbonates	Cosmic spherules
Quartz	Iron oxides	Zeolites	Opal	
Feldspars	Manganese oxides		Phosphates	
Micas	Francolite			
Amphiboles	Barite			
Pyroxines	Celestite			
Pyroclastic material	Calcite			
Rutile	Aragonite			
Anatase	Dolomite			
Haematite	Quartz overgrowth			
Goethite	Anatase (?)			
Calcite				
Dolomite				
Iron oxides				
Manganese oxides				

Note: The quantitatively important minerals are underlined.

(Table 6.1 is reproduced from CHESTER and ASTON, 1976) trends and the percentage contribution made by the lattice-held (lithogenous) fraction to the total element content of the studied elements in the (W.K.B.) sediments may be summarized, in decreasing order, as follows:

Element:	Al >	K >	Fe >	Cr >	Mg >	Cu >	Ni >	Mn >	Na >	Zn =	Sr >	Pb
Percentage lattice-held character	97	90	80	77	66	61	53	47	32	31	31	0

It is unfortunate that the above data cannot be compared with similar data of ancient marine sediments, due to the scarcity of published data. Therefore the observed trends in the (W.K.B.) and (W.B.) sediments are compared with each other, as well as with the trends observed by PAPAVASILIOU (1979) in the sediments of the Indian Ocean, and by CHESTER and MESSIHA-HANNA (1970) in N.Atlantic deep-sea sediments, in Table (6.2). This comparison shows that some of the elements in the (W.K.B) sediments, such as Mg, Sr, Cr, Cu and Na, display comparatively a weaker association with the lattice-held (lithogenous) fraction when compared with their counterparts in the (W.B.) sediments. Similarly elements Mn, Zn and Ni show a stronger association with the lattice-held (lithogenous) fraction. This variation may firstly be caused by the nature of components present in the (W.K.B.) sediments, and secondly by the lattice position of these elements in the various mineral phases. Other details of this variation are described in discussion in the forthcoming pages.

b) Data Analysis

(i) Geochemical Correlations:

A self-explanatory summary of the geochemical correlations observed between the abundances of lattice-held elements and mineral phases is presented in Table (6.1C). It shows a very strong positive correlation, significant at the 0·01% level, between illite, kaolinite and chlorite with the lattice-held elements. It indicates that detrital clay minerals, illite, kaolinite and chlorite, control the major variance of the elements Al, K, Mg, Na, Ni and Cr by containing them in their lattices (WEAVER and POLLARD, 1973). It also shows that C_{org} and pyrite respectively control significant amounts of Cu and Ni, Fe and Cu. It confirms the views of CHESTER and HUGHES (1967) that during the leaching of sediments

TABLE (6.2): Comparison of the average values of elements % contribution to the total element content by the lattice-held fraction in the sediments

Present work: (i) (W.K.B.) Sediments	(a)	Al > K > Fe > Cr > Mg > Cu > Ni > Mn > Na > Zn = Sr > Pb
	(b)	97 90 80 77 66 61 53 47 32 31 31 0
(ii) (W.B.) Sediments	(a)	Al > K > Cr > Fe > Mg > Cu > Sr > Ni > Na > Mn > Zn > Pb
	(b)	98 90 85 80 69 67 47 43 36 28 20 0
Indian Ocean Sediments PAPAVASILIOU(1979)	(a)	Ti > Al > Fe = Cr > Pb = Li > K > Mg > Cu > Ni > Zn > Na > Mn > Sr > Ca
	(b)	99 98 96 96 91 91 89 89 75 72 69 57 51 34 8
North Atlantic Deep-sea Sediments CHESTER *et al.*(1970)	(a)	Fe V Cr Ba Ni Cu Co = Ga Mn Sr
	(b)	82 > 71 > 69 > 61 > 55 > 44 > 42 42 > 32 > 17

Note: (a) Elements studied.

(b) Average value of the percentage contribution made to the total element content by the lattice-held (lithogenous) fraction in the studied sediments.

Explanation of Table (6.1A)

1 = Soluble leached in gr.

2 = Insoluble leached in gr.

3 = % Leached material relative to total amount.

4 = % of calcite ($CaCO_3$).

5 = Soluble non-$CaCO_3$ material = Total soluble % - % $CaCO_3$.

6 = Weight % of the residue.

7 = Sample position in the sequence.

8 = % leached by 10% acetic acid.[3]

TABLE (6.1A): Weights of soluble and insoluble materials (in gr. and %) after leaching with acid-reducing agents[2] representative samples of the Oxford Clay and Kellaways Formations from the Winterborne Kingston Borehole sediments. Comparison of calcite ($CaCO_3$) contents with the amount of dissolved material in 10% acetic acid.

Sample No.	1	2	3	4	5	6	7	8
WBK- 5	0·4940	0·5060	49·40	50·00	1·40	50·60	U.O.C.	50·00
WBK-15	0·3640	0·6360	36·40	33·00	3·40	63·60		33·50
WBK-25	0·3750	0·6250	37·50	33·00	4·50	62·50		33·80
WBK-28	0·2795	0·7205	27·95	25·00	2·95	72·05	M.O.C.	26·30
WBK-34	0·3240	0·6760	32·40	28·20	4·20	67·60		28·00
WBK-38	0·2795	0·7205	27·95	24·20	3·75	72·05		24·40
WBK-43	0·2900	0·7100	29·60	26·00	3·60	71·00	L.O.C.	26·50
WBK-53	0·2365	0·7635	23·65	20·00	3·65	76·35		20·80
WBK-55	0·2245	0·7755	22·45	20·00	2·45	77·55	K.F.	20·75
WBK-58	0·1940	0·8060	19·40	18·30	1·10	80·60		18·05
WBK-61	0·2065	0·7935	20·65	20·00	0·65	79·35		20·65
WBK-64	0·1960	0·8040	19·60	19·00	0·60	80·40		19·50

Note: 1. In each case one gram sample was used.
2. Acid-reducing agent = 1M-hydroxylamine hydrochloride and 25%($^v/_v$) acetic acid.
3. 10% Acetic acid was used to dissolve the amount of total carbonates (calcite).

TABLE (6.1B): Summary of the partial mineral analysis in the bulk rock samples and the percentages of the major and minor elements associated with the lattice-held (lithogenous) fractions in the (W.K.B.) sediments.

Sample No.	WBK-5	WBK-15	WBK-25	WBK-28	WBK-34	WBK-38	WBK-43	WBK-53	WBK-55	WBK-58	WBK-61	WBK-64
Components:												
Minerals: (%)												
ILL	6.36	22.30	18.25	28.10	26.39	29.92	27.17	34.92	34.59	35.81	34.00	33.41
SMEC	18.72	9.15	12.04	6.41	12.45	10.88	8.89	2.12	3.29	3.52	4.18	2.57
CHLR	<1	2.79	1.10	5.92	2.99	4.35	4.45	5.83	5.50	5.87	6.28	3.08
KAOL	<1	5.54	5.11	8.87	7.97	9.25	8.89	11.13	11.53	13.50	12.03	11.31
TClays	26.50	39.80	36.50	49.30	49.80	54.40	49.40	53.00	54.90	58.70	52.30	51.40
C_{org}	1.00	2.08	2.27	2.09	1.70	1.61	4.44	4.49	2.48	2.33	3.15	4.78
Pyt	1.50	2.20	3.70	1.60	2.40	2.10	3.60	3.20	3.10	3.00	2.60	2.70
Elements: (p.p.m.)												
Mn	19.80	25.30	22.80	39.50	40.70	49.13	52.80	63.20	62.30	61.40	51.52	60.42
Zn	4.93	1.54	0.00	45.60	31.00	36.87	73.88	13.68	49.90	0.95	48.00	70.00
Sr	28.80	28.05	0.00	31.00	21.80	30.75	35.60	41.00	39.25	38.50	37.46	39.70
Ni	0.00	39.60	34.00	53.20	45.90	52.40	62.12	61.54	60.34	65.52	66.00	94.83
Cu	36.40	50.20	58.80	55.60	47.00	50.00	77.80	68.00	64.30	65.22	79.20	84.60
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	77.50	86.30	67.40	76.60	65.40	76.15	81.06	83.60	84.81	65.58	78.50	81.21

/contd.over

TABLE (6.1B) contd.

Sample No.	WBK-5	WBK-15	WBK-25	WBK-28	WBK-34	WBK-38	WBK-43	WBK-53	WBK-55	WBK-58	WBK-61	WBK-64
Components:												
Elements: (%)												
Al	96·35	97·50	95·00	97·00	96·00	98·00	98·00	98·00	98·50	97·72	97·50	98·00
Fe	75·75	70·20	73·00	70·00	75·00	81·00	82·00	81·00	83·70	87·70	89·80	90·00
Mg	38·05	57·00	47·00	72·00	65·00	70·00	67·00	74·00	72·13	73·11	75·00	77·00
Na	5·13	0·00	3·50	24·00	0·00	17·00	37·00	46·00	55·74	77·03	47·92	56·00
K	85·12	89·00	85·00	90·00	87·00	90·00	90·00	96·00	91·73	95·54	90·00	92·00

by the acid-reducing agents, sulphides and metals tightly bound with the organic material remain unattacked.

(ii) R-mode Factor Analysis:

R-mode factor analysis of the lattice-held chemical data of 12 representative samples of the (W.K.B.) sediments was carried out to verify the results of the geochemical correlations summarized in Table (6.1C).

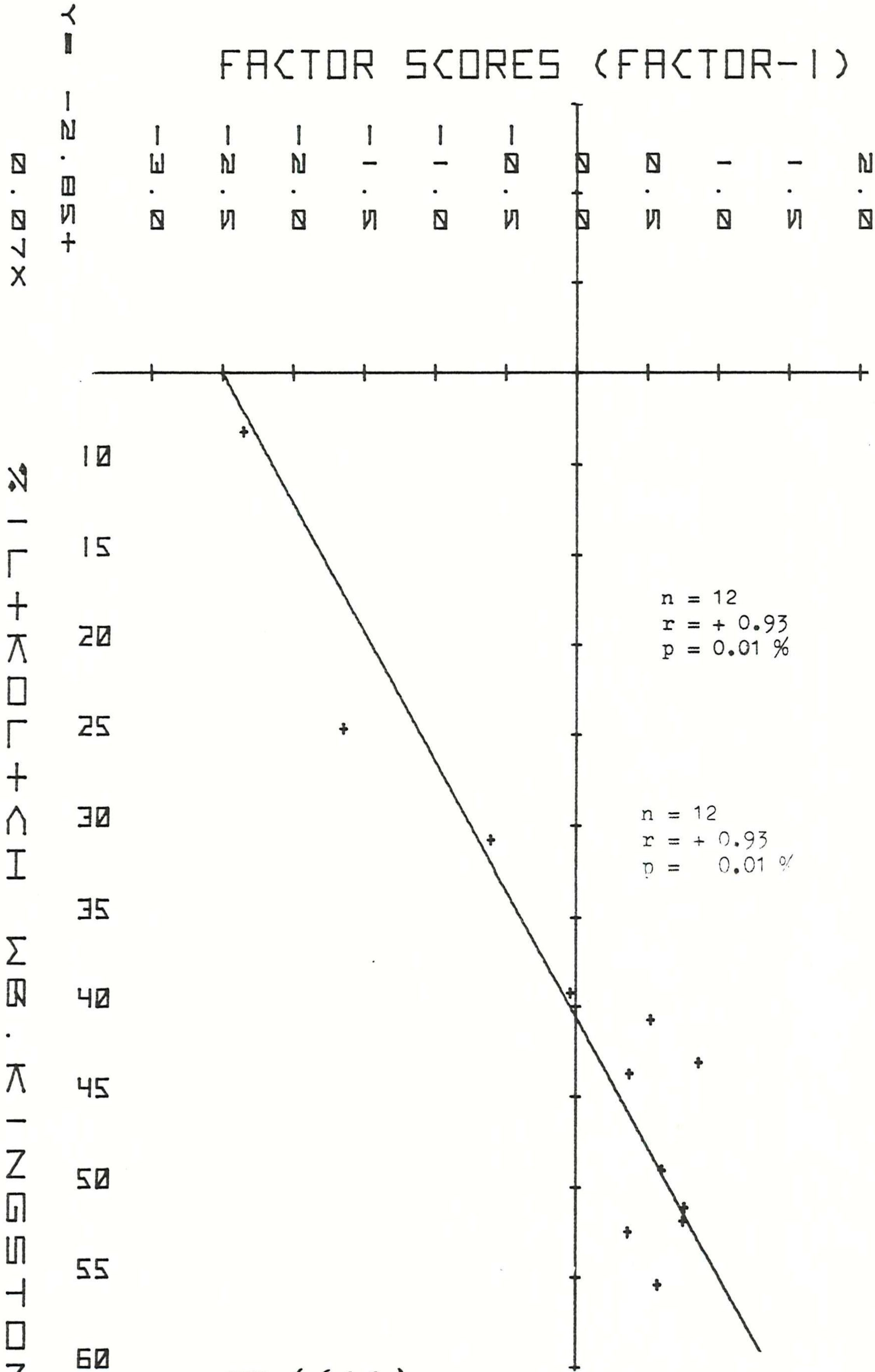
Three factors were extracted which explained 81·81% of the total variance; none of the factors is bi-modal. The Promax Factors loadings with $K_{min} = 5$ and the inter-factor correlations are given in Table (6.1D). A summary of the Promax Factor matrix, indicating the levels of significance of the components loaded in the respective factors, is given in Table (6.1F). Factor scores on the Promax Factors are tabulated in Table (6.1E).

Factor (F-1)

This factor explains 47·16% of the total variance. It shows very strong positive loadings of the elements Al, K, Mg, Na, Cr, and Ni, and a low loading of Cu. Considering this association of elements, this factor may be designated the 'detrital clays' factor. This interpretation is in agreement with the conclusions drawn in Factor (F-1) of the bulk rock chemistry, described in Chapter Five. It is further confirmed by Figure (6.1.1), showing a very strong positive correlation ($r = +0{\cdot}93$; significant at the 0·01% level) between the combined abundances of detrital clay minerals (illite + kaolinite + chlorite), determined in the bulk rock samples, and the factor scores of (F-1). There is a good agreement between the observations summarized in Tables (6.1F and 6.1C). All these elements are found in the lattice structure of illite, kaolinite and chlorite (WEAVER and POLLARD, 1973).

Factor (F-2)

It explains 20·31% of the total variance. It shows very strong loadings of Fe, Zn and Cu, and a low loading of Ni; all these elements are known for their chalcophile nature. Table (6.1C) shows a very strong positive correlation of these elements with C_{org} and pyrite, highly significant at the 0·01% level, with the exception of Zn, which is only significantly correlated at the 10% level. This factor is therefore interpreted as the 'C_{org} + pyrite' factor. Sulphides and elements tightly



n = 12
r = + 0.93
p = 0.01 %

n = 12
r = + 0.93
p = 0.01 %

FIG. (6.1.1)

TABLE (6.1C): Summary of the correlations showing the correlation coefficients for 5% and 0·01% levels of significance shown by the minerals (lithogenous phases) and the abundances of elements determined in the lattice-held fractions of the 12 leached samples of the Oxford Clay and Kellaways Formations from the (W.K.B.) sediments.

Significance levels		IL	KOL	CH	SMEC	T.C.	L.G.F.	C_{org}	Pyt.
+ve	5%	LHCr, LHCu, C_{org}	LHCr, LHCu, C_{org}	LHNa, RNa	NIL	LHCr	LHCr, LHCu, C_{org}	L.G.F., ILL, KAOL, IL, KOL, LHZn*	C_{org} LHZn*
	0·01%	Depth, LHAl LHMg, LHNa, LHK, LHNi, LGF, RAl, RNa, RK, CCAl, CCK, T.C, ILL, KAOL, CHLR, KOL, CH.	Depth, LHAl, LHMg, LHNa, LHK, LHNi, LGF, RAl, RNa, RK, CCAl, CCK, T.C, ILL, KAOL, CHLR, IL, CH.	Depth, LHAl LHMg, LHK, LHCr, LHCi LGF, RAl, RK, CCAl, CCK, T.C, ILL, KAOL, CHLR, IL, KOL.	CCFe, Cal SMECT.	Depth, LHAl, LHMg, LHNa, LHK, LHNi LGF, RAl, RNa, RK, CCAl, CCK, ILL, KAOL, CHLR, IL, KOL, CH.	Depth, LHAl, LHMg, LHNa, LHK, LHNi, Ral, RNa, RK, CCAl, CCK, T.C, ILL, KAOL, CHLR, IL, KOL, CH.	Depth, LHCu, LHNi	LHFe, LHCu
-ve	0·01%	CCFe, Cal, SMECT, SMEC.	CCFe, Cal, SMECT, SMEC.	Cal, SMECT, SMEC.	Depth, LHAl, LHNa, LHK, LHCr, LHNi, LGF, RAl, RNa, CCAl, CCK, C_{org}, T.C, ILL, KAOL, CHLR.	CCFe, Cal, SMECT, SMEC.	CCFe, Cal, SMECT, SMEC.	SMEC	RMg
	5%	NIL	NIL	CCFe	LHMg, LHCu, RK	QTZ	NIL	SMECT	NIL

Note: For 10 degrees of freedom the levels of significance for correlation coefficients are as follows:

10% ≥ 0·49
5% ≥ 0·57
0·01% ≥ 0·70

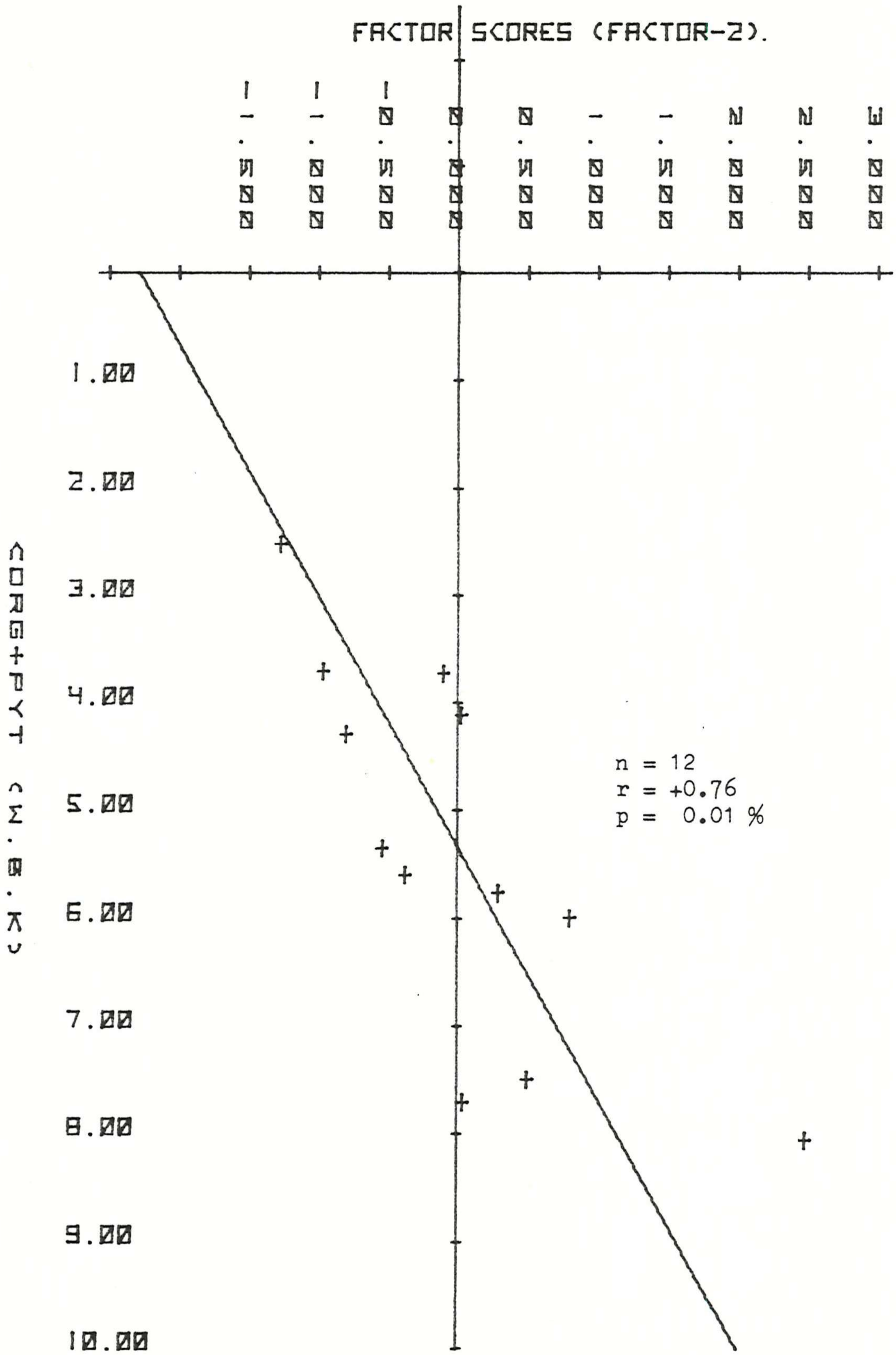
* indicating a correlation significant at the 10% level.

bound with organic material are not attacked by the acid-reducing agent (CHESTER & HUGHES, 1967). The present conclusions agree with the conclusions drawn in Factor (F-2), described in Chapter Five. It is further confirmed by Figure (6.1.2), which shows a very strong positive correlation ($r = +0{\cdot}76$; significant at the 0·01% level) between the combined abundances of 'C_{org} + pyrite' and the factor scores of Factor (F-2). The correlation of Factor (F-2) with Factor (F-1) is positive, and much stronger than its negative correlation with Factor (F-3), and confirms the well-established stronger association of detrital clays with C_{org} and sulphides in the sediments deposited under marine conditions.

Factor (F-3)

This factor explains only 14·34% of the total variance, which indicates its subordinate role in the studied sediments. It contains very strong loadings of Mn and Sr, associated with a moderate loading of Zn. The summary given in Table (6.1C) does not show any correlation of Mn and Sr with the listed phases, which suggests that the lattice-held contents of Mn and Sr in the studied sediments are associated with phases other than the reported ones. Table (6.1B) shows that higher lattice-held percentages of Mn and Sr are associated with the samples from WBK-43 to WBK-64. However, no particular trends between the abundances of clays and the lattice-held elements in these samples exist, which is additional evidence of the association of Mn and Sr with phases other than clays. On the basis of these observations, and a knowledge of the occurrence of the Mn-oxides/hydroxides phase in the factor analysis of bulk rock, described in Chapter Five, it is interpreted that the lattice-held manganese indicates the presence of Mn-oxides/hydroxides.

The occurrence of Mn-oxides/hydroxides in marine sediments is well known. According to STRUNZ (1957), at least four MnO_2 modifications occur in nature. DEGENS (1965) mentioned that the bulk of manganese oxides is composed only of two minerals, namely pyrolusite and cryptomelane. The same author further stated that two other manganese oxides, i.e. psilomelane and δ-MnO_2, are less common. CORNELIUS et al. (1977) mentioned the occurrence of a secondary mineral of manganese called 'psilomelane', $(Ba^{2+},Mn^{2+})_3(O,OH)_6Mn_8^{4+}O_{16}$. The same authors mentioned that psilomelane contains small amounts of Mg, Ca, Ni, Co, Cu and Si. CALVERT and PRICE (1977) quoted ANDRUSHCHENKO and SKORNYAKOVA (1969), who have reported the



FACTOR SCORES (FACTOR-2).
-1.500
-1.000
-0.500
0.000
0.500
1.000
1.500
2.000
2.500
3.000
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
CORG+PYT (M.B.K)
n = 12
r = +0.76
p = 0.01 %

FIG.(6.1.2)

TABLE (6.1D): Promax Factor loadings with K_{min} = 5 and correlations between Promax Factors for K_{min} = 5 for the 12 leached samples of the Oxford Clay and Kellaways Formations, Winterborne Kingston Borehole sediments.

Components	(F-1)	(F-2)	(F-3)
LH Al_2O_3	0·90		
LH MgO	0·79		
LH Fe_2O_3		0·82	
LH Na_2O	0·67		
LH K_2O	0·92		
LH Zn		0·85	0·47
LH Cr	0·71		0·26
LH Cu	0·42	0·63	
LH Mn			0·86
LH Sr			0.80
LH Ni	0·83	0·31	
Per Cent Explanation	47·16	20·31	14·34

Correlations between Promax Factors for K_{min} = 5

F-1	1·0000		
F-2	0·1862	1·0000	
F-3	0·2900	-0·1312	1·0000
	F-1	F-2	F-3

/contd.over

TABLE (6.1D) contd.

(i) Cumulative explanation = 81·81%

(ii) Factor loadings $<$ 0·26 were omitted.

(iii) The values of loadings represent values of correlation coefficients for the 5% and 1% levels of significance. For 10 degrees of freedom these are:

5% level $\geqslant$ 0·57

1% level $\geqslant$ 0·70

TABLE (6.1E): Scores on Promax Factors of 12 leached samples of the (W.K.B.) sediments.

(F-1)	(F-2)	(F-3)
-2•372	-1•280	1•101
-0•620	-0•807	-0•191
-1•661	0•796	-2•641
0•847	0•975	0•541
-0•055	0•017	-0•207
0•360	-0•112	0•328
0•513	2•478	1•073
0•746	0•032	0•284
0•737	-0•380	0•654
0•565	-0•545	-0•284
0•347	0•285	-0•288
0•592	0•491	-0•368

TABLE (6.1F): Summary Table of Promax Factors Matrix for the (W.K.B.) Sediments, showing the significance levels of the loaded components in the respective factors.

Significance levels		(F-1)	(F-2)	(F-3)
+ve	10%	LHCu	Nil	LHZn
	5%	LHNa	LHCu	Nil
	0·01%	LHAl, LHMg, LHK, LHCr, LHNi	LHFe, LHZn	LHMn, LHSr
-ve	0·01%	Nil	Nil	Nil
	5%	Nil	Nil	Nil

Cumulative explanation = 81·81%

For 10 degrees of freedom the levels of significance for the correlation are:

10% $\geqslant$ 0·49
5% $\geqslant$ 0·57
0·01% $\geqslant$ 0·70

occurrence of psilomelane and pyrolusite in the growth layers of the marine nodules. According to these authors, the minerals mentioned above are very fine-grained and it is very difficult to identify them by ordinary optical study.

The association of Mn and Sr in this factor may be due either to a common source of both elements from terrestrial or marine plants and animals (RANKAMA and SAHAMA, 1950), or it may be due to the probable substitution of Sr^{2+}(1·21Å) for Ba^{2+}(1·44Å) or for Ca^{2+}(1·08Å) in the structure of the psilomelane, due to the close similarity of the ionic radii of these elements. The association of Zn^{2+}(0·74Å) with Mn^{2+}(0·80Å) may be due either to substitution, or it may be due to the strong adsorptive ability of hydrated MnO_2 for metal Zn, as mentioned by KRAUSKOPF (1956).

The inter-factor correlations shown in Table (6.1.1) indicate the strongest positive correlation ($r = +0{\cdot}29$) between factors (F-3) and (F-1), the detrital clay factor. It is commonly known that detrital clay minerals are produced by weathering of the existing rocks in the area of the provenance. READ (1976, pp.504-508) mentioned that manganese oxides are produced by the alteration of rocks containing Mn-bearing minerals (chiefly silicates), and so there is a common origin for both Mn-oxides/hydroxides and clay minerals. READ (op.cit.) further mentioned that Mn-oxides thus produced aggregate together as nodules and layers in the residual clays being formed on the outcrops of the weathered rocks. It provides further evidence of the association of Mn-oxides/hydroxides with residual clays in particular, and sediments in general.

c) Discussion

During the data analysis in the foregoing pages, it was observed that some elements displayed characteristic trends, showing the variations of the amounts of the lattice-held elements in the studied sediments. Some of the salient points are enumerated and discussed, as follows.

(1) It was noticed that, in general, the elements Si, Al and Ti showed enhanced values, in Appendix (6.1A), in the leached samples when compared with the re-calculated chemistry on a carbonate-free basis. It indicates that these elements in the leached samples are very strongly associated with the lattice-held fraction. It is commonly known that these elements occupy the octahedral layers (WEAVER & POLLARD, 1973) of the clay minerals, and cannot be easily

removed.

(2) Elements such as Mg, K and Na showed depleted amounts in the leached residue of all the samples. This depletion is due to the lattice position of these elements in clays and other leachable components. Elements K and Na are known to occupy the inter-layer position in illite, montmorillonite and chlorite, and element Mg in the inter-layer position of the mixed-layer minerals (WEAVER and POLLARD, 1973). Being located in the inter-layer positions, these elements can be removed with much greater ease than the elements located in other layers of the clays. The present sediments contain all three clay minerals mentioned above.

(3) Elements such as Fe, S and P showed depleted amounts in the residue of all the samples. This depletion, particularly of P, is due to its strong association with the carbonate phases, the most soluble phase in the acid-reducing agent. The depletion of Fe and S is due to partial attack of the acid-reducing agents on the sulphide phases and also due to association of Fe and S with organic material.

(4) The studied elements in Table (6.1B) show an increasing trend of the lattice-held character of the elements from the (U.O.C.) sediments to the (K.F.) sediments. There appear to be no particular trends between the abundances of the lattice elements and the individual phases in the sediments. The only trend of increase with the depth demonstrated is by the abundance of total clays.

(5) Pb showed its entire association with the non lattice-held (non-lithogenous) components. It may be associated loosely with C_{org} and sulphide phases.

(6) Zn and Sr showed the second lowest lattice-held character. This is due to the association of Sr with the carbonate phase and Zn being loosely associated with C_{org} and sulphide phases.

(7) The depletion of Mg and Sr in the present sediments, as compared to the (W.B.) sediments, may be due to the absence of dolomite in these sediments and the lattice position occupied by these elements.

(8) The lower lattice-held character of Na in the present sediments may be due to the presence of minor amounts of Na-bearing feldspar in these sediments as compared to the (W.B.) sediments, and the lattice position of Na.

(9) The higher lattice-held abundances of elements Zn, Mn, Ni, Cr and Sr in the (W.K.B.) sediments, as shown in Table (6.3), strongly suggest the origin of these elements as being from basic igneous rocks. According to KRAUSKOPF (1979, pp.544-45), basalt contains the enriched abundances of the elements Zn, Mn, Ni, Cr and Sr. CHESTER et al. (1976) reported much enhanced abundances of these metals in the lattice-held fractions of the Cretaceous and pre-Cretaceous zeolitic clays, which are reproduced in Table (6.4). Figure (6.3) clearly shows the enhanced abundances of elements Mn, Zn, Ni, Na and Fe in the lattice-held fraction of the (W.K.B.) sediments, as compared to the (W.B.) sediments. It demonstrates the likely basic igneous rocks origin of these elements in the (W.K.B.) sediments.

On the basis of the observed lattice-held characters of the studied elements in the present sediments, they may be divided into four groups (CHESTER and MESSIHA-HANNA, 1970). Group One contains elements which exhibited lattice-held character > 80%. Group Two includes elements showing lattice-held character of the range from 61 - 80%. Group Three shows the elements which display lattice-held character of the range from 20-60% and Group Four those elements from 0-20%. The proposed groups showing the lattice-held character from lower to higher values are as follows:

Group One:	K and Al	(> 80%)
Group Two:	Cu, Mg, Cr and Fe	(61-80%)
Group Three:	Sr, Zn, Na, Mn and Ni	(20-60%)
Group Four:	Pb	(0-20%).

The elements of Group One (> 80%) are strictly of lithogenous (detrital) origin. Al showed the highest lattice-held character as compared to K, due to its location in the octahedral layer of the clay minerals. The elements in Group Two (61-80%) are enriched in the basic igneous rocks, such as basalt, and indicate the influence of basic igneous material on the detritus of the studied sediments. Moreover these elements are usually located in the tetrahedral and inter-layer positions of the clay minerals and can be relatively easily removed. The elements in Group Three (20-60%), in the studied sediments, are either associated with the soluble or easily soluble phases, such as sulphides and carbonates, or the phases with which they are associated are present in minor amounts such as Mn, which reflects the presence of a minor amount of Mn-oxides/hydroxides. PAPAVASILIOU (1979), in the study of partitioning patterns of elements in Indian Ocean sediments, reported lower lattice-held character of elements such as Mn, Na, Zn, Ni and Sr and attributed it to their association with the soluble or easily soluble phases such as carbonates, sulphides and NaCl present in the sediments of the Indian Ocean.

CHESTER and MESSIHA-HANNA (1970), in the studies of N.Atlantic deep-sea sediments, mentioned association of lattice-held elements in four groups. Group I (> 80%) contains only Fe, Group II (60-80%) V, Cr and Ba, Group III (20-60%) Ni, Cu Co, Ga and Mn, and Group IV (< 20%) contains only Sr. There is a great similarity of the lattice-held characters of the elements grouped by the present author in Groups Two and Three with the elements in Groups II and III, as mentioned by CHESTER and MESSIHA-HANNA (op.cit.). Pb is the only element in Group Four which showed its 100% association with the non-lattice-held fraction.

d) Conclusions

The study in the foregoing pages leads to the conclusions as follows:

(1) Most of the studied elements show a higher lattice-held content ranging from 60 to 97%.

(2) Nickel shows 53% lithogenous character, which may be due to its origin in easily soluble sulphide phases associated with C_{org}.

(3) Elements such as Zn and Sr both showed 31% lithogenous character, while Mn showed 47% lithogenous character. This may be due to the occurrence of minor amounts of Mn-oxides/hydroxides in the studied sediments.

(4) Na showed only 32% lithogenous character, which may be due to its presence in the exchangeable position in the structures of clay minerals.

(5) Pb showed its 100% association with the non-lattice-held (non-lithogenous) fraction; it may be associated with the diagenetically produced phases of sulphides, carbonates and C_{org}.

FIGURE (6.3)

This figure shows a Log-Log geochemical diagram to explain the origin and distribution of main major and minor elements studied in the lattice-held fractions of the (W.K.B.) and (W.B.) sediments. BOSTRÖM *et al.* (1974 and 1976) produced a geochemical graph of Log-Log values to explain the origin and distribution of major and minor elements in their studied sediments. The diagonal line is drawn on 1:1 ratio basis. According to BOSTRÖM *et al.*(1976) the immobility of Al and Ti makes them excellent markers of the extent a sediment model can satisfactorily explain the composition of a given sediment. All values represent Log_{10} (concentration in %). Elements below the diagonal line, in the present case Mg, must have an additional source to the (Y, vertical) ordinate in the graph. Elements such as Mn, Zn, Ni, Na and Fe above the diagonal line indicate a different provenance for the (W.K.B.) sediments.

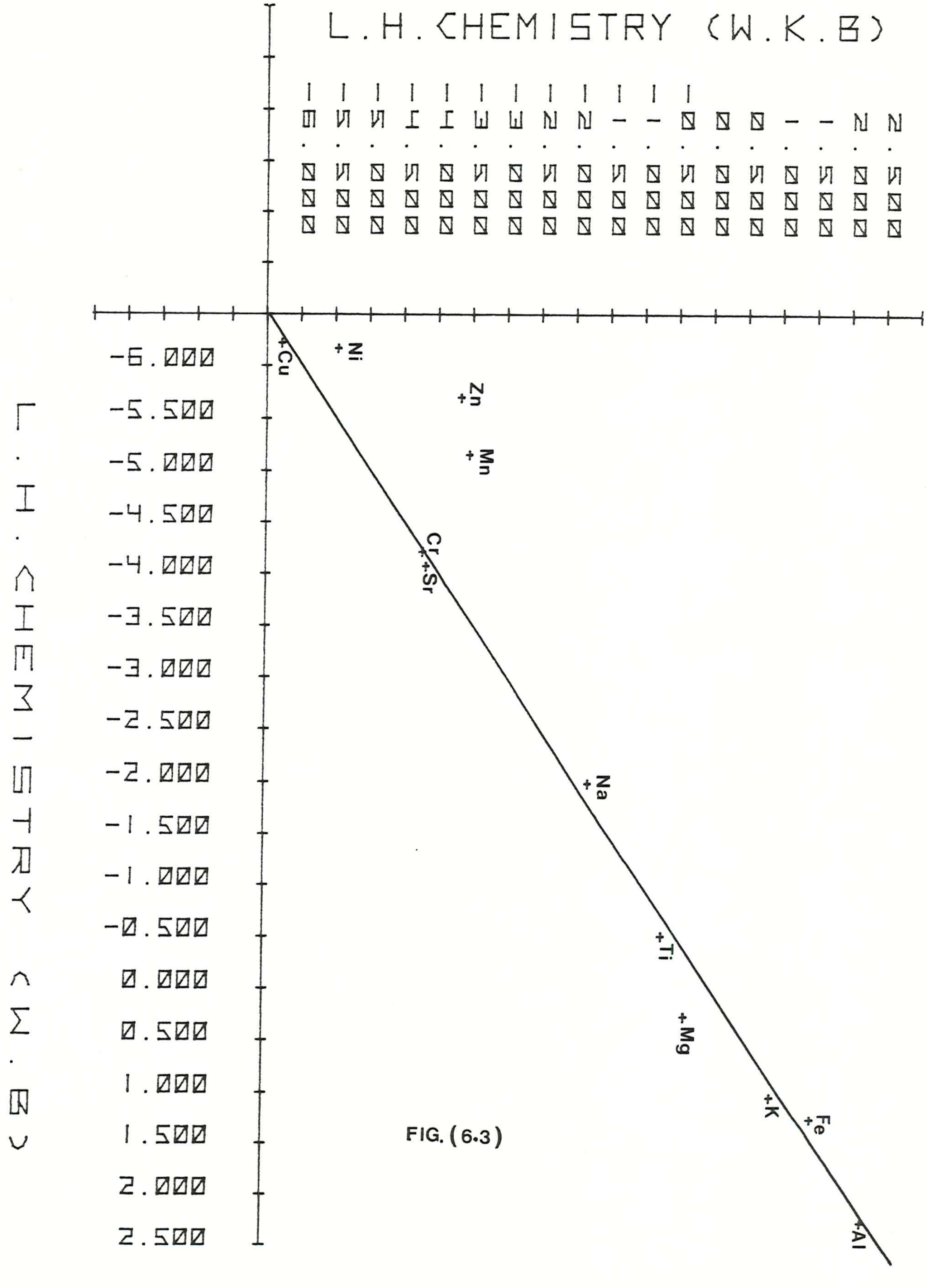

L.H. CHEMISTRY (W.K.B)
-6.000
-5.500
-5.000
-4.500
-4.000
-3.500
-3.000
-2.500
-2.000
-1.500
-1.000
-0.500
0.000
0.500
1.000
1.500
2.000
2.500
L.H. CHEMISTRY (W.K.B)
-6.000
-5.500
-5.000
-4.500
-4.000
-3.500
-3.000
-2.500
-2.000
-1.500
-1.000
-0.500
0.000
0.500
1.000
1.500
2.000
2.500
Cu
Ni
Zn
Mn
Cr
Sr
Na
Ti
Mg
K
Fe
Al

FIG. (6.3)

6.2 Partitioning Geochemistry of the Main Major and Minor Elements in the (W.B.) Sediments

a) Results

All the results of the leaching study of the (W.B.) sediments are tabulated in Tables (6.2A, 6.2B and 6.3) and Appendices (6.2A, 6.2B and 6.2C). Tables (6.2A and (6.2B) respectively show the weight loss in the sample and a summary showing the percentages of the lattice-held elements and the abundances of the minerals etc. present in the bulk rock samples of the studied sediments. The average values of the lattice-held chemistry and components present in both the borehole sediments are compared in Table (6.3). A comparison of the concentrations of elements in the lattice-held fractions of the (W.B.) and (W.K.B.) sediments, with the concentrations of elements in the lattice-held fractions in ancient sediments reported by CHESTER et al. (1976), is shown in Table (6.4). A comparison of the chemical composition of the lattice-held (lithogenous) fractions of the (W.B.) and (W.K.B.) sediments, with the chemical composition of the average terrigenous material, average near-shore muds and average shales, is shown in Table (6.5).

Table (6.3) shows comparatively stronger lattice-held character of elements such as Al, Mg, Na, Cu, Cr and Sr, and a weaker lattice-held character of elements Ni, Mn and Zn, when compared with their counterparts in the (W.K.B.) sediments. The lattice-held character of Pb and Fe in the sediments of both boreholes is identical. This variation reflects the nature and provenance of the components present in the studied sediments. It also indicates the lattice positions where these elements were placed in the lattice-held components of the (W.B.) sediments. The sediments of the (W.B.) in Table (6.3) also display higher average abundances of illite and total clays, as compared with the sediments of the (W.K.B.). The higher lattice-held character of elements Al, Cr and Cu in the sediments of the (W.B.) may be related to the higher abundances of illite and total clays, that of Mg and Sr to the presence of diagenetically produced carbonate phase (ferroan dolomite), and that of Na to the presence of Na-bearing feldspar present in these sediments. The lattice-held copper in the (W.B.) sediments demonstrated a much stronger association with detrital clays (illite, kaolinite and chlorite), significant at the 0·01% level, as shown in Table (6.2C), as

TABLE (6.2A): Weights of soluble and insoluble materials (in gr. and %) after leaching with acid-reducing agents[2] the representative samples of the Oxford Clay and Kellaways Formations from the Warlingham Borehole sediments. Comparison of carbonates(T) contents with the amount of dissolved material by 0·1N HCl.

Sample No.	1	2	3	4	5	6	7	8
BR-134	0·5815	0·4185	58·15	56·76	1·39	41·85	U.O.C.	57·27
BR-278	0·4530	0·5470	45·30	44·00	1·30	54·70		43·30
BR-627	0·2455	0·7545	24·55	24·44	0·11	75·45		24·00
BR-826	0·3630	0·6370	36·30	36·52	0·22	63·70	M.O.C.	36·00
BR-988	0·4580	0·5420	45·80	44·00	1·80	54·20		44·60
BR-1301	0·2480	0·7520	24·80	25·16	0·00	75·20		27·00
BR-1424	0·3410	0·6590	34·10	32·00	2·10	65·90	L.O.C.	32·00
BR-1583	0·2310	0·7690	23·10	22·35	0·75	76·90		21·32
BR-1734	0·0900	0·9100	9·00	7·00	2·00	91·00		7·00
BR-1755	0·1345	0·8655	13·45	12·00	1·45	86·55	K.F.	12·00
BR-1771	0·0288	0·9712	2·88	3·00	0·00	97·12		3·00

Note:
1. One gram of each sample was used.
2. Acid-reducing agent = 1M-hydroxylamine hydrochloride and 25%(^{V}/v) acetic acid.
3. Carbonates(T) = calcite + dolomite.
4. 0·1N HCl was used to dissolve the carbonates(T).

Explanation of Table (6.2A)

1 = Soluble leached in gr.

2 = Insoluble leached in gr.

3 = % leached material relative to total amount.

4 = % of carbonates(T)[3]

5 = Soluble non-carbonate material = % total soluble material - % carbonates(T).

6 = Weight % of residue.

7 = Sample position in the sequence.

8 = % leached by 0.1N HCl[4] (Carbonates(T)).

TABLE (6.2B): Summary of the partial mineral analyses in the bulk rock samples and the percentages of the major and minor elements associated with the lattice-held (lithogenous) fractions of the (W.B.) sediments.

Sample No.	BR-134	BR-278	BR-627	BR-826	BR-1301	BR-1424	BR-1583	BR-1734	BR-1755	BR-1771	BR-988
Components:											
Minerals: (%)											
ILL	16.83	16.64	33.97	28.29	32.27	26.07	36.17	45.15	29.03	49.47	23.90
MLYR	8.80	4.42	6.18	7.07	7.36	7.26	8.22	10.20	6.80	11.42	3.51
CHLR	<1	2.34	5.15	2.65	2.63	4.27	2.74	5.83	3.17	3.80	3.51
KAOL	0.00	2.60	6.17	6.20	6.31	5.13	7.67	11.65	6.35	11.42	3.87
TClays	25.89	26.00	51.48	44.21	52.04	42.74	54.81	72.83	45.36	76.11	35.15
C_{org}	0.45	1.20	0.84	1.00	1.14	3.22	3.76	5.71	2.25	4.65	1.52
Pyt.	0.90	0.80	0.24	1.27	2.66	1.76	2.08	2.02	2.38	2.90	1.74
Dol.	27.00	5.40	4.70	3.42	3.93	8.36	2.00	1.25	1.20	3.00	20.56
Elements: (p.p.m.)											
Mn	10.42	0.00	50.16	41.60	0.00	11.50	43.81	76.41	69.88	n.d.	0.00
Zn	0.00	2.63	70.00	40.38	12.76	24.24	48.83	42.59	59.70	36.21	10.71
Sr	34.73	40.24	51.17	n.d.	51.66	43.54	41.43	67.60	48.72	83.62	53.51
Ni	10.71	8.00	72.50	34.37	36.58	47.20	60.42	60.00	57.89	81.82	0.00
Cu	11.11	62.50	61.11	73.68	73.68	76.19	72.22	84.21	78.95	82.86	66.67
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	37.50	0.00
Cr	83.10	83.50	94.30	91.66	89.68	86.27	92.42	94.52	94.96	93.62	69.81

/contd.over

TABLE (6.2B) contd.

Sample No.	BR-134	BR-278	BR-627	BR-826	BR-1301	BR-1424	BR-1583	BR-1734	BR-1755	BR-1771	BR-988
Components:											
Elements: (%)											
Al	97·44	98·21	99·09	98·87	96·00	97·87	99·01	97·18	98·54	98·18	92·91
Fe	60·89	67·24	84·67	83·44	87·28	77·67	89·11	91·72	84·26	92·38	66·09
Mg	49·11	69·60	79·41	75·00	74·48	58·08	71·51	82·61	76·36	76·92	45·71
Na	0·00	23·08	46·87	4·37	32·25	66·67	31·82	50·00	67·86	54·28	0·00
K	84·85	89·20	94·09	93·50	86·25	90·50	94·14	89·84	97·51	93·02	77·83

compared to the (W.K.B.) sediments, in which it is weakly (5% level) associated with only kaolinite, as shown in Table (6.1C). It explains the higher lattice-held character of Cu in the (W.B.) sediments. Element Cr is known for its entirely lithogenous origin (CHESTER and ASTON, 1976; RILEY and CHESTER, 1971). The higher percentage of the lattice-held character demonstrated by Cr in the (W.B.) sediments may be due firstly to higher abundances of illite and total clays; secondly, it may be related to the nature of the initial detritus, which is believed to be dominantly composed of re-cycled material, probably contributed by the weathering of the sediments of the London platform, believed to exist nearby to the north of the location of Warlingham. The higher lattice-held character of Cr may equally suggest that the present clay minerals,which hold these elements in their lattices, were initially produced from a detritus influenced by basic igneous components. According to KRAUSKOPF (1979, pp.544-45), basic igneous rocks contain enriched values of elements Fe, Cr, Cu, Mg, etc. The depletion of elements Mn, Zn and Ni in the lattice-held fractions of the (W.B.) sediments as compared to their abundances in the (W.K.B.) sediments, shown in Table (6.3), suggests either their association with soluble fractions of the (W.B.) sediments, or their origin from basic igneous rocks in the (W.K.B.) sediments. Manganese in the bulk rock samples of the (W.B.) sediments showed its much stronger association with soluble phases, such as carbonates and ferric oxides/hydroxides, as explained in Factors (F-3) and (F-4) in Chapter Five. Similarly the bulk rock study in Chapter Five showed that maximum variance of Zn and Ni is associated with 'adsorption' factor (F-2). The observed trends of the lattice-held character of the elements in the studied sediments, like the (W.K.B.) are in decreasing order as follows:

Element:	Al >	K >	Cr >	Fe >	Mg >	Cu >	Sr >	Ni >	Na >	Mn >	Zn >	Pb
Percentage lattice-held character:	98	90	85	80	69	67	47	43	36	28	20	0

b) Data Analysis

(i) Geochemical Correlations:

The geochemical correlations observed between the lattice-held elements and the existing phases in the (W.B.) sediments are summarized in Table (6.2C). It shows that the major variance of elements such as Al, K, Cu and Ni is controlled by the detrital clays (illite, kaolinite and chlorite), as indicated by very strong positive correlation, significant at the 0·01% level. A minor amount of variance of elements Cr, Ni, Na and Zn is also controlled by the clays, as indicated by a weaker correlation, significant at the 5% level. Mixed-layer mineral is the only mineral in these sediments which shows a strong association (0.01% level) with Cr. This relationship supports the views expressed earlier regarding the provinance of the clay minerals present in the studied sediments, particularly the mixed-layer mineral

(ii) R-mode Factor Analysis

Three factors were extracted which explained 73·17% of the total variance. Factors (F-1) and (F-3) are bimodal factors, showing loadings of elements in positive and negative phases. The Promax Factor loadings with $K_{min} = 4$, and the inter-factor correlations, are given in Table (6.2D). A summary of the Promax Factors, indicating the significance levels of the loaded elements in the respective factors, is given in Table (6.2F). Factor scores shown on the Promax Factors are tabulated in Table (6.2E).

Factor (F-1)

This factor explains 39·36% of the total variance. It shows very strong positive loadings of lattice-held elements such as Mn, Zn, Ni, and a low negative loading of Sr. The loading of Mn, being highest, suggests that phases containing Mn have played a vital role over the control of the variance of the other two elements. Considering the anticipated dominant role of the said phases, this factor is interpreted as the Mn-oxides/hydroxides factor. These oxides are known to scavenge trace elements such as Cu and Ni from river or sea-water. CHESTER and MESSIHA-HANNA (1970) and CHESTER and ASTON (1976) mentioned that detrital material could contain phases like hydrous Mn or Fe-oxides which precipitated from weathering solutions. COOK (1974) also suggested that Mn may be present as oxides/hydroxides associated with detrital clays in anoxic sediments. The association of Mn with Fe-oxides/hydroxides is explained in Factor (F-3) in Chapter Five. The strong loadings of lattice-held Mn, significant at the 0·01% level, as shown in Table (6.2F) do not show any correlation with the phases listed in Table (6.2C), except a weak correlation, significant at the 5% level,of the lattice-held Zn with chlorite. It strongly suggests that the abundance of the lattice-held Mn in the (W.B.) sediments is

TABLE (6.2C): Summary of the correlations, showing the correlation coefficients for 5% and 0·01% levels of significance, shown by the minerals (lithogenous phases) and the abundances of elements determined in the lattice-held fractions of the 10 leached representative samples of the Oxford Clay and Kellaways Formations from the (W.B.) sediments.

Significance Level		IL	KOL	CH	MLYR	T.C.	L.G.F.	C_{org}	DOL
+ve	5%	LHCr,RFe	LHCr,LHNi, RMg,RFe	Depth, LHNa, LHK,LHZn, CCK,C_{org}		LHCr	LHAl,LHK,LHCr, LHCu,RAl RNa,RK,CCAl, C_{org}	LHAl,LHCr, L.G.F., RAl,KAOL, CH.	MIXLYR, LHSr * LHMg *
	0·01%	Depth,LHAl, LHK,LHCu, LHNi,LGF RAl,RMg, RK,CCAl, CCK,C_{org}, T.C,KAOL, KOL,CH.	Depth,LHAl, LHK,LHCu, LGF,RAl,RK, CCAl,CCK C_{org},T.C, KAOL,IL,CH.	LHAl,LHCu, LHNi,LGF RAl,RMg,RK, CCAl,T.C, KAOL,CHLR, IL,KOL.	LHCr	Depth,LHAl, LHK,LHCu LHNi,LGF RAl,RMg, RK,CCAl, CCK,C_{org}, KAOL,IL, KOL,CH.	Depth, LHNi, T.C,KAOL, IL,KOL,CH	Depth,LHCu, T.C,IL,KOl.	
-ve	0·01%	CAL.	CAL,DOL.	MIXLYR.		CAL.	CAL,DOL.		
	5%	DOL,MIXLYR.	MIXLYR.	CCFe,CAL, DOL.	ILL.	DOL.	LHMg,CCMg, CCFe, MIXLYR.	LHMg,CCFe, CAL.	Depth,LHAl, LHK, LHCu, LHNi,LGF,RAl, RK,T.C,KAOL, IL,KOL.

Note: For 8 degrees of freedom the levels of significance for the correlation coefficients are:

10%	≥	0·54
5%	≥	0·63
0·01%	≥	0·76

* Correlation only significant at the 10% level.

TABLE (6.2D): Promax Factor loadings with K_{min} = 4 and correlations between the Promax Factors for K_{min} = 4 for 10 leached samples of the Oxford Clay and Kellaways Formations, Warlingham Borehole sediments.

Components	(F-1)	(F-2)	(F-3)
LH Al_2O_3		-0·89	
LH MgO			0·635
LH Fe_2O_3		-0·65	0·608
LH Na_2O			-0·688
LH K_2O		-0·845	
LH Zn	0·88		
LH Cr			-0·505
LH Cu		-0·775	-0.402
LH Mn	0·95		
LH Sr	-0·44		
LH Ni	0·65		-0·292
Per Cent Explanation	39·36	18·73	15·08

Cumulative Explanation = 73·17%

Correlations between Promax Factors for K_{min} = 4

F-1	1·0000		
F-2	-0·2769	1·0000	
F-3	-0·3126	0·1731	1·0000
	F-1	F-2	F-3

Note: (i) Cumulative explanation = 73·17%

(ii) Factor loadings $<$ 0·29 were omitted.

(iii) The values of loadings represent values of correlation coefficients for the 10%, 5% and 0·01% levels of significance. For 8 degrees of freedom these are:

10%	$\geq$ 0·54
5%	$\geq$ 0·63
0·01%	$\geq$ 0·76

TABLE (6.2E): Scores on Promax Factors for 10 leached samples of the (W.B.) sediments.

(F-1)	(F-2)	(F-3)
-0·588	2·399	0·666
-0·964	0·820	0·234
2·337	-0·433	0·011
0·374	-0·548	0·902
-1·293	-0·308	1·462
-0·775	-0·810	0·525
-0·155	-0·290	-1·443
0·191	-0·427	-0·302
0·558	-1·067	-1·322
0·315	0·665	-0·731

TABLE (6.2F): Summary Table of Promax Factors Matrix for the (W.B.) Sediments

Significance Levels		(F-1)	(F-2)	(F-3)
+ve	10%	LHNi	NIL	LHMg, LHFe
	5%	NIL	NIL	
	0·01%	LHZn, LHMn	NIL	NIL
-ve	0·01%	NIL	LHAl, LHK, LHCu	NIL
	5%	NIL		LHNa
	10%	NIL	LHFe	LHCu

For 8 degrees of freedom the significance levels for the correlation coefficients are:

10% $\geqslant$ 0·54
5% $\geqslant$ 0·63
0·01% $\geqslant$ 0·76

TABLE (6.3): Summary of the results showing the average values of chemical analyses of bulk rock, lithogenous fractions, residues and re-calculated chemistry on a carbonate-free basis with mineral abundances of 12 samples of the (W.K.B.) and 11 samples of the (W.B.) sediments.

Winterborne Kingston Borehole Sediments							Warlingham Borehole Sediments						
1	2	3	4	5	6	7	1	2	3	4	5	6	7
(%)							(%)						
Al	6·00	8·76	8·96	8·78	97	99·8	Al	6·96	9·24	10·60	9·31	98	99·2
Fe	3·72	4·18	3·61	4·61	80	90·7	Fe	2·91	3·35	3·40	4·15	80	80·7
Mg	0·62	0·66	0·84	0·97	66	68·0	Mg	1·23	1·24	0·86	1·48	69	83·8
Na	0.41	0.16	0.25	0.55	32	29·0	Na	0·25	0·13	0·17	0·33	36	39·4
K	1·85	2·32	2·35	2·49	90	93·0	K	2·15	2·69	2·71	2·90	90	92·8
Ti	0·47	n.d.	0·47	0·44	n.d.	n.d.	Ti	0·39	n.d.	0·57	0·54	n.d.	n.d.
Si	19·26	n.d.	29·65	26·24	n.d.	n.d.	Si	19·79	n.d.	29·51	27·67	n.d.	n.d.
(p.p.m.)							(p.p.m.)						
Pb	48	0	n.d.	66	0	0	Pb	17	0	n.d.	23	0	0
Cu	20	18	"	26	61	67	Cu	20	19	"	27	67	70
Zn	509	245	"	697	31	35	Zn	47	32	"	64	20	37
Ni	56	41	"	76	53	54	Ni	40	20	"	55	43	36
Cr	132	141	"	177	77	80	Cr	114	141	"	155	85	91
Sr	340	149	"	n.d.	31	44+	Sr	231	163	"	n.d.	47	n.d.
Mn	440	277	"	"	47	63+	Mn	150	55	"	"	28	n.d.

/contd.over

TABLE (6.3) contd.

Winterborne Kingston Borehole Sediments							Warlingham Borehole Sediments						
1	2	3	4	5	6	7	1	2	3	4	5	6	7
(%)							(%)						
* ILL	28						* ILL	31					
* KOAL	10						* KOAL	6					
* CHLR	4						* CHLR	3					
* SMEC	8						MLYR	7					
T.C.	48						T.C.	55					
C_{org}	3						C_{org}	2.5					
Pyt.	3						Pyt.	2					
							Dol.	7					

Explanation of Table (6.3)

1. List of the studied components.
2. Average values on absolute basis of total elements content of the studied samples.
3. " " " " calculated in the lattice-held fraction.
4. " " " " determined in the leached residue by Beta-probe.
5. " " " " re-calculated on carbonate-free basis.
6. " " " the percentage of elements associated with the lattice-held fraction.
7. " " " " " " " calculated from the re-calculated values of elements at (5) and the amount of elements determined in the lattice-held fractions at (3).

* Abundances of clay minerals, i.e. illite, kaolinite, chlorite and smectite, re-calculated in the bulk rock samples.

TABLE (6.4): Comparison of the average trace element concentrations (p.p.m.) in the lattice-held fraction of the Burmuda Rise D.S.D.P. sediments (CHESTER *et al.*, 1976) and the average trace element concentration (p.p.m.) in the lattice-held fractions of the (W.K.B.) and (W.B.) sediments of the Oxford Clay and Kellaways Formations.

	Mn	Ni	Cu	Pb	Zn	Cr	Fe(wt%)
Pliocene(?)/Miocene(?) Clays	196	80	40	26	104	163	5•1
Middle Eocene zeolitic Clays	856	180	167	20	152	159	4•6
Upper Cretaceous zeolitic Clays	1610	137	112	28	135	120	5•8
Cretaceous(?) zeolitic Clays	705	66	29	25	71	123	5•2
Present work:							
(a) (W.K.B.)sediments	277	41	18	0	245	141	4•18
(b) (W.B.) sediments	55	20	19	0	32	141	3•35

TABLE (6.5): Comparison of chemical composition of the lithogenous fractions of the (W.K.B.) and (W.B.) sediments with the chemical compositions of 'average terrigenous material', 'average near-shore muds', and 'average shales'.

	(W.K.B.) Sediments			(W.B.) Sediments					
Elements	(a)	(b)	(c)	(a)	(b)	(c)	1	2	3
Major (%)									
Al	8·76	2·170	11·97	9·24	2·223	12·49		9·20	8·10
Fe	4·18	1·430	3·94	3·35	1·209	3·66	4·83	4·70	4·90
Mg	0·66	-0·415	1·14	1·24	0·215	1·28		1·40	1·58
Na	0·16	-1·832	0·50	0·13	-2·040	0·75		0·90	1·10
K	2·32	0·841	2·86	2·69	0·989	3·40		2·50	2·25
Ti	0·47	-0·755	0·50	0·39	-0·562	0·53	0·46	0·45	0·48
Minor (p.p.m.)									
Pb	0	-	84	0	-	25	20	20	20
Cu	18	-6·319	26	19	-6·266	27	48	50	57
Zn	245	-3·709	253	32	-5·745	88	95	90	78
Ni	41	-5·497	70	20	-6·215	73	55	80	90
Cr	141	-4·261	192	141	-4·261	191	100	100	100
Sr	149	-4·206	151	163	-4·116	105	< 250	400	431
Mn	277	-3·586	196	55	-5·203	174	850	850	880

Explanation of Table (6.5)

(a) Average values of the elements determined in the lithogenous fractions in the respective Borehole sediments.

(b) Log$_{10}$ values of the chemical analysis shown at (a)

(c) Average chemical abundances for 12 clay fraction ($\leq 2\mu$) samples.

(1) Average chemical analysis of the Near-Shore Muds (WEDEPOHL, 1960)

(2) " " " " " Average Shales (KRAUSKOPF, 1979)

(3) " " " " " Terrigenous Material (BOSTRÖM et al., 1976).

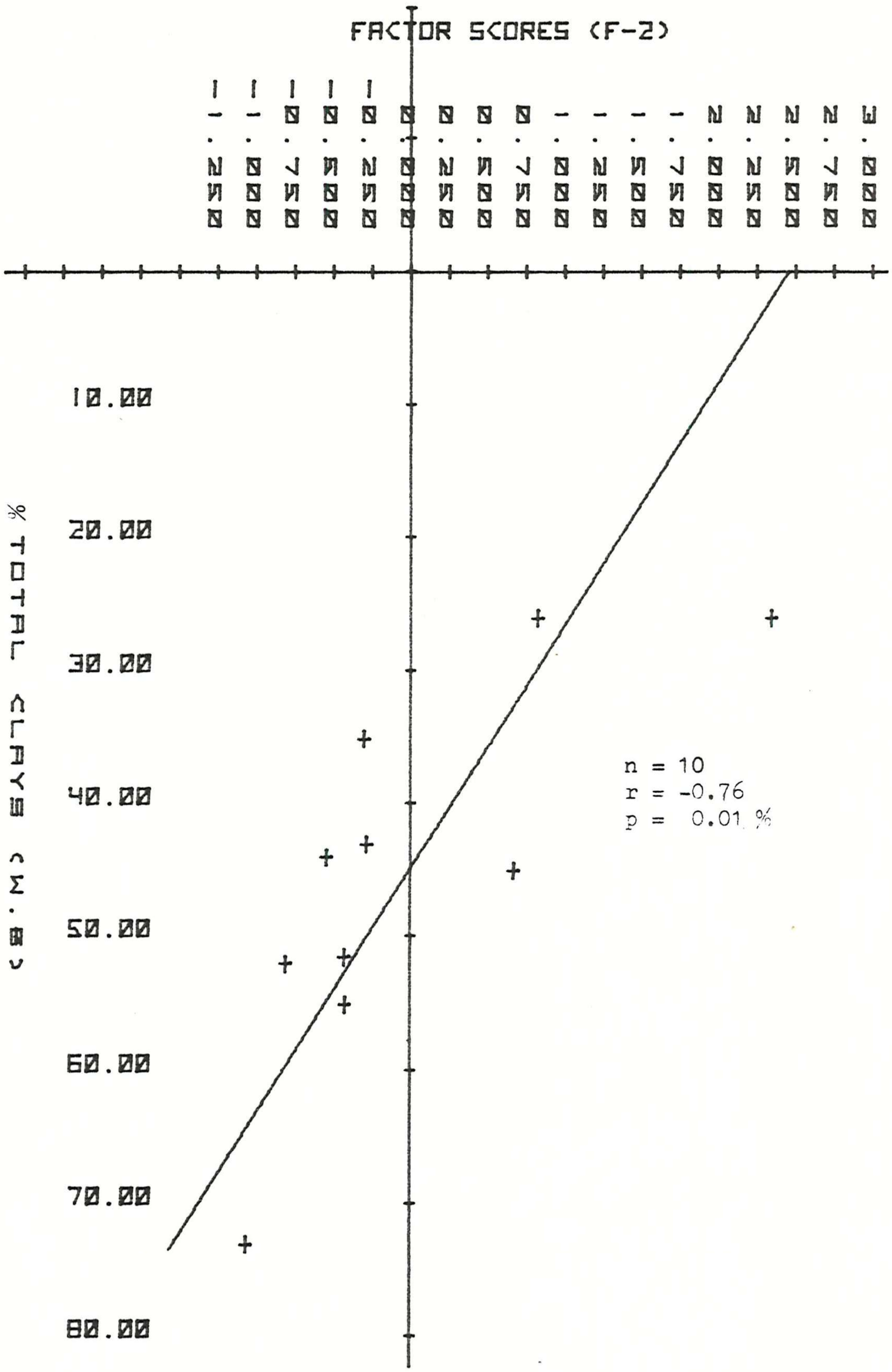

FACTOR SCORES (F-2)
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
% TOTAL CLAYS (W.B)
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
n = 10
r = -0.76
p = 0.01 %

FIG.(6.2.1)

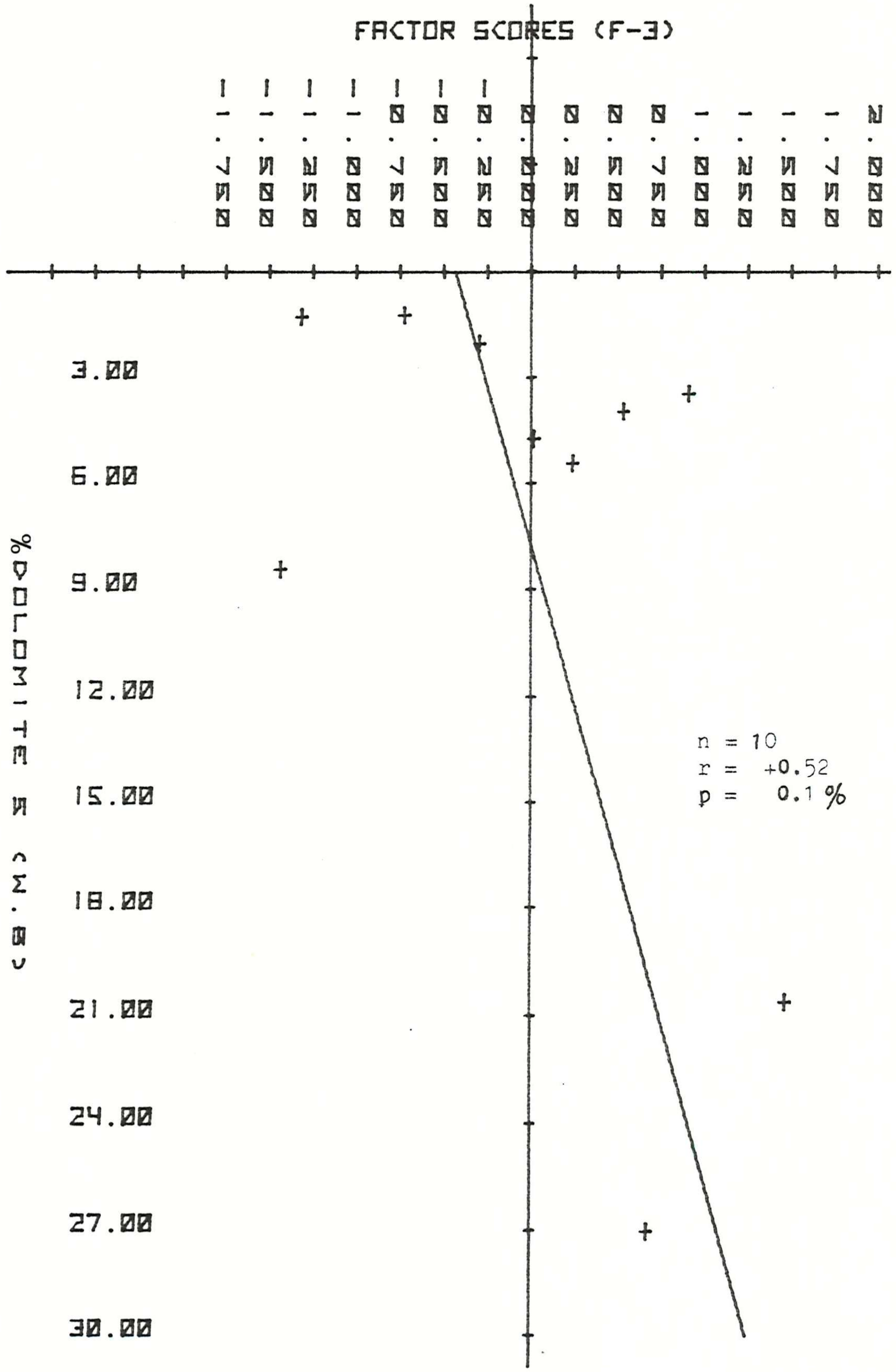
associated with a phase other than those listed in Table (6.2C), like the (W.K.B.) sediments, which in all probability is Mn-oxides/ hydroxides.

Factor (F-2)

This factor explains 18·73% of the total variance. It shows strong loadings of Al, K, Cu and Fe only in the negative phase. The high loadings of Al and K, being lithophile elements, suggest that this phase represents the control of detrital clay minerals over the loaded elements. Therefore this factor is interpreted as the total clay factor. The inter-factor correlations in Table (6.2D) indicate that Factor (F-2) is strongly and negatively correlated with Factor (F-1), which has been interpreted as Mn-oxides/hydroxides factor. The strong relationship of the detrital clays with Mn-oxides/hydroxides has been mentioned in Factor (F-1). Figure (6.2.1) shows a very strong negative correlation ($r = -0{\cdot}76$; significant at the 0·01% level) between the abundances of total clays, shown in Appendix (3.2), and the factor scores of Factor(F-2), tabulated in Table (6.2E). This confirms that the major variance of the lattice-held amounts of Al, K, Cu and Fe is controlled by the total clays in their lattices. There is a marked difference in the associations of the lattice-held elements with clay factors in the samples from the two boreholes. The clay factor of the (W.K.B.) contains elements such as Mg, Cr, Ni and Na, in addition to Al and K, and this clearly suggests a strong influence of the basic igneous rocks on the detritus of the sediments of the (W.K.B.) as compared to those of the (W.B.). The interpretation of Factor (F-2) of the (W.B.) sediments is further confirmed by the results summarized in Tables (6.2C and 6.2F).

Factor (F-3)

This factor shows strong positive loadings of elements Mg and Fe, and a strong negative loading of Na, and moderate to low negative loadings of Cr, Cu and Ni. The association of Mg and Fe in the positive phase suggests the occurrence of dolomite(ferroan). According to the observations of PAPAVASILIOU (1979), some dolomite is leached by the acid-reducing agent. The sediments of the (W.B.) contain dolomite(ferroan), and it is therefore possible that the present association of the lattice-held Mg and Fe reflects the presence of the unattacked fraction of the said dolomite. Therefore this factor is interpreted as the 'dolomite'



n = 10
r = +0.52
p = 0.1 %

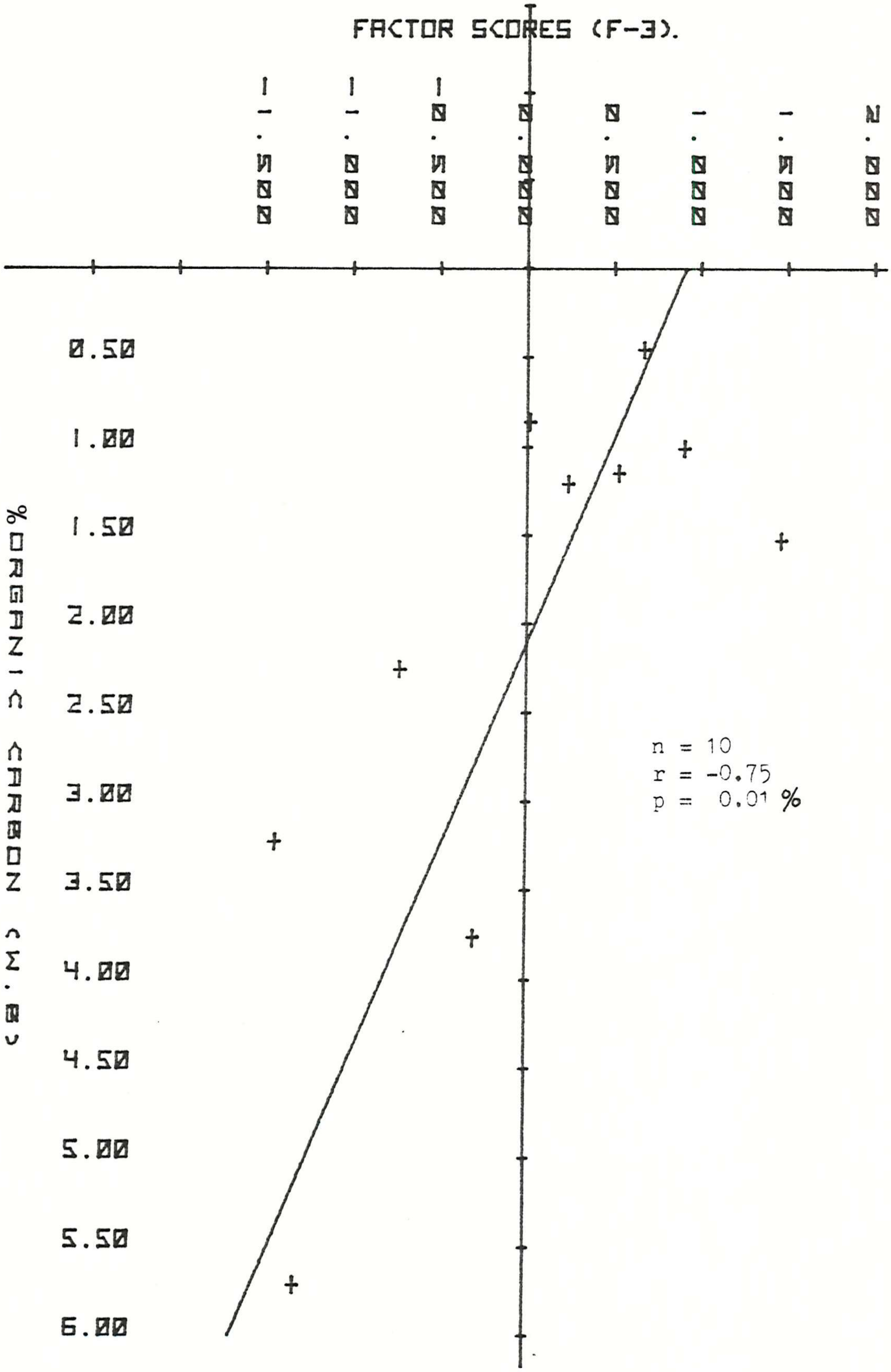
FIG.(6.2.2)

factor controlling the variance of Mg and Fe. The inter-factor correlations in Table (6.2D) indicate a very strong negative correlation (r = -0·3126) of Factor (F-3) with Factor (F-1). The negative phase of Factor (F-1) shows only one loading of Sr. The relationship of Sr with dolomite and the origin of dolomite in these sediments have been explained in Factor (F-4) in Chapter Five. Figure (6.2.2) shows a medium strong positive correlation (r = +0·52; significant at the 0·1% level) between the abundances of dolomite in the studied samples, tabulated in Appendix (3.2), and the factor scores of Factor (F-3), shown in Table (6.2E). The scatter shows that points are departed from the regression line, which confirms that a significant proportion of dolomite was leached by the acid-reducing agents, as observed by PAPAVASILIOU (1979). This interpretation of Factor (F-3) is further confirmed by the two summaries given in Tables (6.2C and 6.2F).

The negative phase of this factor shows strong loading of Na, moderate loadings of Cr and Cu, and a very low loading of Ni. The inter-factor correlations in Table (6.2D) indicate a strong positive correlation of Factor (F-3) with (F-2), indicating the strong relationship of the phases of the two factors. Factor (F-2) has been interpreted as the 'total clays' factor. Table (6.2C) shows that, among clay minerals, chlorite is the only mineral which showed association with the lattice-held Na. The presence of Na in this factor may be due to the described relationship with chlorite, as well as being due to the presence of Na-bearing feldspar. The other two elements, i.e. Cr and Cu, show association with organic carbon; the association of Cu is much stronger than that of Cr, being strongly correlated, significant at the 0·01% level, as shown in Table (6.2C). The association of minor elements such as Cr and Cu with organic material is well documented (PRICE, 1976). The association of organic carbon with clays in marine sediments is also a well-established fact. The positive correlation of Factor (F-3) with Factor (F-2), which represents clays, also confirms this relationship. Figure (6.2.3) shows a strong negative correlation (r = -0·75; significant at the 0·01% level) between the abundances of C_{org}, shown in Appendix (3.2), and the factor scores of Factor (F-3), tabulated in Table (6.2E), which also confirms the derived conclusions.

c) Discussion

Some of the more geochemically significant features noticed in the



n = 10
r = -0.75
p = 0.01 %

FIG.(6.2.3)

results tabulated in the tables and appendices are listed.

(1) Element Ti showed enriched values in the leached residue in all the samples except BR-1583 and BR-1755, as shown in Appendix (6.2A). It indicates that Ti in all the samples is present in the strongest lattice-held part of the clays.

(2) Element Al showed enriched values in the residue in most of the samples with the exception of BR-988, BR-1301 and BR-1583. This may be due to the degraded nature of clays in those samples.

(3) Fe showed depleted amounts in most of the samples, with the exception of BR-627, BR-1424, BR-1734 and BR-1771, which showed enriched values. These samples, as shown in Table (6.2B) contain the high abundances of dolomite, chlorite and pyrite, in samples BR-627 and BR-1424, and the highest abundances of chlorite, kaolinite, C_{org} and a significantly higher amount of total clays in sample BR-1734. Sample BR-1771 contains the highest abundances of illite, mixed-layer(illite-montmorillonite), kaolinite, pyrite, total clays, and a significantly high amount of C_{org}. This sample in Table (6.2B) also shows the highest abundances of lattice-held elements such as Ni, Cu, Sr, Pb, Cr and Fe. These associations explain the observed relationships.

(4) Mg showed much depleted amounts in the residue of all the samples, due to its association with dolomite and chlorite; both minerals are significantly leached by the acid-reducing agent (PAPAVASILIOU, 1979). Elements Mg and Sr show high abundances in sample BR-1734, which contains higher abundances of mixed-layer, illite and chlorite; it confirms the relationship of Mg and Sr with the mentioned minerals.

(5) Na is depleted in all the samples except BR-278 and BR-988. The observed depletion of Na in the majority of the samples suggests its structural position most probably in the inter-layer position of clay minerals. The slightly higher amount of Na in the residues of samples BR-278 and BR-988 may suggest the presence of Na-bearing feldspar in these samples.

(6) K showed depleted values in all the samples, with the exception of BR-278 and BR-1771. It is well-known (WEAVER and POLLARD, 1973) that K occupies the inter-layer position in the structure of clay minerals; therefore it can be relatively easily leached out.

The slightly high value of K in samples BR-278 and BR-1771 may be related to the presence of K-bearing minerals in BR-278, and the highest abundance of illite and total clays in sample BR-1771 respectively.

(7) Phosphorus is depleted in all the samples due to the obvious reason of its association with carbonate minerals, the most soluble phases, present in the studied sediments.

(8) Sulphur showed depleted values in all the samples except samples BR-627, BR-1424, BR-1734 and BR-1755. It may be related to the variable abundances of pyrite in these samples.

(9) Pb showed entirely non-lattice-held (non-lithogenous) character in all the samples except BR-1771, which contains the highest abundance of total clays, illite, mixed-layer and pyrite. Pb may be associated with any of these phases.

On the basis of the observed lattice-held characters of elements in the studied sediments, they may be grouped into four main groups, exactly on the same basis as was done in the case of the (W.K.B.) sediments. The proposed groups are as follows:

Group One:	Cr, K, Al	(> 80%)
Group Two:	Cu, Mg, Fe	(61 - 80%)
Group Three:	Zn, Mn, Na, Ni, Sr	(20 - 60%)
Group Four:	Pb	(0 - 20%)

Group One: It contains elements Cr, K and Al, which are strictly of lithogenous origin and belong to the lithophile group. These elements are detrital in origin. The association of Cr in this group suggests a strong influence of the detrital (lithogenous) material on the studied sediments. Cr is known for its detrital origin (RILEY and CHESTER, 1971; CHESTER and ASTON, 1976). The higher abundance of illite and total clays in the (W.B.) sediments may also be responsible for the observed trends.

Group Two: This group contains only three elements, i.e. Cu, Mg and Fe, as compared with the same group in the (W.K.B.) sediments, which contains Fe, Cr, Mg and Cu elements. This association suggests a lower influence of the basic igneous rocks on the detritus, because here Mg and Fe are due to the presence of dolomite.

Group Three: It contains the same elements as grouped in Group Three of the (W.K.B.) sediments, but with different lattice-held trends. It indicates similar relationships of the elements and phases as observed in the (W.K.B.) sediments. The striking difference is that elements such as Zn and Mn in the (W.B.) sediments are associated with easily soluble phases, and Sr with a lithogenous fraction.

Group Four: It shows only one element, i.e. Pb, which displayed its entire association with a non-lithogenous fraction, and indicates its non-lithogenous origin.

d) Conclusions

The observations of the leaching study lead to the following conclusions:

(1) Elements Cu, Mg, Fe, Cr, K and Al showed a higher lattice-held character, ranging from 67% to 98%. It may be due to higher abundances of the individual clay mineral species, total clays and dolomite etc., present in the studied sediments. These relationships also reflect a strong influence of a detrital phase on the sediments of the (W.B.).

(2) Nickel showed only 43% lattice-held character, indicating its association mainly with the easily soluble phases such as sulphides and organic matter.

(3) Mn and Zn respectively showed 28% and 20% lattice-held character, which is much lower than observed in the (W.K.B.) sediments. It indicates the presence of Mn-oxides and easily soluble compounds of Zn in the studied sediments.

(4) Na showed 36% lattice-held character, which is slightly higher than observed in the (W.K.B.) sediments. It reflects the presence of Na-bearing feldspar and a stronger association of Na with clays in the (W.B.) sediments.

(5) Sr showed 47% lattice-held character, which is much higher than the (W.K.B.) sediments. It is due to its association with Mn-oxides/hydroxides and dolomite in the (W.B.) sediments.

(6) Pb showed an identical character in both the boreholes, and seems to be of non-detrital origin.

CHAPTER SEVEN

MINERALOGY AND GEOCHEMISTRY OF THE CLAY FRACTION ($< 2\mu$) OF THE (W.K.B.) AND (W.B.) BOREHOLE SEDIMENTS

1. Mineralogy
2. Geochemistry

7.1 Mineralogy of Clay Fraction ($< 2\mu$)

Introduction

1. Aims of the Study:

The purpose of the study of mineralogy of clay fractions ($< 2\mu$) of sediments of the Oxford Clay and Kellaways Formations from the (W.K.B.) and(W.B.) samples was to (i) identify the clay mineral species present in these sediments; (ii) to observe the stratigraphic and geographic variations of the clay mineral suites; (iii) to quantify the abundances of clay minerals; and lastly (iv) to observe if there is any relationship between the abundances of clay minerals and the chemical components in the studied sediments. Characteristics of the common clay minerals are shown in Table (7. 1).

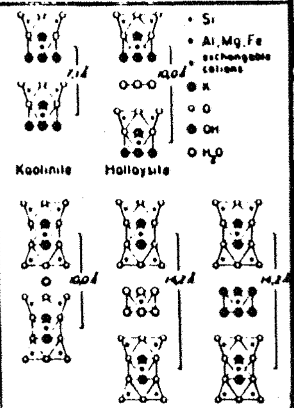
2. Identification of Clay Minerals:

The various clay mineral species present in the sediments of the two boreholes were identified by running specially prepared oriented slides of the clay fraction ($< 2\mu$) on a Philip's PW1010 X-ray Diffractometer. Details regarding the sample preparation and the diffractometry etc. are given in Chapter Two (2.II.1(a) & 2.II.1(b)).

The presence of specific clay mineral species was detected by the (001) reflections of the individual species. The clay fraction of the (W.K.B.) sediments indicated the presence of clay mineral species such as illite, kaolinite, chlorite and smectite (montmorillonite-illite mixed-layers). The clay fraction of the (W.B.) sediments contains the same species, with the exception of smectite, which has been replaced by a non-expanding mixed-layer clay mineral. BROWN (1954) called such mineral 'degrading illite'. The peak positions on which the various clay mineral species were identified, after various treatments which help in their identification, are shown in Figures (7.1a & 7.1b) and Table (2.6) in Chapter Two. Figures (7.1a & 7.1b) also show the variations of the crystallinity of illite, kaolinite and the expandability of the smectite with respect to the depth in the boreholes.

3. Semi-Quantitative Estimation of Clay Minerals:

Many methods are published for the estimation of relative abundances of clay minerals in sediments. Each method has its merits and demerits, but none of the methods can claim to be 100% satisfactory.

CLASSIFICATION OF PRINCIPAL CLAY MINERALS IN SEDIMENTS (EXCLUDING IMPURE MINERALS AND AMORPHOUS PHASES)								Basal diffraction spacings (Å) Various treatments				Mineral	Structural Cartoon
LAYERS	POPULATION OF OCTAHEDRAL SHEET	EXPANSION	GROUP	SPECIES	CRYSTALLOCHEMICAL FORMULA	SPACE GROUP	STRUCTURE (SCHEMATIC)	Air Dried	Glycolated	300°C	550°C		
Two-Sheet (1 1)	Dioctahedral	Non-Swelling	Kaolinite	Kaolinite Dickite Nacrite	$Al_4(OH)_8[Si_4O_{10}]$	Cc or P1 Cc Cc or R3c		7, 3·5 etc	7	7	Destroye	Kaolinite	
		Non-Swelling and Swelling	Halloysite	Halloysite Metahalloysite	$Al_4(OH)_8[Si_4O_{10}] \cdot (H_2O)_4$ $Al_4(OH)_8[Si_4O_{10}]$	Cm							
	Trioctahedral	Non-Swelling	7Å-Chlorite (Septechlorite)	Berthierine ("Kaolin-Chamosite")	$(Fe^{2+},Fe^{3+},Al,Mg)_6(OH)_8[(Al,Si)_4O_{10}]$	Cm							
Three-Sheet (2 1)	Dioctahedral	Swelling	Montmorillonite * (Smectite)	Montmorillonite Beidellite Nontronite	$\{(Al_{2-x}Mg_x)(OH)_2[Si_4O_{10}]\}^{-x}Na_x \cdot nH_2O$ $\{Al_2(OH)_2[(Al,Si)_4O_{10}]\}^{-x}Na_x \cdot nH_2O$ $\{(Fe^{3+}_{2-x}Mg_x)(OH)_2[Si_4O_{10}]\}^{-x}Na_x \cdot nH_2O$	Monoclinic		14, 7, 3·5 etc	17	10	10	Montmorillonite	
		Non-Swelling	Illite * (hydromica)	Illite-Varieties	$(K,H_3O)Al_2(H_2O,OH)_2[AlSi_3O_{10}]$	C2/m or Cm		10, 5, 3·33 etc	10	10	10	Illite	
	Trioctahedral	Swelling	Vermiculite **	Vermiculite	$(Mg,Fe)_3(OH)_2[AlSi_3O_{10}]Mg \cdot (H_2O)_4$	Cc		14, 7, 3·5 etc	14	10	10		
Three-Sheet-One-Sheet (2 2)	Trioctahedral	Non-+ Swelling	14Å-Chlorite ** (Normal Chlorite)	Chlorite-Varieties	$(Al,Mg,Fe)_3(OH)_2[(Al,Si)_4O_{10}]Mg_3(OH)_6$	Monoclinic		14, 7, 3·5 etc	14	14	14	Chlorite	

* also trioctahedral varieties } less common
** also dioctahedral varieties }
\+ swelling chlorites are rare and intermediate forms between vermiculite and chlorite

▭ Octahedral Sheet
⏢ Tetrahedral Sheet
K Potassium Ions

TABLE (7.1): This table shows the characteristics of clay minerals. It has been modified from Table 1 given by DEGENS (1965).

FIG.(7.1a): Showing the effects of glycolation on clay mineral species from three different depths in the Winterborne Kingston Borehole. Details of each sample are as under:

S.No.	Depth in B/H	V/h ratio	C.I.W.	C.I.I. 2θ degrees	C.I.K. 2θ degrees
A. WBK-5	480 m.	0·70	3·00	0·40	0·30
B. WBK-30	558 m.	0·45	4·40	0·20	0·25
C. WBK-62	663 m.	0·43	5·16	0·24	0·23

FIG.(7.1b): Showing the effects of glycolation on clay mineral species from three different depths in the Warlingham Borehole. Details of each sample are as under:

S.No.	Depth in B/H	C.I.W.	C.I.I. 2θ degrees	C.I.K. 2θ degrees
A. BR-145	961·30 m.	2·08	0·70	-
B. BR-1123	1032·50 m.	2·70	0·50	0·40
C. BR-1852	1060·40 m.	2·40	0·50	0·20

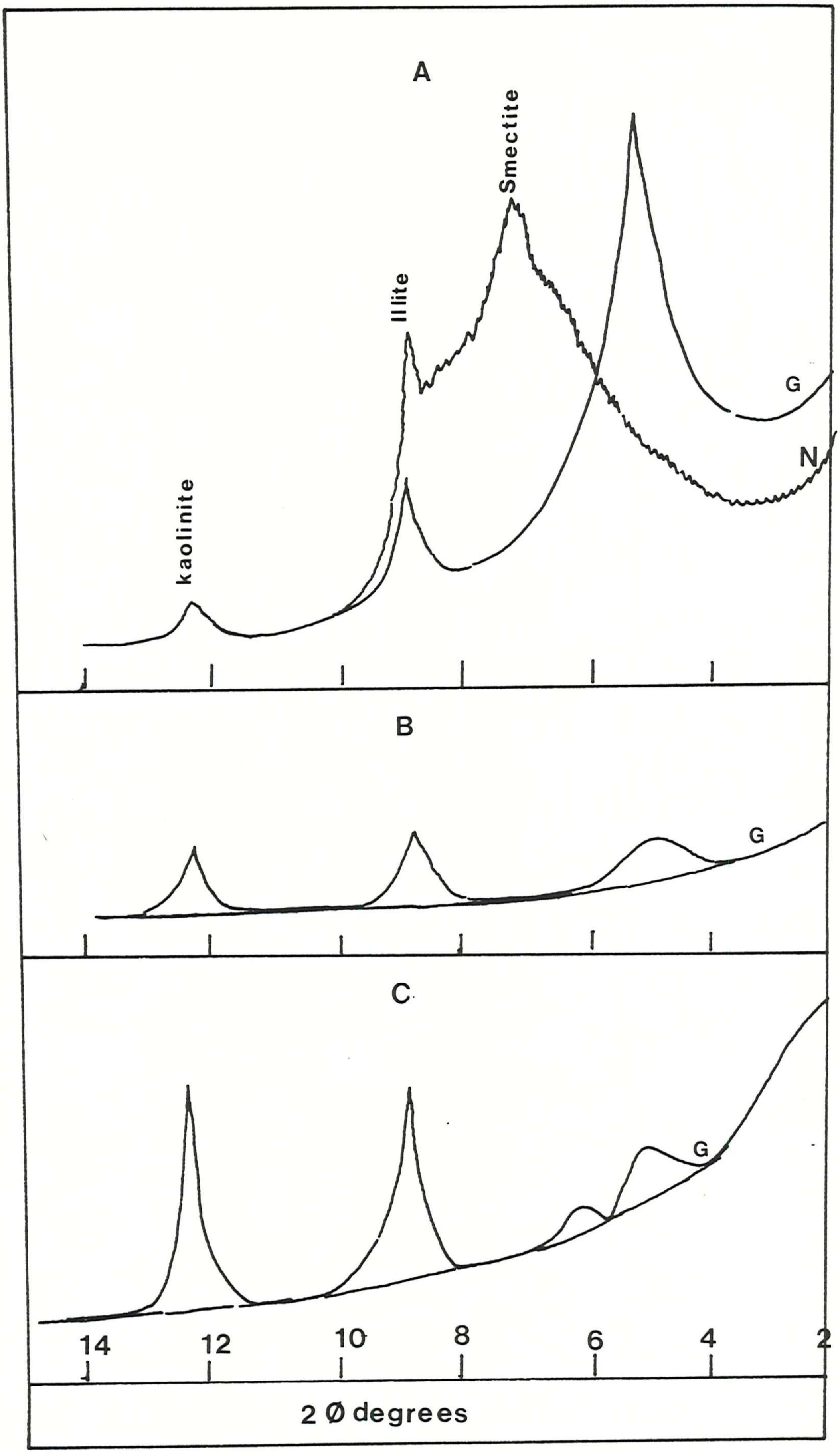


FIG (7·1a)

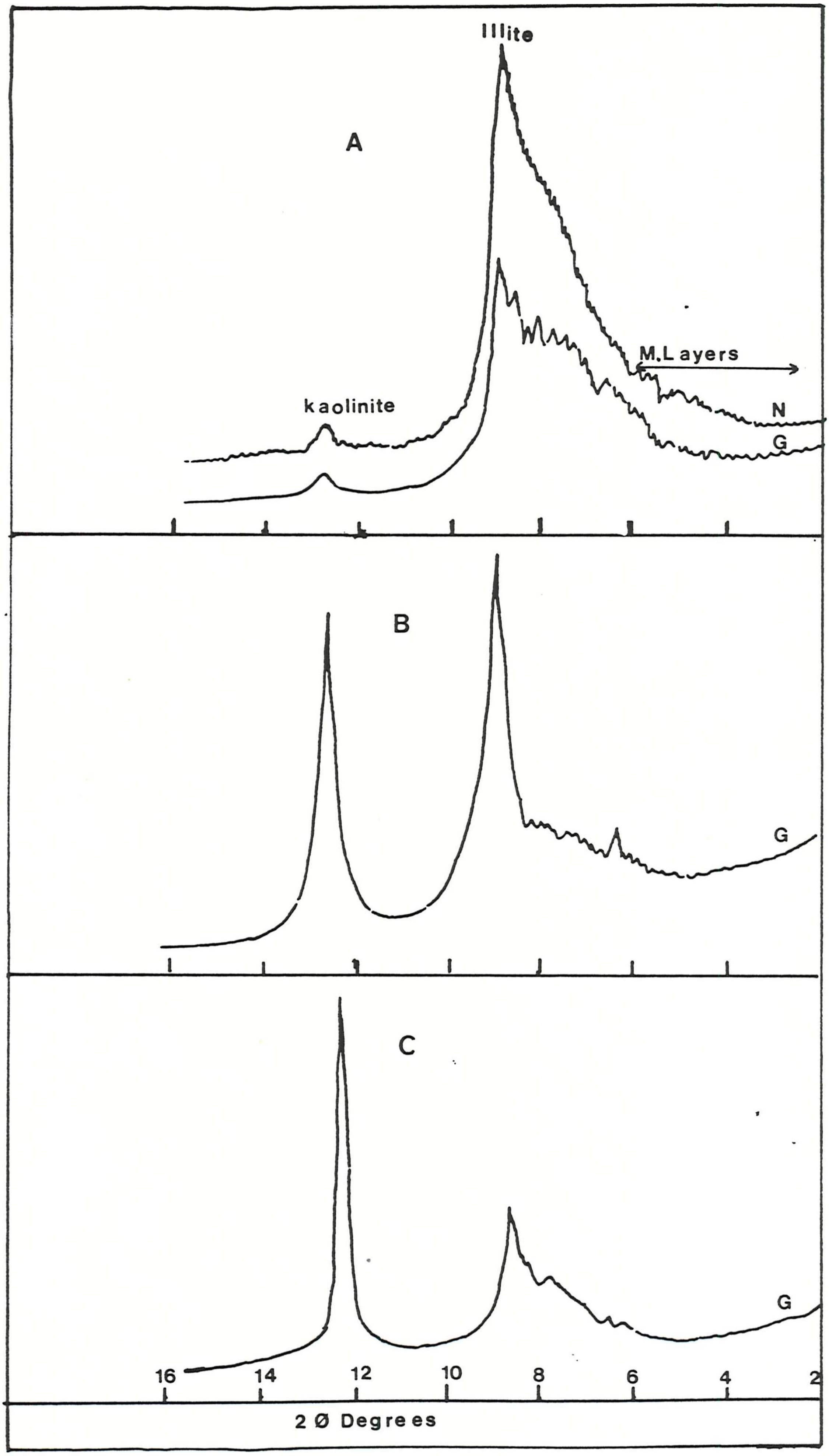

Illite
A
kaolinite
M.Layers
N
G
B
G
C
G
16
14
12
10
8
6
4
2
2 Ø Degrees

FIG (7·1b)

In the present study, a method used by MATTER (1974) was applied. The main reason for the selection of this method was the great similarity of the clay mineral species in the present sediments with those calculated by MATTER (op.cit.). In this method the areas under the peaks of 17Å for smectite, 10Å for illite and 7Å for kaolinite and chlorite were measured on the glycolated slides, Kaolinite and chlorite give a common peak at 7Å, and for this reason it is difficult to estimate how much of the 7Å peak belongs to kaolinite and how much to chlorite. BISCAY (1964 & 1965) and MATTER (1974) recommended that the 7Å peak can be divided between chlorite and kaolinite areas according to the peak height ratio at 3·53 to 3·55Å and 3·57 to 3·60Å respectively. Unfortunately, peaks mentioned above were not distinct in the majority of the samples of the two boreholes; therefore, this technique was not generally applicable for resolving the chlorite and kaolinite areas. Discrimination between chlorite and kaolinite in the present samples was achieved by such treatments as acid digestion (1:1 HCl) and heating of the samples at 550°C for two hours. Details regarding these treatments are given in Chapter Two (2.II.1(a) and 2.II.1(b)). For the estimation of the relative abundances of clay minerals, illite was used as an internal standard, and the remaining clay minerals were compared with it. The relative abundances were calculated by multiplying the peak areas of individual clay minerals on a glycolated slide by the factors as follows:

17Å peak area for smectite	x	$^1/_4$
10Å peak area for illite	x	$^1/_1$
7Å peak area for kaolinite	x	$^1/_2$
7Å peak area for chlorite	x	$^1/_2$
11·04Å to 14Å area for mixed layer mineral	x	$^1/_3$

The above results were normalized to 100%. The relative abundances of the clay minerals thus obtained for the (W.K.B.) and (W.B.) samples are tabulated in Appendices (7.1A and 7.2A) respectively.

4. Previous Work:

Clay mineral suites of the Oxford Clay sediments have been studied by many workers, including FREEMAN (1956, 1958 & 1964), COSGROVE and SALTER (1966), PERRIN (1971), JACKSON (1972), JACKSON and FOOKES (1974), WEIR and RAYNER (1974), ATTEWELL and TAYLOR (1973), and RUSSELL (1977). These authors studied clay mineral suites in specific parts of the Oxford Clay Formation. None of these authors have studied the clay mineral suites of the complete succession of the Oxford Clay Formation. FREEMAN (op.cit.) mentioned that illite is the dominant and kaolinite is the subsidiary clay mineral in the Oxford Clay sediments. PERRIN (op.cit.) stated that the Lower Oxford Clay from the S.E. Midland areas contains only two clay minerals, i.e. illite (65 to 80%) and kaolinite (20 to 35%). The same author reported that the Upper Oxford Clay from the Dorset area contains illite (40 to 70%), smectite (5 to 40%), kaolinite (11 to 31%) and chlorite (4 to 10%). JACKSON and FOOKES (op.cit.) mentioned that the Lower Oxford Clay contains illite (54 to 75%), kaolinite (21 to 45%) and chlorite (from 0 to 4%). ATTEWELL and TAYLOR (op.cit.) reported the presence of mixed-layer clay minerals, but quantified them with illite. RUSSELL (op.cit.), during a study of the effects of weathering on the physical and chemical properties of some Mesozoic clays, collected from the seven weathering profiles from the Midlands and southern England, has mentioned the presence of illite, kaolinite, chlorite, mixed-layer minerals and montmorillonite in the sediments of the Oxford Clay. He stated that illite is the most abundant clay mineral (30 to 55%). WEIR and RAYNER (op.cit.) reported the presence of an interstratified ($\approx$45% expanding and 55% non-expanding interlayers) illite-smectite from the weathered Oxford Clay from Denchworth series soil. CHOWDHURY (1980), in the study of the Corallian sediments, examined clay minerals in a few samples from the Upper Oxford Clay. He mentioned the presence of illite, kaolinite, chlorite and mixed-layer minerals. The clay mineral findings of the present author are in good agreement with the findings of the earlier workers.

5. Stratigraphic Variations of Clay Minerals:

The relative abundances of the clay minerals in the (W.K.B.) and (W.B.) sediments show variable relationships with depth in the boreholes, as shown in Figures (7.3a and 7.3b). The observed variations provide some clues regarding the genetic relationship of clay minerals and their provenance, conditions of weathering, transportation and rates of sedimentation etc. of the studied sediments. Table (7.1A3) exhibits a sympathetic relationship of illite, kaolinite and chlorite with depth, and an antipathetic relationship with smectite. These variations clearly suggest, for the entire sequence, a common source for illite, kaolinite and chlorite, and a separate source for smectite. The sediments of the (W.B.) in Table (7.1B3) indicate an antipathetic relationship of illite, mixed-layer minerals and chlorite with depth and kaolinite. These trends suggest a common source for the described minerals in the (W.B.) sediments. Here kaolinite is the only mineral which showed a sympathetic relationship with depth in the borehole. It may suggest the near-shore and offshore nature (shifting of shorelines) for the deposition of the sediments at the Warlingham site. The sympathetic relationships of illite, kaolinite and chlorite in the (W.K.B.) sediments and the antipathetic relations of these minerals in the (W.B.) sediments with depth may be related to a number of factors, such as rock types from which these minerals were derived, the nature of the weathering and the rate of deposition for the respective borehole sediments.

The relative abundances of illite might have been calculated over-generously, particularly in the case of the (W.B.) samples, due to the presence of mixed-layer minerals, which do not expand on glycolation. This created a problem in the accurate counting of areas for illite and mixed-layer minerals. To solve this problem, the illite peak on the glycolated slide was extended, as shown by the broken lines in Figure (7.1c). The illite area was counted from 'a-b' within the extended peak. This extension of the illite peak sometimes may not be very accurate as compared to the original illite peak. Therefore, it is possible that areas counted for the illite peak in this way may be exaggerated and could ultimately give over-generous estimations of illite abundances. Tables (7.1A3 and 7.1B3) show the average values of clay minerals of 12 samples for the sediments of each borehole, from the divisions of the Oxford Clay and Kellaways Formations. These tables also show the average values of K_2O determined in the bulk rock samples, and are on an absolute basis. Assuming that all K_2O is associated with illite, abundances of illite are calculated and are shown in parenthesis. These vallues are much lower than the values determined by the X.R.D. and therefore confirm the over-generous estimation of illite.

6. Crystallinity of Clay Minerals:

The crystallinity indices of clay minerals, particularly of

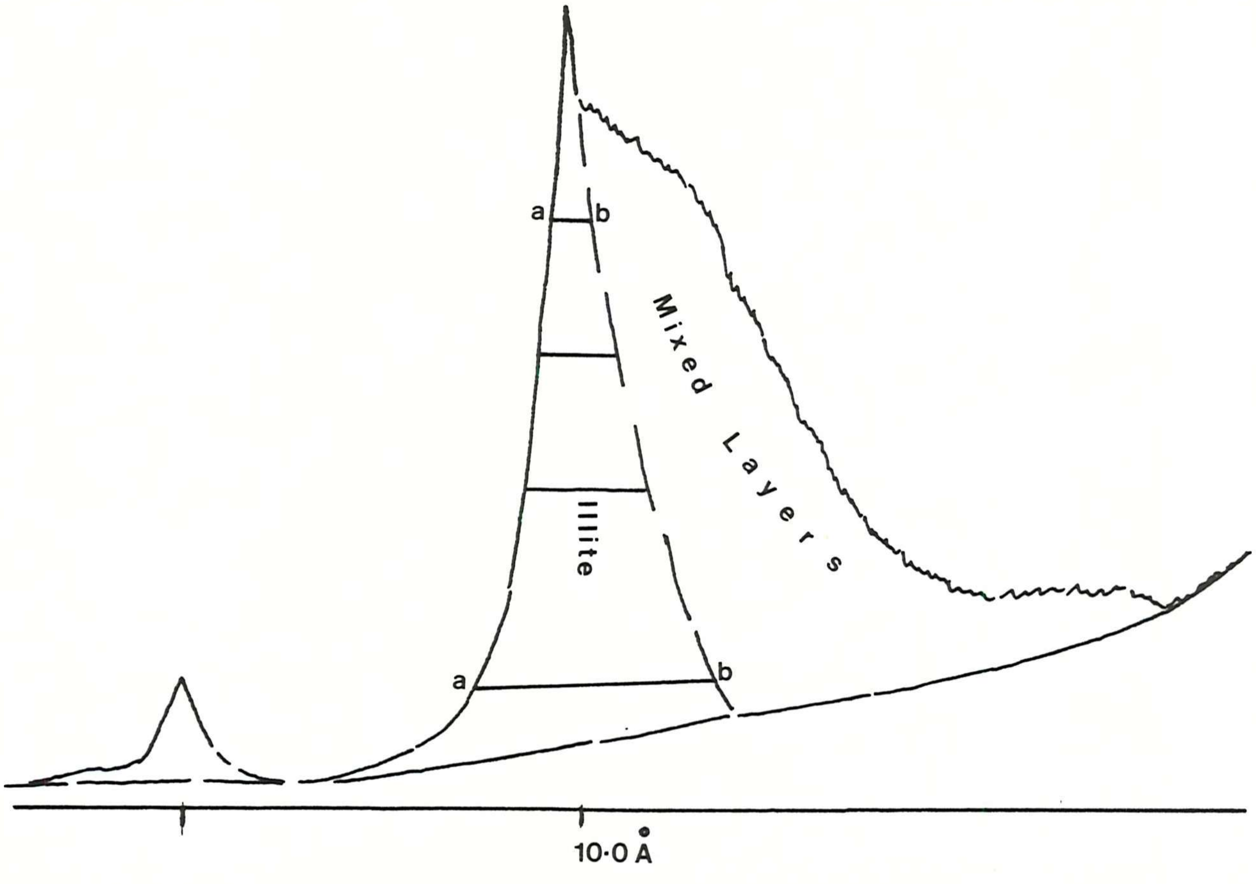


FIG.(7.1c): Shows how the area for the illite peak was measured on a glycolated slide. The remaining area towards the 2θ degrees was counted as mixed-layer minerals.

illite, have been studied by many workers. According to KUBLER (1967) the 10Å peak of illite varies in character with increasing depth of burial, and also with increasing temperature. The peak becomes sharper and narrow as these effects progress. Two main indices are proposed for the quantification of these changes. These indices have been used widely by many workers as indicators to distinguish between diagenetic states, anchizone or transitional grades and epizone or greenschist metamorphism. WEAVER (1960, 1961) determined the 'sharpness ratio' of the 10Å and 10·5Å peaks minus background for the crystallinity of illite, and on this basis established zones of very weak metamorphism. JARON (1967) mentioned that crystallinity of illite decreases upwards in a weathering profile. CHAMLEY (1967, 1968) used the data of the crystallinity of illite in the Mediterranean muds to disclose the evidence of the climatic changes during the Quaternary. It is known that under cold conditions of climate, less weathering takes place; therefore, illite in such sediments shows a better crystallinity. DUNOYER DE SEGONZAC (1969, 1970) stated that detrital illite displays a higher crystallinity because the particles are large. Fine granular particles are more sensitive to degradation and hydration during the processes of weathering and transportation; due to this reason the siltstones show better crystallinity than the fine-grained clays or shales. DUNOYER DE SEGONZAC (op.cit.) stated that palaeogeographic conditions influence the crystallinity of illite as a consequence of the effects of weathering. The same author further mentioned the great influences of geochemistry and the burial diagenesis of the sediments on the crystallinity of clay minerals. BRAZIER et al. (1979) studied the crystallinity of illite in the Devonian and Carboniferous pelitic rocks in the south-west of England, and distinguished the grades of metamorphism.

In the present study the crystallinity of illite and kaolinite were measured. Crystallinity of illite was measured as 'sharpness ratio' proposed by WEAVER (1960, 1961), in which the heights of 10Å and 10·5Å peaks are measured by minimising the background, and a ratio is calculated which gives the crystallinity of illite. The value of this ratio increases with the increase in the sharpness of the illite peak, and is directly proportional to the true crystallinity of illite. Another method for the measurement of crystallinity is that proposed by KUBLER (1968) which is also called 'Peak-width' or 'Kubler index' (DUNOYER DE SEGONZAC et al., 1968). In this method the width of the 10Å peak at half height above the background was measured in 2Θ degrees. The width of the peak reduces with the increase of sharpness of the peak, so this index is inversely proportional to the true crystallinity of illite.

The crystallinity of kaolinite was also measured by measuring the width at half height of the (001) reflection of kaolinite at 7·12Å above the background. The illite crystallinity was determined on the glycolated slides due to the presence of mixed-layer minerals, and that of kaolinite on the heated slides, due to the presence of chlorite.

The crystallinity indices determined for illite and kaolinite for the (W.K.B.) and (W.B.) sediments are tabulated in Appendices (7.1A and 7.2A) respectively. Figure (7. 2a) illustrates the methods used for the determination of crystallinity indices. Tables (7.1A3 & 7.1B3) show the trends of the crystallinity indices of illite and kaolinite with respect to the depth in the respective boreholes. From these tables, it is clear that the sediments of the (U.O.C.) contain poorly crystalline illite in both boreholes. The best crystallinity of illite in the (W.K.B.) sediments is present in the (K.F.) samples, and in the (W.B.) sediments it is associated with the (M.O.C.) samples. On the whole, the (W.B.) sediments exhibit a poor crystallinity as compared with the (W.K.B.) sediments. It means that the (W.B.) sediments, on the whole, contain a more degraded type of illite than the sediments of the (W.K.B.). This variation may be related to the type of source rocks for the respective sediments. This information supports the idea of a recycled sedimentary provenance for the (W.B.) sediments, and an igneous or metamorphic provenance for the (W.K.B.) sediments. This information may also give some clue regarding the conditions of weathering, as suggested by JARSON (1967). The poorest crystallinity of illite exhibited by the (U.O.C.) sediments of both the boreholes may suggest the intensive nature of weathering in the areas of the supply of detritus and at the time of deposition. The better crystallinity of illite in the (M.O.C.) and (L.O.C.) sediments of the (W.B.) may be related to a number of factors such as rate of sedimentation, lack of weathering, effects of burial and probably a prolonged contact of sediments with the sea-water. Degraded illite may be aggraded by the substitution of

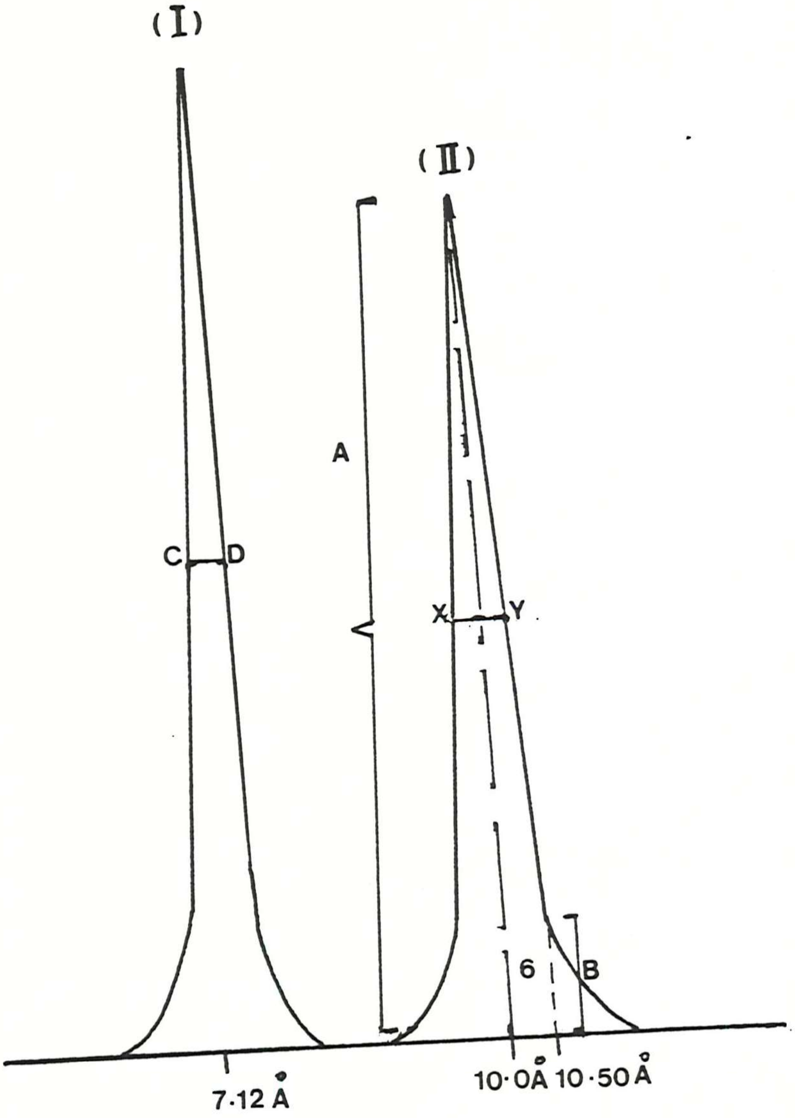


FIG.(7.2a): Measurement of crystallinity of kaolinite (I) at 7·12Å and illite (II) at 10·0Å respectively (KUBLER, 1968; WEAVER, 1960 & 1961).

potassium from the sea-water, as a result of prolonged contact of sediments with sea-water.

7. Estimation of Expandable Layers in Smectite

Sediments of the (W.K.B.) only contain smectite composed of expandable layers. A careful observation of the X.R.D. diffractograms shows concentration of smectite in the Upper Oxford Clay, which is also shown in Table (7.1A3), which shows an antipathetic trend of the abundances of smectite with depth. The smectite in the Upper Oxford Clay contains higher amounts of expandable layers ($>$ 60 and $<$ 80%). There exists a gradual decrease in the percentage of expandable layers in smectite with the increase of depth in the bore-hole, as is shown by the trends of V/h and V/P ratios in Table(7.1A3).

The nature of interstratification in mixed-layer illite-montmorillonite has been studied by many workers including REYNOLDS and HOWER (1970), HOWER and MOWATT (1966), PERRY and HOWER (1970), WEAVER (1956), WEIR and RAYNER (1974), ESLINGER and SAVIN (1976) and BISCAY (1965).

Knowledge of the average percentage of expandable layers in illite/smectite is very important in the study of clay minerals. Studies of clay minerals in D.S.D.P. sediments have shown that random mixed-layers illite/smectite, having a very high percentage of expandable layers, are mainly authigenic and co-exist with zeolites and low contents of detrital minerals, e.g. illite, chlorite,kaolinite, feldspar, and quartz (GIESKES and KASTNER, 1975; ESLINGER and SAVIN, 1976). ESLINGER and SAVIN (1976) mentioned that illite-smectite mixed-layers, having lower percentages of expandable layers, are mainly detrital in origin, and are associated with significant amounts of detrital clay minerals such as illite, kaolinite, chlorite and other detrital components, which may include feldspar and quartz, etc.

REYNOLDS and HOWER (1970) stated that randomly mixed-layers illite-smectite,peaking at 17Å after glycolation, contain between 40% to 100% expandable layers. These authors have proposed a method for the estimation of the expandable layers in mixed-layer minerals, based on the fact that the d-values of $(001)_{10}$ illite/$(002)_{17}$ smectite and $(002)_{10}$ illite/$(003)_{17}$ smectite in glycolated samples vary according to

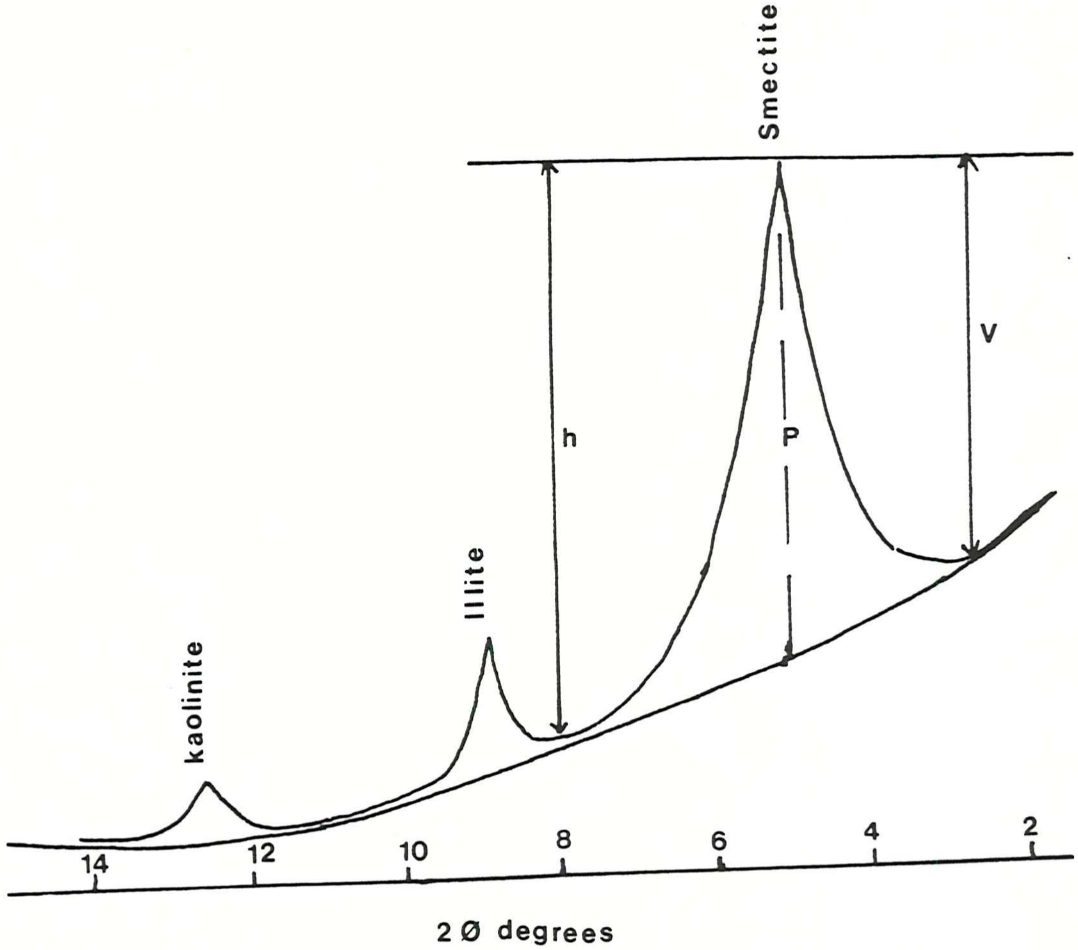


FIG.(7.2b): Shows the method of measurement of crystallinity and per cent expandable layers in smectite.

REYNOLDS & HOWER (1970) } V/h = 0·37, indicates 60% montmorillonite
and
ESLINGER & SAVIN (1976) } V/h = 0·77, indicates 80% montmorillonite

BISCAY (1965) mentioned V/P gives % of expandable layers; if the ratio is 1 it means 100% montmorillonite.

the composition of layers. ESLINGER and SAVIN (1976) proposed a method for the estimation of expandable layers on the basis of the 17Å peak of illite-smectite. They used the l/h parameter, where 'l' is the peak to trough distance on the low angle side and 'h' is the peak to trough distance on the high angle side of the 17Å peak. The l/h parameter shows a directly proportional relationship with the expandable layers. According to these authors "the calculated diffraction profiles of REYNOLDS and HOWER (1970) indicate that l/h values of 0·39 and 0·77 correspond to 60% and 80% of the expandable layers respectively.

This method of estimation of percentage of expandable layers seems to be more realistic in relation to the first one, described earlier, because the 17Å illite/smectite peak in glycolated samples is always distinct. BISCAY (1965) used the V/P ratio, where 'V' represents the depth of the 'valley' on the low angle side of the peak and 'P' indicates the height of the peak above the background. According to BISCAY (<u>op.cit</u>.), the V/P ratio indicates the degree of crystallization of the smectite within the mixed-layers illite/smectite. If the value of V/P is high, it indicates good crystallization, which may suggest that smectite is of authigenic origin. BISCAY (<u>op.cit</u>.) further mentioned that V/P values of 1 or just below 1 indicate a "perfectly to well-crystalline" nature of smectite, and the lower values indicate poor crystallization.

In the present study both parameters suggested by ESLINGER and SAVIN (1976) and BISCAY (1965) were measured for all the samples of the (W.K.B.) sediments. The l/h parameter of ESLINGER and SAVIN (<u>op.cit.</u>) is expressed as V/h. The measured values of V/h and V/P are tabulated in Appendix (7.1A). There is a good agreement between the two parameters in general, and both have shown an antipathetic trend for crystallinity with depth in the borehole. The highest and lowest average values of the V/h and V/P correspond to the highest and lowest averages of smectite, as shown in Table (7.1A3). Figure (7. 2b) shows the method for the determination of both parameters.

8. <u>Description of Clay Minerals</u>:

Sediments of both the boreholes contain the same species of clay minerals, with the exception of mixed-layer minerals. The sediments of the (W.K B.) contain expanding mixed-layer minerals, dominantly composed of montmorillonitic layers, and are called 'smectite'. The sediments of the (W.B.) contain an entirely different type of mixed-layer (non-expanding) minerals, and in the present thesis these are called by the name of 'mixed-layer minerals'. BROWN (1954), during a study of soil clays from Ireland, found a similar clay mineral in association with illite, chlorite, vermiculite and kaolinite, and called it 'Degrading illite'. Due to the complicated nature of mixed-layering in these minerals, no attempt has been made to identify the specific layer types. A description of each clay mineral species is given as follows:

Table (7.1.8a)

(a) ILLITE	(W.K.B.)	(W.B.)
Range	24 to 67%	58 to 77%
Highest abundance	63·75% (K.F.)	66·50% (U.O.C.)
Lowest abundance	42·60%(U.O.C.)	62·00% (K.F.)

The term 'illite' was proposed by GRIM et al. (1937) as a group name, after the State of Illinois in the U.S.A. Illite is the abundantly present mineral in the sediments of both the boreholes at present under observation. The average values of illite of 63 samples in the (W.K.B.) and 78 samples in the (W.B.) sediments are 53·54% and 65·63% respectively, which is in general agreement with the average values of illite in the Oxford Clay sediments, reported by other workers. Illite showed a sympathetic relationship with depth, kaolinite, chlorite and an antipathetic relationship with smectite in the (W K.B.) sediments. It showed a sympathetic relationship with mixed-layer minerals and chlorite, and an antipathetic relationship with kaolinite and depth in the (W.B.) sediments. These relationships are shown in Figures (7. 3a & 7.3b) and Tables (7.1A3 & 7.1B3) respectively.

The sediments of the (U.O.C.) of both the boreholes contain a comparatively much degraded type of illite, as indicated by the broad nature of the 10Å peaks of illite shown in Figures (7. 1a & 7.1b). The WEAVER'S index or the sharpness ratio of the 10Å and 10·5Å peaks minus background was measured, as suggested by WEAVER (1960) for all the samples, and in the present thesis is expressed as C.I.W. This ratio gives an indication of the crystallinity of illite; better crystallinity

TABLE (7.1A1): Summary Statistics of Clay Mineralogy - (W.K.B.) Sediments

CLAY MINERALS	MEAN	VARIANCE	S.DEVIATION	S.E. OF MEAN	SKEWNESS	KURTOSIS
ILLITE	* 57·583	93·356	9·6621	2·7892	-1·876 **	4·078 **
KAOLINITE	* 18·917	36·083	6·0069	1·7341	-1·001	1·472
SMECTITE	* 15·833	274·700	16·5740	4·7845	1·890 **	3·594 **
CHLORITE	* 7·666	8·788	2·9644	0·8557	0·1303E-01	-1·826

TABLE (7.1A2): Correlation Coefficient Matrix of (W.K.B.) Sediments ($< 2\mu$)

	DEPTH	ILLITE	KAOLINITE	SMECTITE	CHLORITE
DEPTH	1·0000				
ILLITE	0·8599	1·0000			
KAOLINITE	0·7520	0·7997	1·0000		
SMECTITE	-0·8829	-0·9837	-0·8694	1·0000	
CHLORITE	0·6094	0·6199		-0·6229	1·0000

n = 12

For 10 degrees of freedom the correlation coefficients for 5% and 0·01% levels of significance are as follows:

5% $r \geqslant \pm 0{\cdot}576$

0·01% $r \geqslant \pm 0{\cdot}707$

*Mean values of 12 representative samples of the clay fraction ($< 2\mu$) from the (W.K.B.)

TABLE (7.1A3): Distribution of the clay minerals in the studied sequences of the Oxford Clay and Kellaways Formations

WINTERBORNE KINGSTON BOREHOLE SAMPLES

	ILLITE %	KAOLINITE %	SMECTITE %	CHLORITE %	V/h	V/P	C.I.W.	C.I.I.	C.I.K.	K_2O %	% Expandable Layers
U.O.C.	42·60	8·40	45·16	3·84	0·58	0·67	3·36	0·34	0·33*	1·54	$>$60% $<$80%
M.O.C.	58·31	17·70	16·61	7·38	0·46	0·56	4·12	0·30	0·29$^+$	2·17	" "
L.O.C.	60·38	21·77	10·08	7·77	0·45	0·55	3·85^x	0·32^x	0·29^x	2·19	" "
K.F.	63·75	21·08	5·33	10·50	0·43	0·51	4·53	0·27	0·26	2·59	" "

TABLE (7.1B3) WARLINGHAM BOREHOLE SAMPLES

	ILLITE	KAOLINITE	MIXED-LAYER	GHLORITE	V/h	V/P	C.I.W.	C.I.I.	C.I.K.	K_2O
U.O.C.	66·50	7·69	21·00	4·72	n.d.	n.d.	2·03	0·74	0·40	2·36
M.O.C.	66·26	12·26	14·70	6·68	"	"	2·39	0·59	0·38	2·50
L.O.C.	65·41	14·47	14·12	5·94	"	"	2·37	0·60	0·36	2·55
K.F.	62·00	23·70	10·40	3·90	"	"	2·13	0·69	0·28	2·30

Note: (i) V/h = Ratio of the peak to trough distance (V) on the low angle side of 17Å peak to the peak to trough distance (h) on the high angle side of 17Å peak (REYNOLDS& HOWER, 1970; ESLINGER & SAVIN, 1976).

(ii) V/P = Ratio of the valley depth (V) on the low angle side of 17Å peak and the height (P) of the 17Å peak (BISCAY, 1965).

(iii) C.I.W.= Ratio of the peak sharpness of illite peak at 10Å and 10·5Å (WEAVER, 1960).

(iv) C.I.I.= Crystallinity index of illite, i.e. width at half height of 10Å peak, in 2θ degrees.

(v) C.I.K.= Crystallinity index of kaolinite, i.e. width at half height of 7·12Å peak, in 2θ degrees.

x = Average of 10 samples
\+ = Average of 12 samples
* = Average of 18 samples.

(vi) K_2O values recorded for the sediments of both boreholes are the absolute values.

illites giving higher values of this ratio. The value of C.I.W. increases with the sharpness of the illite peak, and therefore is considered a measure which is directly proportional to the true crystallinity of illite. The lowest values of C.I.W. in the studied sediments exist in the (U.O.C.) sediments of both the boreholes and confirm the degraded nature of illite.

The crystallinity of illite is also measured by another method, suggested by KUBLER (1968), as described in Section 7.6. This corroborates the conclusions drawn above. The large variation in crystallinity in the (U.O.C.) between the two sites strongly suggests two different provenances for the clays in the respective sediments. The source rock for the (W.B.) sediments is probably re-cycled sedimentary material from the Paleozoic rocks of the East Anglian massif (Kent, 1980). The sedimentary nature of the source rock is suggested by the degraded nature of illite and its poor degree of crystallinity.

DUNOYER DE SEGONZAC (1969) stated that changes in the crystallinity of illite takes place due to weathering effects. He also mentioned that the crystallinity of illite can be related to the facies of sediments; detrital illite, being coarser in particle size, will exhibit a high crystallinity,and fine-grained particles of illite being more sensitive to degradation and hydration during weathering and transportation, will display a poor crystallinity. For these reasons, detrital siltstones, composed of larger particles, generally contain more crystalline illite as compared to the fine-grained clays and shales. Further, the above author explained that aggradation of illite by interstitial waters/solutions,during early diagenesis,is carried out more easily in porous rocks in which solutions can easily circulate. Thus sandstones contain better crystalline illite than shales.

Additionally, variations of crystallinity of illite in sediments may be controlled by the geochemistry of the environments and the chemistry of the illite. The ordering of illite lattices, which determines the crystallinity of illite, occurs at a rate dependent on the chemical composition of illite particles and of environments (DUNOYER DE SEGONZAC, 1970). According to this author, the levels of aluminium in the octahedral layers and of sodium in the inter-layer positions, play a major role in the development of the crystallinity of illite. ESQUEVIN (1969) suggested that a high Al(Fe + Mg) ratio in the octahedral layer favours the recrystallization of illite. DUNOYER DE SEGONZAC (1969), after many observations, confirmed the suggestion of ESQUEVIN (op.cit.). As far as the level of inter-layer sodium is concerned, it is known that phyllosilicates take up sodium poorly, and it is easily and preferentially replaced by magnesium in the inter-layers, and then by potassium (the 'equivalence level' of POWERS, 1959).

Tables (7.1A1 & 7.1B1) show the summaries of the statistics from the data of 12 representative samples of the clay fraction ($< 2\mu$) of both the borehole sediments. Table (7.1A2) shows the correlation coefficients shown by the clay minerals and depth in the borehole in the (W.K.B.) sediments. This table shows a very strong positive correlation (significant at the 99·99% level) of illite with depth ($r = +0{\cdot}859$), kaolinite ($r = +0{\cdot}799$) and a very strong negative correlation for smectite with depth ($r = -0{\cdot}984$), significant at the 99·99% level. Illite showed a strong positive correlation with chlorite ($r = +0{\cdot}620$), significant at the 95% level. The very strong positive and negative correlations of illite (with kaolinite and chlorite positively, and smectite negatively) clearly indicate a detrital origin of the illite and a separate provenance for the smectite.

Table (7.1B2) shows the correlation coefficients shown by the clay minerals and depth in the borehole in the (W.B.) sediments. This table does not show any correlation of illite with other clay minerals, which may be due to over-generous estimation of illite in the (W.B.) sediments, as mentioned earlier. The sympathetic trends of illite with mixed-layer minerals and chlorite shown in Table (7.1B3), which are inversely related to kaolinite and depth, may suggest a relationship of illite with mixed-layer minerals and chlorite. Possibly there are two types of illite present in these sediments, i.e. a primary illite produced by the weathering of the parent rock, and a small amount of illite probably formed by the alteration of either smectite, or mixed-layer minerals, or sediments rich in mixed-layer and chlorite minerals. By the degradation of smectite and chlorite in sedimentary

TABLE (7.1B1): Summary Statistics of Clay Mineralogy - (W.B.) Sediments

CLAY MINERALS	MEAN	VARIANCE	S.DEVIATION	S.E.OF MEAN	SKEWNESS	KURTOSIS
ILLITE	* 66·000	12·000	3·4641	1·0000	1·701 **	3·675 **
KAOLINITE	* 11·667	18·061	4·2498	1·2268	-1·846 **	5·742 ****
MIXED-LAYERS	* 16·333	46·606	6·8269	1·9707	2·477 **	7·025 ****
CHLORITE	* 6·000	5·818	2·4121	0·6963	-0·466	0·845

TABLE (7.1B2): Correlation coefficient matrix of (W.B.) sediments ($< 2\mu$)

	DEPTH	ILLITE	KAOLINITE	MIXED-LAYERS	CHLORITE
DEPTH	1·0000				
ILLITE		1·0000			
KAOLINITE	0·7122		1·0000		
MIXED LAYERS			-0·8512	1·0000	
CHLORITE				-0·5907	1·0000

n = 12

For 10 degrees of freedom the correlation coefficient for 5% and 0·01% levels of significance are as follows:

5% $r \geqslant \pm 0{\cdot}576$

0·01% $r \geqslant \pm 0\ 707$ (****)

* Mean values of 12 representative samples of the clay fraction ($< 2\mu$) from the (W.B.)

rocks, a degraded illite is produced. The highest abundances of illite and mixed-layer minerals and the lower amount of chlorite in the (U.O.C.) of the (W.B.) shown in Table (7.1B3) support the transformation of smectite into degraded type of illite and mixed-layer minerals. The poorest degree of crystallinity of illite in the (U.O.C.) sediments, shown in Table (7.1B3) further supports the idea of conversion of smectite or chlorite into degraded illite and mixed-layer minerals.

(b) KAOLINITE:

Table (7.1.8b)

	(W.K.B.)	(W.B.)
Range:	2 to 26%	0 to 34%
Highest abundance:	21·80% (L.O.C.)	23·70% (K.F.)
Lowest abundance:	8·40% (U.O.C.)	7·69% (U.O.C.)

Kaolinite, like other clay minerals, is a phyllosilicate, and its structure is composed of one octahedral and one tetrahedral layer, which give approximately a basal reflection (001) peak at 7Å when run on the X.R.D.

Kaolinite in the studied sequences shows higher abundances in the (L.O.C.) sediments in the (W.K.B.) and in the (K.F.) sediments in the (W.B.) samples, as shown in Table (7.1.8b). The lowest abundance of kaolinite is common in the (U.O.C.) sediments of both the boreholes. Appendices (4.1B and 4.2B) show a higher average value of kaolinite in the (W.K.B.) sediments as compared with the (W.B.) sediments. These variations may be related to more than one factor, i.e. provenance, nature of weathering, and the proximity of the shore-lines. The highest abundance of kaolinite in the (K.F.) of the (W.B.) sediments, associated with the highest abundance of quartz, suggests a near-shore deposition of these sediments; it may also indicate an intense chemical weathering in the areas of the source rock. PERRIN (1971) mentioned that, due to low surface charge and the relatively large micelle size of kaolinite, it tends to segregate from 2:1 minerals by differential flocculation and settling, and is thus concentrated in shallow water.

Kaolinite in the (W.K.B.) sediments demonstrated a sympathetic relationship with depth in the borehole, illite and chlorite, and an antipathetic relationship with smectite, which is shown in Figure (7.3a) and Table (7.1A3). These relationships suggest a common source for kaolinite, illite and chlorite, which is further confirmed by the very strong positive correlation of kaolinite with illite (r = +0·799), significant at the 99·99% level. The very strong negative correlation of kaolinite with smectite (r = -0·89), also significant at the 99·99% level, supports a different source rock for its origin. The lowest and highest average values of kaolinite in the (U.O.C.) and the (L.O.C.) and (K.F.) sediments in the (W.K.B.) may be associated with the climatic conditions that existed at the time of deposition. It may also be related to the nature of weathering at the site of weathering and during the transportation of the detritus, differential flocculation and the rate of sedimentation.

Kaolinite in the (W.B.) sediments showed the highest and lowest abundances, respectively, in the (K.F.) and the (U.O.C.) samples, which is shown in Tables (7.1.8b and 7.1B3). It follows more or less the same concentration trend in the sediments of the two boreholes, which suggests that the observed variations in the concentration of kaolinite are related to the rate of sedimentation and to differential flocculation (PERRIN, 1971) in the two boreholes. Many workers described kaolinite as an indicator of palaeogeography (MILLOT, 1964) and the proximity of shore-lines; kaolinite particles, being larger than other clay mineral particles, settle rapidly and are thus deposited near the shore-lines. Abundant concentration of kaolinite in sediments indicates a tropical and humid climate for the region. The maximum concentration of kaolinite in the (K.F.) of the (W.B.) sediments, associated with the highest abundance of quartz, signifies the near-shore type of deposition of these sediments.

DUNOYER DE SEGONZAC (1970) mentioned that kaolinite is very sensitive to the geochemistry of the environments. He further mentioned that destruction or formation of kaolinite, in rocks of sufficient porosity, depends on the contact of the rock with alkali or acidic solutions.

(c) CHLORITE:

Table (7.1.8c)

	(W.K.B.)	(W.B.)
Range:	1 to 12%	0 to 11%
Highest abundance:	10·50% (K.F.)	6·68% (M.O.C.)
Lowest abundance:	3·84% (U.O.C.)	3·90% (K.F.)

Chlorite is known since the last century when WERNER used this term for green foliated minerals, rich in ferrous iron. BARSHAD (1948) and BRINDLEY (1951) provided detailed information regarding the relationship of chlorite with other clay minerals. Chlorite minerals are hydrous silicates of magnesium and alumina, and their structure is made up of alternate mica-like and brucite-like layers. The chlorite minerals are recognised by a series of basal reflections ranging from 14·0 to 14·3Å (001). Iron-rich chlorite gives strong reflections of (002) and (004) and weak reflections of (001) and (003). Identification of chlorite in the presence of kaolinite becomes difficult as the (001) peak of kaolinite at 7·15Å is very close to the (002) peak of chlorite at 7·0 - 7·2Å. Sometimes both minerals give reflections at 7·12Å and 3·55Å; under this situation the identification of both minerals becomes extremely difficult.

Their discrimination in this study has been described earlier. Chlorite showed a sympathetic relationship with depth, illite and kaolinite, and an antipathetic relationship with smectite in the (W.K.B.) sediments (Figure (7. 3a) and Table (7.1A 3). The sequence of the (W.B.) shows an antipathetic relationship of chlorite with depth and kaolinite, and a sympathetic relationship with illite and mixed-layer clay minerals, indicating a strong relationship and a common source of chlorite, illite and mixed-layer minerals.

Tables (7.1A1 and 7.1B1) show the summaries of the statistics of only 12 representative samples of the clay fractions of each borehole; they indicate different mean values of chlorite than those tabulated in the Appendices (4.1B and 4.2B) respectively. Table (7.1A2) shows a strong positive correlation of chlorite with depth ($r = +0·609$) and illite ($r = +0·620$), both correlations being significant at the 95% level. Taking into consideration the sympathetic trends of chlorite with illite (detrital) and the antipathetic trend with smectite (authigenic?) minerals, a detrital origin for the chlorite is indicated. Chlorite in the (W.B.) sediments does not show any correlation with other minerals except its negative correlation with mixed-layer minerals ($r = -0·59$, significant at the 90% level), which is shown in Table (7.1B2). It may be due to a different provenance for the two minerals. Earlier it is mentioned that mixed-layer minerals in the

(W.B.) may be an alteration product of smectite.

(d) MIXED-LAYER MINERALS:

Mixed-layer minerals, according to GRIM (1968) are composed of more than one species of clay minerals. The interstratification in the mixed-layer minerals depends on the composition and the proportion of each layer type associated, and with the degree of regularity or randomness of the interstratification. Mixed-layer minerals, broadly, may be of two types, as follows:

(i) Regular mixed-layer minerals: These minerals display a regular repetition of the different layers composing a mixed-layer mineral. The unit cell in such minerals is equivalent to the sum of the component layers. Such minerals give an integral series of basal reflections when run on the X.R.D.

(ii) Random mixed-layer minerals: These minerals exhibit interstratifications of more than one layer of a random nature, i.e. no regular repetition of layers, as was observed in the regular mixed-layer minerals. Such minerals give a series of non-integral basal reflections on the X.R.D. diffractograms. Many workers, including GRUNER (1934), HENDRICKS and TELLER (1942), BRADLEY (1945) and WEAVER (1956) emphasised the importance of the random mixed-layer minerals in the study of sediments. According to GRIM (1968, p.122), random mixed-layer minerals have an inherent variability and, due to this, it is difficult to assign a specific name to such minerals. Such minerals may be designated as 'mixtures of the layers' involved.

Extensive studies of the mixed-layer minerals in ancient and recent sediments have been carried out by many workers. Some recent workers include WEAVER (1956, 1958 and 1960), WEIR (1965), HOWER and MOWATT (1966), SCHULTZ (1968), GRIM (1968), REYNOLDS (1970), PERRY and HOWER (1970), DUNOYER DE SEGONZAC (1970), GILKES and HODSON (1971), MILLOTS (1971), WEIR and RAYNER (1974), BRADSHAW (1975), ESLINGER and SAVIN (1976), BAQRI (1977), HOFFMAN and HOWER (1979) and PAPAVASILIOU (1979).

According to HOWER and MOWATT (1966) and HELGESON **et al.**, (1969), illite and smectite are the end members of a continuous mixed-layer solid solution series. Therefore, a knowledge of the percentage of expanded layers in mixed-layer minerals is of significant importance. It may give a valid clue regarding the origin of the mixed-layer minerals. According to studies on many D.S.D.P. sediments, random mixed-layer minerals (illite-smectite), having a high percentage of expandable layers, are mainly authigenic in origin and usually are associated with zeolites and low contents of detrital minerals such as illite, kaolinite, chlorite, feldspar and quartz (GIESKES *et al.*, 1975; ESLINGER and SAVIN, 1976). Mixed-layer minerals (illite-montmorillonite), having a low or zero percentage of the expandable layers, are detrital in origin and are associated with significant amounts of detrital minerals such as illite, kaolinite, chlorite, feldspar and quartz (ESLINGER and SAVIN, 1976).

The sediments of the Oxford Clay and Kellaways Formations, at present under study, contain mixed-layer minerals of two types. The sediments of the (W.K.B.) contain an expandable mixed-layer mineral composed of a mixture of montmorillonite and illite, and in the present thesis this is designated as smectite. The expandability of smectite was measured according to the methods described earlier; it ranges between 60% and 80% indicating a dominant proportion of montmorillonitic layer. The sediments of the (W.B.) contain an entirely different type of mixed-layer mineral, which does not show the presence of an expandable component when tested. They do not collapse on glycolation, an indication of the absence of montmorillonitic component. If any of the samples showed the presence of an expandable layer it was very nominal. Therefore the mixed-layer mineral in the (W.B.) sediments is designated as 'mixed-layer mineral'. Details regarding the mixed-layer minerals in each borehole are as follows:

1. Smectite (expandable mixed-layer mineral)

Table (7. 1.8d1)

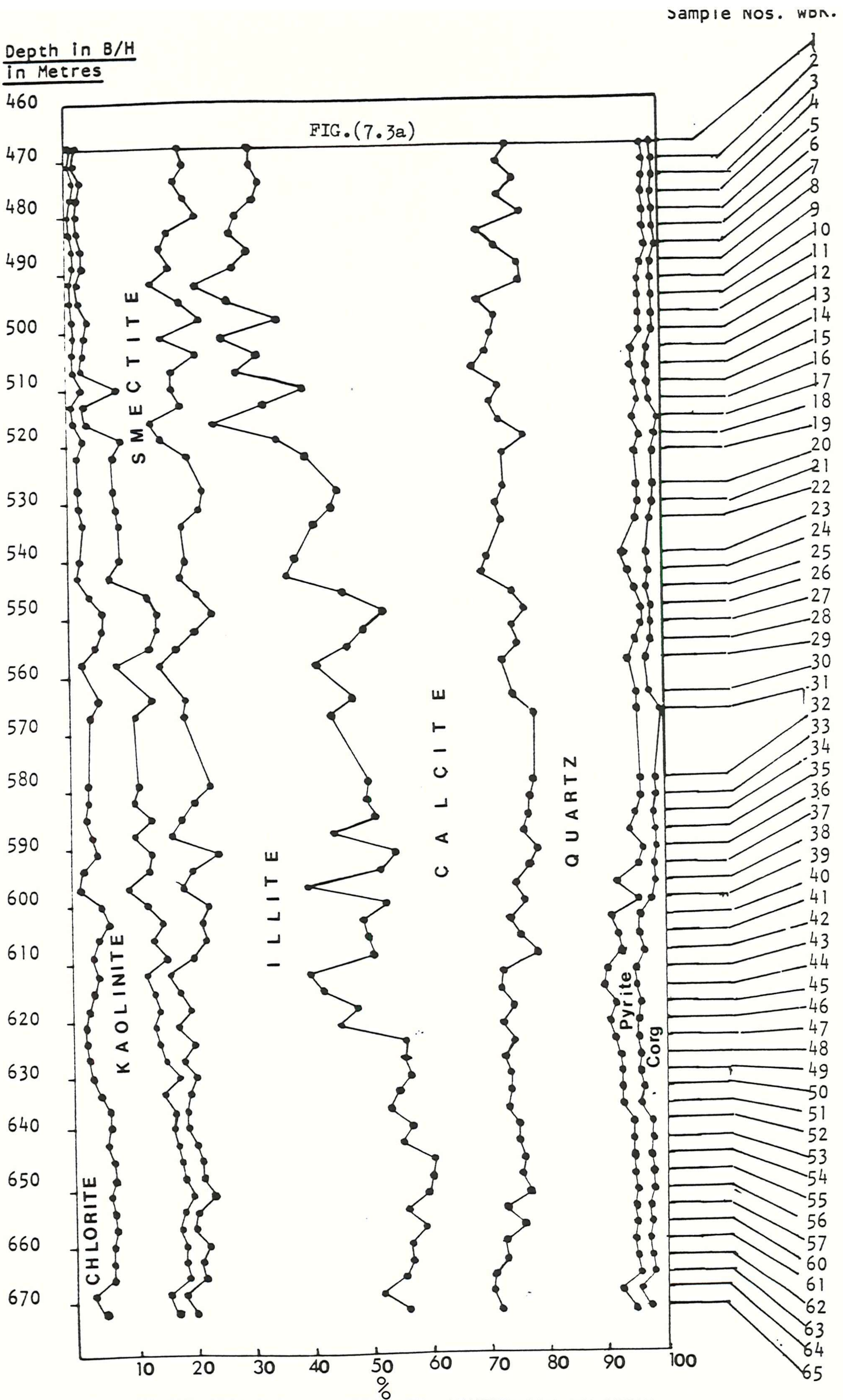
	(W.K.B.)
Range:	4 to 72%
Highest abundance:	45·16% (U.O.C.)
Lowest abundance:	5·33% (K.F.)

GRIM (1968) used the term 'smectite' as a group name for montmorillonite and the aluminous members of this group. According to

GRIM (op.cit.) the generally accepted structure of the smectite currently in use follows the original suggestions made by HOFMANN et al. (1933). Modifications in the structure of smectite were suggested by MAEGDEFRAU and HOFMANN (1937), MARSHALL (1935) and HENDRICKS (1942). According to this concept, the smectite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet (GRIM, 1968, p.78). Smectite (montmorillonite-illite) is characterised by its expanding lattice. According to GRIM (1968, p.80), under ordinary room temperature conditions, when smectite(montmorillonite-illite) is dried, it gives a basal spacing of about 12·5Å, and contains sodium as the exchange ion, and frequently has one molecular layer of water. If calcium or magnesium is the exchange ion, then it gives a c-axis spacing of about 15·5Å and contains two molecular water layers. After glycol treatment, smectite (montmorillonite-illite) gives a series of basal X-ray peaks at 17Å, 8·5Å, 5·7Å, 4·2Å, 3·4Å, etc. Smectite in the present study is found only in the (W.K.B.) sediments. It gave peaks at 14·5Å to 15·5Å for the normal and untreated slides; after glycolation the peak position was shifted to 17Å, as shown in Figure (7.1a). The peak position of smectite indicates that it contains calcium or magnesium as the exchange ion (GRIM, 1968, p.80). Exchange ions present in the studied smectite are mentioned in the description of the structural formula, calculated for smectite present in one of the samples of the (W.K.B.) sediments.

Smectite (montmorillonite-illite) in the (W.K.B.) sediments showed the highest and lowest abundances in the (U.O.C.) and (K.F.) samples, as shown in Table (7.1.8d1). Smectite showed an antipathetic relationship with depth, illite, kaolinite and chlorite, as shown in Figure (7.3a) and Table (7.1A3). This variation of the abundance of smectite may be related to the abundance of the source material which produced smectite. The antipathetic relationship of smectite with detrital minerals such as kaolinite, illite and chlorite indicates a non-detrital origin of smectite. CHOWDHURY (1980) insisted on a volcanogenic origin of smectite in the Corallian sediments from the Dorset coast. PERRIN (1971) mentioned an antipathetic relationship of smectite with kaolinite in the British sediments during the clay mineral study of the sediments.

FIG.(7.3a)



OXFORD CLAY AND KELLAWAYS MINERALOGY, WINTERBORN KINGSTON

The expandability of smectite in the present study was measured by following the methods proposed by REYNOLDS and HOWER (1970), BISCAY (1965) and ESLINGER and SAVIN (1976). The measured parameters are tabulated in the Appendix (7.1A). Details regarding the measurement of these parameters are given in the earlier section. The parameter V/h represents the 1/h parameter mentioned by REYNOLDS and HOWER (op.cit.)and ESLINGER and SAVIN (op.cit.). No attempt was made to quantify the exact amounts of the expandable layers; only a range of expandability was determined based on the values of V/h. REYNOLDS and HOWER (op.cit.) mention that an 1/h value of 0·39 and 0·77 represents 60% and 80% expandable layers respectively. According to BISCAY (op.cit.) a high value of V/P indicates a better crystallinity of montmorillonite. If this ratio is very high and approaches the value of one, it indicates that the mineral is well crystallised and is composed of 100% montmorillonite. The values of V/h and V/P in the present study generally are in good agreement, as shown in Table (7.1A3) and Appendix (7.1A) All values of V/h are more than 0·39 and less than 0·77, which implies that the majority of the samples contain smectite (montmorillonite-illite) having > 60% but < 80% of the expandable layers. Only a few samples (WBK-33,37,47,48,51,52,57,63,64 and 65) showed V/h values < 0·39, and therefore contain < 60% expandable layers. Table (7.1A3) shows the highest and the lowest average values of V/h (0·67) and (0·43) respectively in the (U.O.C.) and (K.F.) sediments, and are associated with the highest and lowest average values of smectite. The highest abundance of smectite and the highest value of V/h in the (U.O.C.) sediments may be related to the abundance of the source material.

Taking into consideration the amounts of the expandable layers (> 60% and < 80%), the smectite in the (W.K.B.) sediments from the Dorset area may be recognised as a randomly interstratified mixed-layer (montmorillonite-illite). Mixed-layer minerals containing 35% to 40% expandable layers are always randomly interstratified (REYNOLDS and HOWER, 1970).

CHOWDHURY (1980), during a study of the Corallian sediments from the Dorset area, also examined a few samples of the Upper Oxford Clay and reported the presence of montmorillonite (up to 30%) associated with illite (45%) and kaolinite (25%) in the Oxford Clay. The same author stated that the contents of montmorillonite in the Corallian sediments are highest (75%) in the Berkshire sediments as compared to 60% in the Dorset samples and 35% in the sediments from the Warlingham Borehole. He concluded that the percentage of expandable clays decreases from the Berkshire area to the Warlingham area, and attributed it to a north-westerly source of the montmorillonite. The origin and provenance of smectite of the present sediments is discussed later.

2. Mixed-layer mineral (non-expanding)

	Table (7.1.8d2) (W.B.)
Range:	6 to 42%
Highest abundance:	21·00% (U.O.C.)
Lowest abundance:	10·40% (K.F.)

The mixed-layer mineral in the (W.B.) sediments, as mentioned earlier, is composed of non-expanding components and therefore differs from the expanding mixed-layer mineral of the (W.K.B.) sediments. The entire sequence of the (W.B.) shows, from top to bottom, a similar type of mixed-layer mineral. Figure (7. 1b) shows that, after glycolation, no expansion takes place in the mixed-layer mineral from three different points in the studied sequence. If any expansion takes place, it is insignificant. The mixed-layer mineral in the (W.B.) sediments demonstrated a sympathetic relationship with illite and an antipathetic relationship with depth and kaolinite, as shown in Figure (7. 3b) and Table (7.1B3). Mixed-layer minerals display an antipathetic relationship with chlorite only in the (U.O.C.); in the rest of the profile it follows a sympathetic trend with chlorite, like illite. The highest amounts of illite and mixed-layer minerals, and the lower amount of chlorite in the (U.O.C.) sediments suggest two possibilities: (a) a genetic relationship of these minerals; (b) effects of weathering on these sediments. RUSSELL (1977) observed an increase in the contents of illite towards the surface in the majority of the studied profiles of the Oxford Clay, during his studies on the effects of weathering on physical and chemical properties of clays, by which he inferred that illite increase cannot be accounted for by chemical weathering of the Oxford Clay materials (hence the increase may be inherited from the fresh clay; but the net rise in abundance towards the surface in the studied profiles suggests that it is weathering-related). DROSTE et al. (1960) stated that

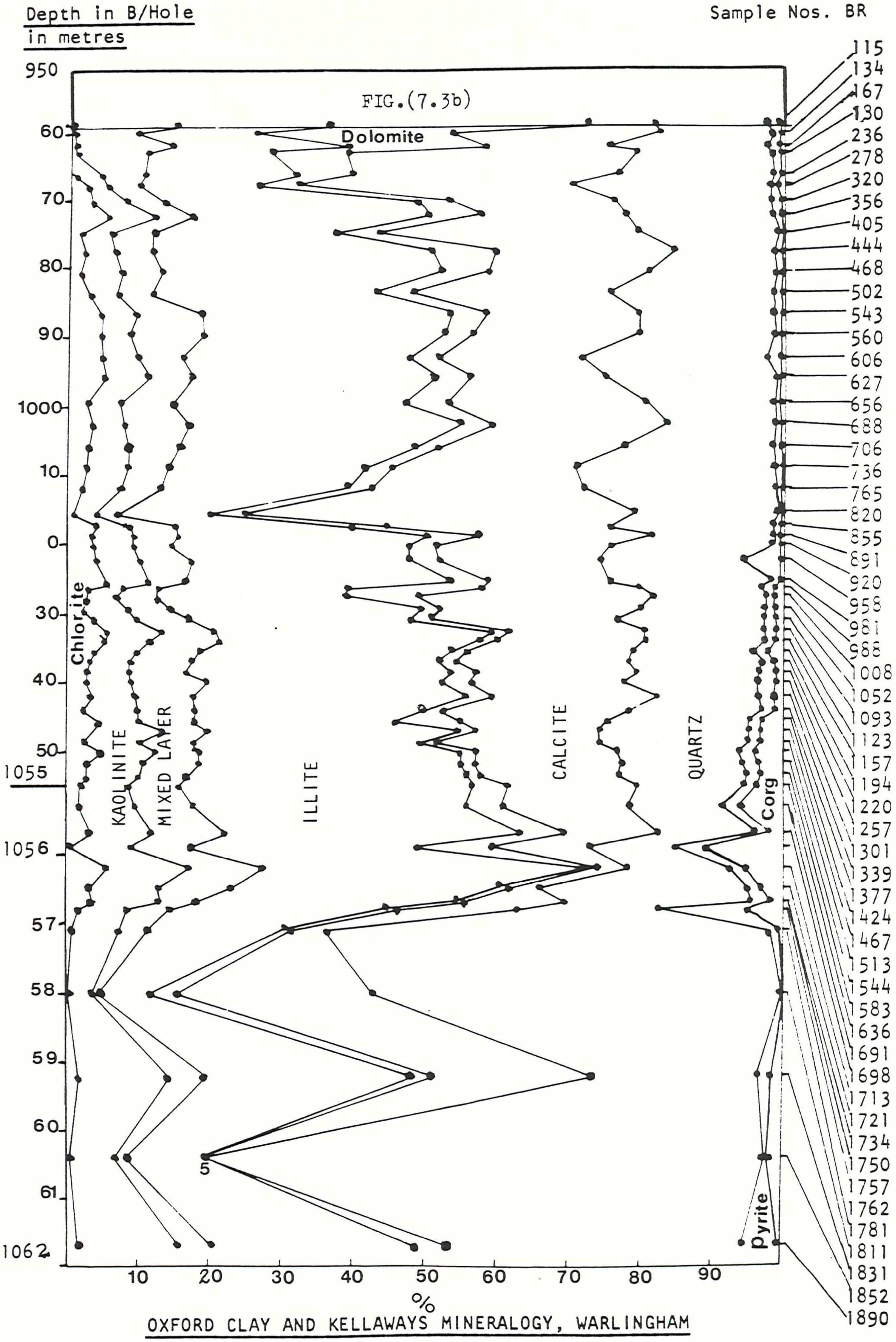


FIG.(7.3b)

OXFORD CLAY AND KELLAWAYS MINERALOGY, WARLINGHAM the abundance of mixed-layer clay minerals may be expected to increase as a result of weathering of illite and chlorite-rich sediments. ATTEWELL and TAYLOR (1973) reported the presence of mixed-layer minerals in the Oxford Clay sediments. The observed relationships of mixed-layers, illite, chlorite, and their inverse relationship with depth in the studied sequence may be explained in the light of the above expressions.

Table (7. 1B2) shows the correlation coefficient matrix of the clay minerals in the (W.B.) sediments. This table shows a very strong negative correlation of mixed-layer minerals with kaolinite (r = -0•85; significant at the 99•99% level). It may be interpreted as due to the antipathetic relationship of the two components. This relationship may also suggest different provenance for the two minerals. The correlation between mixed-layer minerals and chlorite is also negative and significant at the 95% level, as shown in Table (7.1B2). This relationship may be due to the strong inverse relationship of mixed-layer minerals and chlorite, as observed in the (U.O.C.) sediments, which may be due to weathering of chlorite-rich sediments which produced degraded illite and mixed-layer minerals (non-expanding), as suggested by DROSTE et al. (1960).

9. Origin of Clay Minerals

The studied sediments of both the boreholes contain three common clay mineral species, i.e. illite, kaolinite and chlorite. Smectite (montmorillonite-illite mixed-layers) is only present in the (W.K.B.) sediments and a mixed-layer mineral (non-expanding) only in the (W.B.) sediments. The origin of clay minerals, like illite, kaolinite and chlorite, is commonly interpreted as detrital (GRIM, 1968; MILLOT, 1970; DUNOYER DE SEGONZAC, 1970). These three clay minerals in the studied sediments have demonstrated strong positive correlations with typically detrital components such as Si, Ti, Al, Cr, Zr, and total clays, which are shown in Appendices (7.1 D and 7.2 D), and therefore confirm a detrital origin of these minerals. Furthermore, the correlation coefficient matrix of clay minerals only in Table (7.1A2) also indicates very strong positive inter-correlations, significant at the 99•99% level, between these three minerals, and a very strong negative correlation, also significant at the 99·99% level with smectite. These correlation trends undoubtedly confirm a detrital origin for illite, kaolinite and chlorite, and a non-detrital (authigenic?) origin for the smectite. The origin of smectite and mixed-layer minerals needs further explanation.

(a) Smectite

The definition of smectite has been given earlier. Smectite (montmorillonite-illite/illite-montmorillonite, mixed-layers) may be produced in various ways in nature. HALLAM and SELLWOOD (1968) mentioned that at present the smectite is known to be formed by (i) sub-aqueous alteration of tuffs; (ii) by terrestrial weathering of basic igneous rocks, in an alkaline environment, in the presence of magnesium; (iii) by the hydrothermal alteration of the source rock on land surface. MILLOT (1970) stated that a pyroclastic source rock is not always necessary for the formation of montmorillonite. COWPERTHWAITE <u>et al.</u> (1972) mentioned that montmorillonite may commonly be formed by the weathering of ancient rocks (shales, etc.) in hydromorphic, calcimorphic soils in regions of warm climate. These authors further mentioned that, for the formation of a Ca-montmorillonite as an alteration product of silicate rocks, special environments are required which fulfil the following:

(a) High Mg (and to a lesser extent Fe and Ca) concentration.

(b) Low K-concentration.

(c) Moderate to high (alkaline) pH and a low (reducing) Eh potential.

DUNOYER DE SEGONZAC (1970), MILLOT (1970) and JACKSON and SHEARMAN (1959) stated that montmorillonite may be derived from one or more than one of the following:

(i) by degradation of mica during soil weathering;

(ii) by alteration of volcanic ash in or adjacent to the basin of deposition;

(iii) by neo-formation from the elements in the basin of deposition;

(iv) by re-working of the pre-existing smectite-rich sediments in an environment which is neither too rich nor too poor in the ions which induce alteration;

(v) by post-depositional diagenesis.

Many workers, including ROBERTSON (1961), HALLAM and SELLWOOD (1968, 1970), COWPERTHWAITE *et al.* (1972), SELLWOOD and HALLAM (1974), BRADSHAW (1975), JEANS *et al.* (1977) and KNOX (1979), have studied the origin of fuller's earth, montmorillonite and the associated volcanic and igneous components found in the Jurassic sediments in southern England. CHOWDHURY (1980), during the studies of the Corallian sediments from southern England, also studied the origin of montmorillonite present in these sediments. All these authors agreed that 'air-fall' volcanic ash, intimately related to synchronous vulcanism (in the North Sea or elsewhere), is the source material for its origin.

BRADSHAW (1975) noticed a variation of the crystallinity of montmorillonite in the Middle Jurassic sediments of England, which he related to the fluctuations in the intensity of volcanism and the rate of sedimentation. CHOWDHURY (1980) found fresh euhedral biotite, zeolite, apatite and well-crystallized montmorillonite restricted to the early Corallian sediments, to which he attributed, with a short-lived pulse of volcanic activity, the source of montmorillonite. BRADSHAW (*op.cit.*) and HALLAM and SELLWOOD (1970) mentioned that 'air-fall' volcanic ash can be carried in large quantities for hundreds of miles, which rules out the necessity of the existence of an active volcano in the near vicinity of the sedimentation for providing the source rock for the formation of montmorillonite. HALLAM and SELLWOOD (1970), however, mentioned that there is strong evidence of late Mesozoic vulcanicity at no great distance from southern England.

CHOWDHURY (1980) believes that intermediate rocks and the volcanic ash are the most probable source materials for the origin of Corallian montmorillonite. He found recognizable volcanic evidence only in the early Corallian sediments, which he associated with a westerly source. He further noticed a significant decrease in the abundance of montmorillonite from 35% in the *Cardioceras Cordatum & Perisphintes plicatilis* zone to zero percentage in the *Ringsteadia pseudocordata* zone.

The present author did not find any recognizable volcanic evidence such as zeolite, biotite, apatite or cristobalite, etc. in the studied sediments. The absence of these components may be related to the fact that volcanic glass, which on its transformation produces montmorillonite, is unstable in the aqueous environments of sedimentary basins (BRADSHAW, 1975). It may also be related to the distance and the direction of the supply of source material, as pointed out by CHOWDHURY (1980). The only evidence available to the present author is geochemical, i.e. enrichment of certain elements such as Mn, Zn, Ni, Ti and Na, in the clay fraction samples of the (W.K.B.) over the chemistry of the clay fraction of the Lower Calcareous Grit Group sediments from the Dorset coast, as reported by CHOWDHURY (1980). Table (7. 3) and Figures (7.5a & 7.5b) show the enriched values of the mentioned elements. Most of the elements are typically enriched in basalt (KRAUSKOPF, 1979, pp.544-45). CHOWDHURY (1980) proposed an intermediate rock and volcanic ash as a probable source of the Corallian montmorillonite. The enriched values of the above-mentioned elements in the studied sediments and the types of rocks (Intermediate basic) of the Cornubian Highlands (COSGROVE and SALTER, 1966) which probably contributed, after weathering, the major part of the detritus for the Oxford Clay sediments of the (W.K.B.), tend to suggest a similar source of montmorillonite as that proposed for the Corallian sediments by CHOWDHURY (1980). PAPAVASILIOU (1979) reported a similar type of mixed-layer (illite-smectite) from the Indian Ocean sediments, which is volcanogenic in origin.

The absence of directly recognizable volcanic evidence in the studied sediments, in support of a volcanogenic origin for montmorillonite, is not unusual. BRADSHAW (1975), HALLAM and SELLWOOD (1968), SLAUGHTER and EARLEY (1965), KNOX (1979) and CHOWDHURY (1980) did not find direct volcanic evidence in the sediments studied by them.

(b) Mixed-layer mineral

Mixed-layers, as mentioned earlier, are intermediate stages which occur during degradation by weathering and during aggradation by deep diagenesis. The mixed-layers in the (W.B.) sediments, as already mentioned, do not expand on glycolation and therefore indicate the absence of expandable layer in them. After glycolation and heating at $550^{o}C$ for two hours, no distinct change takes place in the mound towards the lower 2θ angle side in the X.R.D. diffractogram of the sample, except that the chlorite peak on heating becomes more distinct. MILLOT (1970, p.17) mentioned a schematic representation of the behaviour of reflections corresponding to X-ray diffraction after different treatments, which explains all possible combinations of mixed-layer minerals; this is reproduced in Table (7.1B4). The X-ray diffraction pattern of the (W.B.) mixed-layers does not follow any of the reflections shown by MILLOT (op.cit.). The early workers, including ATTEWELL and TAYLOR (1973), COSGROVE and SALTER (1966) and JACKSON and FOOKES (1974) noticed the presence of the mixed-layer mineral in the Oxford Clay but did not treat it as a separate phase, and therefore included it with illite.

DROSTE et al. (1960) mentioned that the abundance of mixed-layer mineral may be increased as a result of the weathering of illite and chlorite-rich sediments. The common trend of illite and mixed-layer mineral, which is antipathetic with depth and chlorite in the (U.O.C.) as shown in Table (7.1B3), seems to be in sympathy with this weathering theory.

The provenance of the Oxford Clay sediments at Warlingham area was most probably the East Anglian massif (KENT, 1980). Pre-existing sedimentary rocks from this source (Silurian-Carboniferous in age) were probably weathered and contributed most of the detritus to the Oxford Clay. Geochemical results tabulated in Table (7. 3) also favour a sedimentogenic source for the (W.B.) sediments.

Taking into consideration these facts, it may be suggested that mixed-layer minerals in the (W.B.) sediments are of a similar origin to the other species, and are thus detrital. The present nature of the mixed-layer minerals in the (W.B.) may equally be related to the tectonic movements that took place in the area, as indicated by the faulting through the early Corallian rocks at Warlingham, mentioned by CALLOMON and COPE (1971, Table 5). DUNOYER DE SEGONZAC (1969), in the study of sediments from 'Logbaba', mentioned that dehydration of clays was almost complete at 75°C (instead of 130°C) and illitization begins at 150°C (instead of 170°C). The same author, in a later publication (1970), stated that compression of sediments plays an important role in the dehydration of clays; it expels the inter-layer water and alkaline interstitial solutions which close up the layers. Therefore, the second possibility may be that the present mixed-layers (non-expanding) were initially of smectite composition, which were later changed by the effects of tectonism to non-expandable mineral-layer clays.

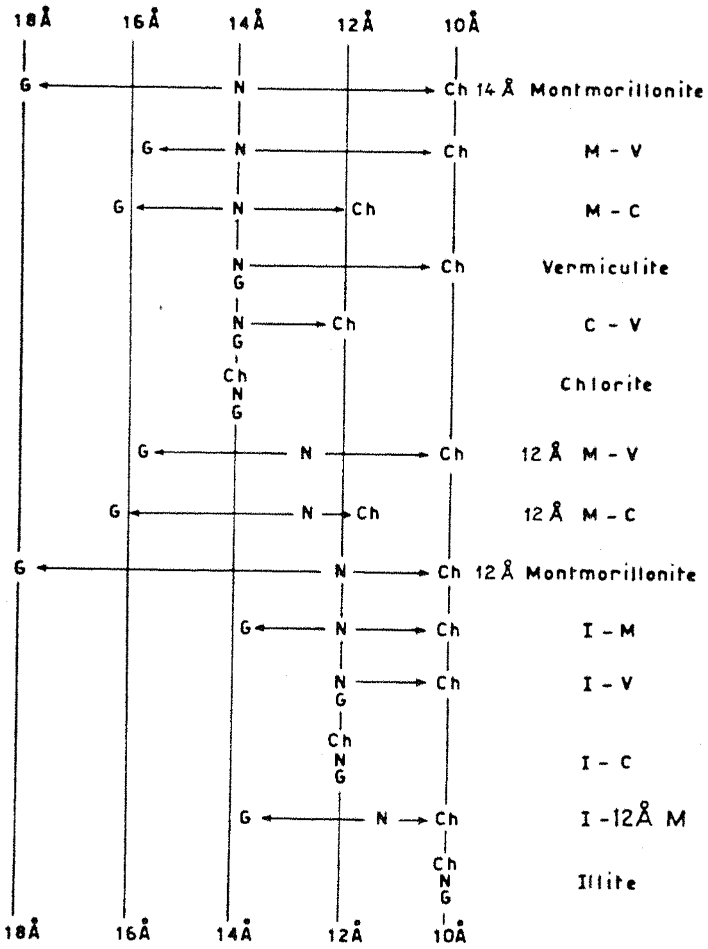


FIG. 2. — *Schematic representation of the behavior of the reflections corresponding to basal spacing during X-ray diffraction after different treatments* (after LUCAS, CAMEZ and MILLOT, 1959).
G: Treatment with glycerol; N: Natural sample; Ch: Heating at 490°.

TABLE (7.1B4) is the reproduction of Figure 2 given by MILLOT (1970).

10. Structural Formulae of Smectite and Illite

(a) Introduction

The structural formulae for two clay minerals, i.e. smectite and illite, studied in the sediments of the Oxford Clay from the (W.K.B.) and (W.B.) samples were calculated based on the method proposed by SCHULTZ (1964). The water content of the studied clay minerals was ignored and the structural formulae were calculated on the basis of 20 oxygens and 4 hydroxyls per structural unit (BROWN and NORRISH, 1952). The structural formula for smectite was calculated for sample WBK-12 and for illite for sample WBK-32 in the (W.K.B.) sediments, and BR-468 from the (W.B.) sediments. The selection of samples was on the basis that they furnished the pre-requisites of SCHULTZ's method, which are listed below:

(1) the clay minerals for which the structural formula is desired must be present abundantly, i.e. > 50% in association with lower abundances of the remaining clay minerals;

(2) a satisfactory chemical and clay mineralogical analysis of the sample must be available;

(3) well established chemical analyses of the clay mineral species, present in the studied sample must be available in the literature.

The chemical and semi-quantitative clay mineral analyses of these samples are shown in Table (7.1A6) and Appendices (7.1B & 7.2B). Illite present in the (W.B.) sediments exhibited a poor degree of crystallinity and is considered much degraded compared with the illite in the (W.K.B.) sediments. For this reason, calculation of a structural formula for the (W.B.) illite was not desirable. However, when it was seen that the structural formula of illite, calculated for WBK-32, gave some clues regarding the provenance of illite, it was felt necessary to calculate a structural formula for the illite present in the (W.B.) sediments in spite of its poor crystallinity.

The calculation of a structural formula for the smectite and illite is very helpful in identifying the clay species. GRIM (1968) mentioned less substitution of Al^{+3} for Si^{+4} in tetrahedral sheet of a well crystallized mica. WEAVER and POLLARD (1973) have mentioned a number of groupings and sub-groupings of micas and smectites, based on the trends of distribution and association of cations in the tetrahedral, octahedral sheets and inter-layer positions, which are listed below:

(1) mica may be divided on the basis of dioctahedral (muscovite) and trioctahedral (biotite);

(2) mica may be classified on the basis of silicon ions in tetrahedral sheet (tetrasilicic; trisilicic; disilicic and monosilicic).

(3) by considering the substitution for silicon by either Al^{+3} or Fe^{+3};

(4) on the basis of cations and their combination in the octahedral sheet: Al^{+3} occurs in muscovite and Mg^{+2} in phlogopite;

(5) most micas contain two or more cations in the octahedral sheet, such as Al, Mg and Fe in association with Mn, V, Cr, Li and Ti in varying amounts;

(6) the most common illite mineral is dioctahedral; it contains Al^{+3} substituted for Si^{+4} in the tetrahedral sheet, which is approximately half the amount substituted for muscovites. GRIM (1968) states that if 2/3 possible positions, in the octahedral sheet are filled, it is called heptaphyllites or dioctahedral minerals.

(7) the dioctahedral illite contains approximately three-quarters of the amount of aluminium associated with minor amounts of Fe^{+3} and one-eighth the amount of divalent cations such as Mg^{+2} and Fe^{+2} in the octahedral sheet, which gives a total negative charge of 0·75, as compared with a value of 1 for muscovite per $(O_{10}(OH)_2)$ unit.

WEAVER and POLLARD (1973) further mentioned that the substitution of a cation of a lower charge for a cation of a higher charge in both the tetrahedral (e.g. Al^{+3} replacing Si^{+4}) and octahedral (e.g. Mg^{+2} replacing Al^{+3}) sheets gives the 2:1 layer a net negative charge which is satisfied by the positive charge due to inter-layer cations.

WEAVER and POLLARD (1973) stated, regarding the expandable clay minerals (2:1), that they show a wide range of chemical composition and layer charges. According to these authors, the most commonly, naturally occurring cations of inter-layer position include sodium calcium, hydrogen, magnesium, iron and aluminium. They also stated that the dioctahedral sub-group of mixed-layer minerals is the most abundantly occurring group in clays. These authors further mentioned that the layer charge on the expanded clays ranges from 0·3 to 0·8 per $(O_{10}(OH)_2)$ unit. The low charged (0·3 - 0·6) expanded clay minerals, according to the above authors, are called montmorillonite and smectite. The low charge (0·3 - 0·6) originates in the octahedral sheet, and a clay mineral bearing such charge is called a dioctahedral mineral. Such a mineral may also be termed dioctahedral smectite or montmorillonite. When a dioctahedral smectite shows a relatively high tetrahedral charge (0·4), it is called 'beidellites'.

(b) Structural Formula of Smectite

The structural formula for the smectite present in sample WBK-12 in the (U.O.C.) of the (W.K.B.) sediments was calculated. It is shown in Table (7.1A5) and is compared with the structural formulae of montmorillonite and smectite given by other workers. The various steps involved in the calculations for the formula of this sample are shown in Table (7.1A4). The well established chemical analyses of clay minerals, such as illite, kaolinite, chlorite and mixed-layer mineral, which were used in the calculations, are shown in Table (7.1A7) which indicates the sources of information. The lattice composition of the calculated formula is not much different from those mentioned for the dioctahedral smectites by WEAVER and POLLARD (1973, pp.58-59). It suggests that the studied smectite in sample WBK-12 is also dioctahedral.

The calculated formula shows a great similarity with those formulae reported by CHOWDHURY (1980) for montmorillonite in the Corallian sediments from the Dorset area, and also with the formula reported by PAPAVASILIOU (1979) for a mixed-layer (illite-montmorillonite) studied by him in the D.S.D.P. sediments from the Indian Ocean; both structural formulae are shown in Table (7.1A5) in columns 2 and 4 respectively. The chemical and mineralogical analyses of these two samples are shown in Table (7.1A6). The tetrahedral sheet of sample WBK-12 shows a lower amount of Al^{+3} (0·25) substituted for Si^{+4} when

TABLE (7.IA4): Showing the various steps involved in the calculation of structural formula for smectite.

Sample WBK-12

Chemical Analysis $\ll$ 2μ Fraction		KAOLINITE: 7%	ILLITE: 39%	CHLORITE: 4%	Remaining constituents assigned to smectite, i.e. A-(B+C+D) = (a)	Molecular Weight of Oxide divided by Cations per Molecule equals - (b)	Cation equivalents times (x) (a/b)	Valence equals -(V) (a/b) x (V)	Charge equivalents = (c.eq.)	Cations per unit cell = f x cation equivalents = f x (a/b)
%	(A)	(B)	(C)	(D)						
SiO_2	50·58	0·07 x 45·65 = 3·19	0·39 x 50·02 = 19·51	0·04 x 26·30 = 1·052	50·58-(3·19 + 19·51 + 1·052 = 26·83	60·0	0·4472	x 4	1·789	7·75
TiO_2	0·75	0·07 x 0·80 = 0·80	0·39 x 0·48 = 0·19	0·04 x 0·22 = 0·009	0·49	80·0	0·0061	x 4	0·024	0·10
Al_2O_3	20·19	0·07 x 37·33 = 2·61	0·39 x 22·19 = 8·65	0·04 x 19·97 = 0·799	8·13	51·0	0·1594	x 3	0·478	2·76
Fe_2O_3	6·58	0·07 x 0·69 = 0·05	0·39 x 2·99 = 1·17	0·04 x 3·24 = 0·130	5·23	80·0	0·0654	x 3	0·196	1·13
MgO	2·25	0·07 x 0·34 = 0·02	0·39 x 3·18 = 1·24	0·04 x 19·66 = 0·786	0·20	40·3	0·0050	x 2	0·01	0·09
CaO	1·02	0·07 x 0·48 = 0·03	0·39 x 0·20 = 0·08	0·04 x 0·29 = 0·012	0·90	56·0	0·0161	x 2	0·032	0·28
Na_2O	0·13	0·07 x 0·20 = 0·01	0·39 x 0·17 = 0·07		0·05	31·0	0·0016	x 1	0·0016	0·03
K_2O	3·17	0·07 x 0·63 = 0·04	0·39 x 6·90 = 2·69		0·44	47·0	0·0094	x 1	0·0094	0·16
									Σ 2·54	

$$f = \frac{\underline{44\ \text{charges per unit cell}}}{\text{charge equivalents (c.eq.)}} = \frac{44}{2\cdot54} = 17\cdot322.$$

STRUCTURAL FORMULA FOR WBK-12 SMECTITE CONTAINING $\gg$60% and $\ll$80% EXPANDABLE LAYERS BASED ON THE METHOD PROPOSED BY SCHULTZ (1964) ON AN($O_{20}(OH)_4$) BASIS:

TETRAHEDRAL SHEET Z = 4
(Si^{+4} Al^{+3})
7·75 0·25 8·00

OCTAHEDRAL SHEET Y = 8
(Al^{+3} Fe^{+3} Ti^{+4} Mg^{+2})
2·51 1·13 0·10 0·10 3·84

INTER-LAYER POSITION
(Ca^{+2} Na^{+} K^{+})
0·28 0·03 0·16 0·47

NET NEGATIVE CHARGE = 0·73
INTER-LAYER CATIONS CHARGE = +0·75

Note: The average chemical analyses of the clay minerals, i.e. illite, kaolinite, chlorite and smectite, used for assigning the cations to the respective clay minerals present in the studied sample, were taken from literature and are tabulated in Table (7.IA7).

TABLE (7.1A5): Structural formulae for smectite and illite, calculated from the chemical analysis of clay fraction ($< 2\mu$) of the Oxford Clay from the (W.K.B.) and (W.B.) samples, and their comparison with the structural formulae for similar clay minerals reported by other workers, on a $O_{20}(OH)_4$ basis

	1	2	3	4	5	6	7	8	9
TETRAHEDRAL SHEET:									
Si^{+4}	7·75	7·56	7·85	7·80	7·20	7·77	7·30	7·56	6·75
Al^{+3}	0·25	0·44	0·15	0·20	0·80	0·27	0·70	0·44	1·25
Sum:	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00
OCTAHEDRAL SHEET:									
Al^{+3}	2·51	2·56	2·51	2·63	2·82	2·48	2·76	1·56	2·77
Fe^{+3}	1·13	0·70	0·74	0·89	0·68	0·87	0·53	0·91	0·45
Fe^{+2}	n.d.	0·12	0·03	-	-	-	-	0·024	0·188
Ti^{+4}	0·10	0·04	-	0·097	-	0·15	0·09	0·20	0·05
Mg^{+2}	0·10	0·67	0·78	0·31	0·52	-	0·52	1·30	0·56
Sum:	3·84	4·09	4·06	3·93	4·02	3·50	3·90	4·00	4·02
INTER-LAYER CATIONS:									
Ca^{+2}	0·28	0·27	-	0·22	-	0·09	0·19	0·26	0·023
Na^{+}	0·03	0·07	0·78	0·07	0·66	0·23	0·16	0·156	0·043
K^{+}	0·16	-	0·01	0·10	0·58	1·20	0·89	0·88	1·023
Mg^{+2}	-	0·10	-	-	-	-	-	-	-
Sum:	0·47	0·44	0·79	0·39	1·24	1·52	1·24	1·256	1·09

/contd.over

TABLE (7.1A5) contd.

	1	2	3	4	5	6	7	8	9
CHARGES:									
(a) Tetrahedral Sheet:	-0·25	-0·44	-0·15	-0·20	-0·46	-0·27	-0·70	-0·44	-1·25
(b) Octahedral Sheet:	-0·48	-0·48	-0·63	-0·43	-0·80	-1·35	-0·72	-1·14	-0·65
Net Charge	-0·73	-0·92	-0·78	-0·63	-1·26	-1·62	-1·42	-1·58	-1·90
(c) Inter-layer position:	+0·75	+0·81	+0·79	+0·61	+1·24	+1·61	+1·43	+1·56	+1·87
% OF EXPANDABLE LAYERS:	79%	-	-	79%	≈45%				

Explanation of Table (7.1A5):

1. Sample No.WBK-12 from the Upper Oxford Clay (W.K.B.) from Dorset.
2. Sample No.1 L.C.G. from the Corallian sediments, Dorset coast, reported by CHOWDHURY (1980).
3. Redhill montmorillonite (Aptian, Surrey), reported by WEIR (1965).
4. Sample No.33-1 from D.S.D.P. sediments from the Indian Ocean, reported by PAPAVASILIOU (1979).
5. Interstratified illite-smectite from the weathered Oxford Clay from Denchworth Series Soil, reported by WEIR and RAYNER (1974).
6. Sample No. WBK-32, from the Middle Oxford Clay (W.K.B.) from Dorset.
7. Sample No.BR-468 from the Upper Oxford Clay (W.B.).
8. Sample No.16-4 from the D.S.D.P. sediments of the Indian Ocean (PAPAVASILIOU, 1979).
9. BROWN and NORRISH (1952) calculated formula for illite-2, using the chemical analyses given by GRIM *et al*.(1937).

compared with other samples in Table (7. 1A5), with the exception of the 'Redhill montmorillonite sample in column 3 (0·15 Al^{+3}), which WEIR (1965) stated contains a very large proportion of the expandable layers. PAPAVASILIOU (1979) has reported 79% expandable layers in column 4 (sample No.33-1). Since this sample shows a very close similarity to WBK-12, as regards the distribution of cations in the tetrahedral,octahedral sheets and inter-layer position, and also of the net negative charge, it suggests that sample WBK-12 also contains a similar amount of expandable layers to that of sample 33-1. The expandable layers were measured for the (W.K.B.) samples by measuring the V/h and V/P ratios, and these are tabulated in Appendix (7.1B), which indicates that sample WBK-12 contains expandable layers from 60% to 80%. HOWER and MOWATT (1966) stated that there exists a relationship between the percentage expandable layers in smectite and that of fixed inter-layer cations, i.e. (K + Na) in illites and mixed-layer illite-smectite. PAPAVASILIOU (1979) tested the percentage of expandable layers in the illite-smectite, which he measured on the X-ray diffractograms, by plotting the percentage expandable layers and percentage of fixed inter-layer cations (K + Na) - Figure (7.4). This figure shows the plots of six samples from the Indian Ocean, including sample 33-1, and also the data of expandable layers and fixed inter-layer (K + Na) cations reported by HOWER and MOWATT (1966). The amount of fixed inter-layer cations (K + Na) of sample WBK-12 is known (0·19%). This value, when applied to Figure (7.4), as indicated by the vertical line A-B, gives approximately 79-80% expandable layers. This observation confirms the range of expandable layers determined by the X.R.D. method for the (W.K.B.) samples in the present study.

The low lattice charge shown on sample WBK-12 seems to be the result of the lower substitution of Al^{+3} for Si^{+4} in the tetrahedral sheet. The lowest and highest lattice charges associated with the lowest and highest Al^{+3} substitution for Si^{+4} in the tetrahedral sheets of the samples shown in columns 4 and 5 confirm the above inference.

The structural formula calculated for sample WBK-12 shows some differences when compared with the structural formulae of montmorillonite reported by CHOWDHURY (1980) from the Dorset Corallian sediments (column 2, Table (7.1A5)). This comparison shows a lower substitution

Fig.(7.4):

The relationship between per cent expandable (smectite) layers and the fixed inter-layer cations (K + Na) in illites and mixed-layers illite/smectite, as defined by HOWER and MOWATT (1966). The crosses (X) represent the illite and M.LI/Sm samples used by the above authors to define this relationship. The small triangles (▲) represent the points where the $(K+Na)_n$ values from the six chemical formulae of M.LI/Sm and illites from Site 223, D.S.D.P. samples meet the line representing the above relationship. The fixed inter-layer cations, i.e. (K+Na) value of sample WBK-12 meets the line at point 'B'. From these points the approximate % of expandable layers for sample WBK-12 and other samples may be determined if the calculated chemical formulae are accurate. Thus it is possible to compare the % expandability derived by X-R diffractograms and by chemical analysis. Fig.(7.4) has been reproduced from PAPAVASILIOU (1979).

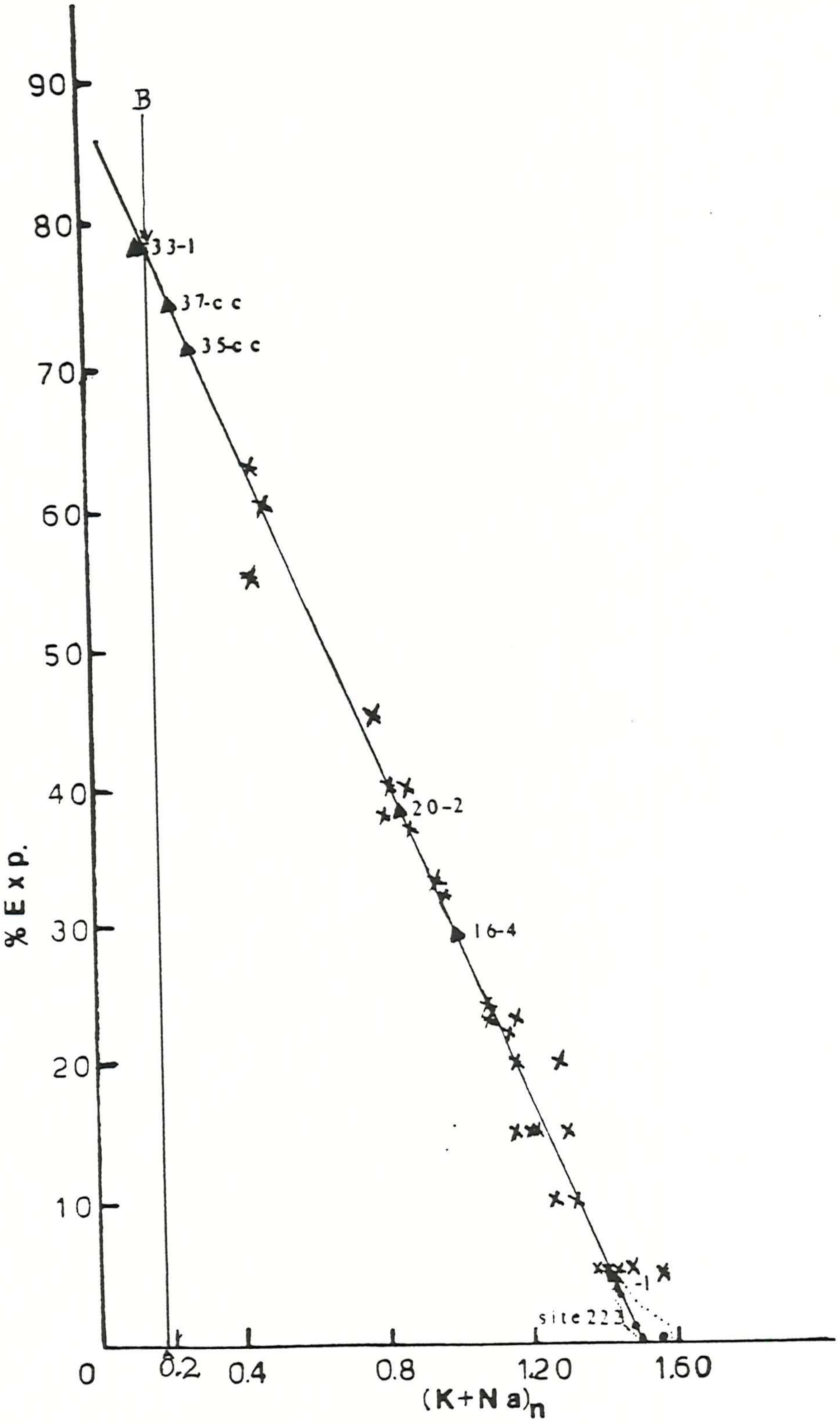

90
80
70
60
50
40
30
20
10
0
% Exp.
B
33-1
37-cc
35-cc
20-2
16-4
-1
site 223
0.2
0.4
0.8
1.20
1.60
(K+Na)$_n$

FIG. (7.4)

TABLE (7.1A6): Chemical composition of the studied clay fraction samples and comparison with the chemical composition based on the structural formulae for smectite and illite calculated by other workers, as shown in Table (7.1A5)

Chemical Composition	1*	2*	3*	4*	5*	6*	7*
SiO_2	50·58	56·60	64·80	54·76	58·58	54·85	49·73
TiO_2	0·75	0·46	-	0·67	-	1·03	0·85
Al_2O_3	20·19	20·34	24·60	15·13	24·98	23·28	23·50
Fe_2O_3	6·58	6·23	4·25	6·72	7·24	5·55	5·70
FeO	n.d.	0·92	0·21	-	-	-	-
MgO	2·25	2·86	2·83	1·62	2·90	2·01	2·42
CaO	1·02	1·10	-	1·16	0·01	0·51	1·01
Na_2O	0·13	0·20	3·15	1·06	2·77	0·55	0·46
K_2O	3·17	2·80	0·04	1·88	3·63	3·77	4·44
H_2O^+	n.d.	9·50	n.r.	n.r.	n.r.	5·65	n.d.
LOI	15·25		n.r.	n.r.	n.r.	n.d.	10·27
	99·92	101·01	99·88	83·00	100·11	96·93	98·38
Mineral Composition:							
ILLITE	39	30	n.r.		n.r.	(42) 60	(50) 73
KAOLINITE	7	-	n.r.		n.r.	19	10
SMECTITE	50	62	n.r.		n.r.	(29) 11	(39) 16
CHLORITE	4	-			n.r.	10	1
QUARTZ		8	n.r.				

* Sample numbers are shown in Table (7.1A4)

Figures shown in brackets for illite are calculated from the % of K_2O, and for smectite are the modified values.

n.r = not recorded; n.d = not determined.

of Al^{+3} for Si^{+4} in the tetrahedral sheet; a lower amount of Al^{+3}, Mg^{+2} and a much higher concentration of Fe^{+3} and Ti^{+4} in the octahedral sheet. In the inter-layer position it shows approximately the same amounts of Ca^{+2}, a lower amount of Na^{+}, no Mg^{+2}, and a higher concentration of K^{+} ions. These variations explain the lower charges shown by sample WBK-12.

WEIR and RAYNER (1974) studied the structural formula of an inter-stratified illite-smectite from the weathered Oxford Clay in the Denchworth Series Soil, and this is shown in column 5 of Table (7.1A5). This sample shows the highest amounts of Al^{+3} substituted for Si^{+4} in the tetrahedral sheet and very high amounts of Al^{+3} and Mg^{+2} in the octahedral sheet. It also shows very high values of the fixed inter-layer cations (K + Na) and, according to HOWER and MOWATT (1966), it must contain lower amounts of the expandable layers. According to WEIR and RAYNER (1974), it contains approximately 45% expandable layers. As a consequence of distribution and proportions of cations in the tetrahedral, octahedral sheets and inter-layer position, this sample shows a very high lattice charge.

(c) Structural formula for illite

The structural formulae of illite for two samples, i.e. WBK-32 from the (W.K.B.) and BR-468 from the (W.B.) sediments, were calculated based on the same method as described earlier for smectite. BROWN and NORRISH (1952) calculated the structural formulae for the hydrous micas and for well-crystallized illites, using a similar method to that proposed by HENDRICKS and ROSS (1941) and GRIM and BRADLEY (1951). One of the illite formulae calculated by BROWN and NORRISH (op.cit.) is reported in column 9 of Table (7.1A5). The mineralogical and chemical analyses of the Oxford Clay samples are shown in Table (7.1A6) and Appendices (7.1B & 7.2B). The calculated structural formulae of illite are shown in columns 6 and 7 of Table (7.1A5) respectively. Both formulae are compared with the structural formulae of illite given by PAPAVASILIOU (1979) and BROWN and NORRISH (1952), which are shown in columns 8 and 9 (Table 7.1A5). The most significant difference between the illite formulae is the very high concentration of Mg^{+2} in the octahedral sheet and Ca^{+} in the inter-layer position in the D.S.D.P. sample, as compared with the Oxford Clay samples. The tetrahedral sheets

TABLE (7.1A7): Average chemical composition of illites, kaolinites, chlorites and mixed-layers illite-smectite from the literature.

Composition	ILLITES[1]	KAOLINITES[2]	CHLORITES[3]	MIXED-LAYERS[4]	5
SiO_2	50·02	45·65	26·30	60·01	44·01
TiO_2	0·48	0·80	0·22	0·22	0·64
Al_2O_3	22·19[6]	37·37	19·97	23·06	26·81
Fe_2O_3	2·99	0·69	3·24	2·10	11·99
FeO	0·25	-	18·69	0·73	-
MgO	3·18	0·34	19·66	4·40	2·43
CaO	0·20	0·48	0·29	0·22	0·11
Na_2O	0·17	0·20	-	0·17	0·07
K_2O	6·90	0·63	-	2·65	4·78
H_2O^+	7·93	13·26	11·55	6·91	8·08

1. WEAVER and POLLARD (1973), average of 3 marine illites.
2. GRIM (1968), average of 5 kaolinite analyses.
3. GRIM (1968), average of 7 chlorite analyses.
4. WEAVER and POLLARD (1973), (TABLE XLVI, column 10, page 109).
5. WEAVER and POLLARD (1973), (TABLE II, column 16, page 9).
6. VAN OLPHEN and FRIPIAT (1979), average of 13 illite samples.

of the Oxford Clay samples, particularly WBK-32, show the lowest Al^{+3} substitution for Si^{+4}, while sample BR-468 shows a higher amount of Al^{+3} substituted for Si^{+4}. GRIM (1968) mentioned that well-crystallized micas display less substitution of Al^{+3} for Si^{+4} in the tetrahedral sheet. Both samples of the Oxford Clay show enriched values of Al^{+3} in the octahedral sheet when compared with the sample shown in column 8, but the sample in column 9 shows the highest amount of Al^{+3} in the octahedral sheet, which is very close to sample BR-468 in column 7, Table (7.1A5). Sample BR-468 also showed appreciable amounts of Mg^{+2} in the octahedral sheet, which are very close to the contents of Mg^{+2} in the sample shown in column 9. Sample WBK-12 does not show any amount of Mg^{+2} in the octahedral sheet. According to WEAVER and POLLARD (1973, p.7), low MgO illites are primarily formed from the alteration of feldspar, as might be expected. PAPAVASILIOU (1979) associated the enriched value of Mg^{+2} in the sample studied by him with the Mg-rich provenance for his illite. He further stated that the most probable source of illite is the metamorphosed part of the Oman ophiolites (GLENNI et al., 1973; SMEWING et al., 1976).

The structural formula of illite for sample WBK-32 shows a high amount of Al^{+3} and no Mg^{+2} in the octahedral sheet. High Na^+ and a very high amount of K^+ occurs in the inter-layer position. These trends of cation distribution suggest that the source rock for this illite was not Mg-rich, but it was rich in K and Na phyllosilicates and tectosilicates. This suggests that illite in the (W.K.B.) sediments most probably originated from the weathering of the acidic igneous rocks (granites?) from the Cornubian Highlands.

FOSTER (1956), WARSAW and ROY (1961), GRIM (1968), and WEAVER and POLLARD (1973) stated that dioctahedral illite dominates over trioctahedral illite in sediments. Illite in the Oxford Clay sediments, at present under study, seems to be dioctahedral. The net negative charge of 1·62 per $(O_{20}(OH)_4)$ unit on the tetrahedral and octahedral sheets (due to substitution of Al^{+3} for Si^{+4} in the tetrahedral and Al^{+3} for Mg^{+2} in the octahedral sheets) in sample WBK-32 is satisfied by the inter-layer cations charge of +1·61.

The structural formula of illite for BR-468 showed, comparatively, a higher amount of Al^{+3} substituted for Si^{+4} in the tetrahedral sheet, and reflects the poor crystallinity and the degraded nature of illite as compared to the illite of WBK-32. It showed a high charge on the tetrahedral and a low charge on the octahedral sheets when compared with the illite of WBK-32. It showed a net negative charge of 0·71 per $(O_{10}(OH)_2)$ unit, while sample WBK-32 showed a little higher net negative charge of 0·81 per $(O_{10}(OH)_2)$ unit; while muscovite gives a net negative charge of 1 per $(O_{10}(OH)_2)$ unit. The charge variation also indicates a better crystallinity for the illite of WBK-32 over the illite of BR-468. Illite in BR-468 is a dioctahedral, as indicated by the three-quarters proportion of Al^{+3} in the octahedral sheet (WEAVER and POLLARD, 1973). The presence of Mg^{+2} (about one-eighth proportion) in the octahedral sheet is of significant importance. It suggests that metamorphic rocks may have contributed some detritus to the (W.B.) sediments. GRIM (1968, p.96) mentioned that there are some dioctahedral illites in which the aluminium is replaced by some iron and magnesium. WEAVER and POLLARD (1973, p.7) mentioned that the MgO content of the 'marine' illite is more abundant than in those formed under non-marine conditions. These authors further stated that the MgO content of 'marine' illite is similar to that of montmorillonite and may indicate that these illites formed from montmorillonite - probably during burial.

(d) Summary

It may be summarized, on the basis of the observations described earlier, that smectite in sample WBK-12 is dioctahedral; it contains a lower net negative charge of 0·73 per $(O_{20}(OH)_4)$ unit and contains approximately 80% expandable layers of montmorillonite. Illites in both samples are dioctahedral, trisilicic, and contain high amounts of Al^{+3} in the octahedral sheets. Illite in WBK-32 contains high amounts of fixed cations, i.e. (K + Na: 1·20 + 0·23 = 1·43%) in the inter-layer position. It showed a net negative charge of 0·81 per $(O_{10}(OH)_2)$ unit, approaching the value of 1 net negative charge per $(O_{10}(OH)_2)$ unit described for muscovite. It is a better crystalline illite as compared with that in BR-468 from the (W.B.) samples. The better crystallinity of this illite is also indicated by higher values of the crystallinity indices, i.e. C.I.W. and C.I.I., recorded in Appendices (7.1B & 7.2B) respectively for both samples. The net negative charge on the illite of BR-468 is 0·71 per $(O_{10}(OH)_2)$ unit, which is lower than that in WBK-12. This suggests the degraded nature of illite, which is further confirmed by the lower amounts of fixed cations (K + Na: 0·89 + 0·16 = 1·05%). The presence of Mg^{+2} in the octahedral sheet of this illite suggests a relationship with a Mg-rich source. Illite in the (U.O.C.) sediments of the (W.B.) samples shows an antipathetic relationship with chlorite, as shown in Table (7. 1B3). This relationship suggests that illite in the (W.B.) samples could have been formed by the weathering of chlorite-rich (low-grade metamorphic) source material.

(e) Conclusions:

On the basis of the account given in the foregoing pages, the broad conclusions are as follows:

1) Illite, kaolinite and chlorite, in the sediments of both the boreholes are detrital in origin. Illite in the (W.K.B.) sediments is more crystalline and less degraded as compared with the illite of the (W.B.) sediments.

2) Smectite (montmorillonite-illite, expanding mixed-layer mineral) in the (W.K.B.) sediments is non-detrital and probably is the alteration product of 'air-fall' volcanic ash of intermediate-basic type.

3) Kaolinite in both the boreholes shows a better crystallinity towards the base of the sediments. The (W.K.B.) kaolinite, as compared with that of the (W.B.), is more crystalline and may be a product of first cycle of sediments.

4) Mixed-layer minerals (non-expanding) in the (W.B.) sediments are detrital in origin.

5) The enriched values of the smectite of better crystallinity in the (U.O.C.) sediments of the (W.K.B.) may be related to a localised pulse of volcanic activity.

6) The smectite contains calcium in the inter-layer position. It is dioctahedral and contains significantly higher amounts (approximately 80%) of the montmorillonitic layers.

7) The illite is dioctahedral in the sediments of both the boreholes. Illite of the (W.K.B.) seems to be derived from an acidic igneous source, while that of the (W.B.) is from the weathering of chlorite-rich sediments. Illite in the (W.K.B.) is more crystalline and contains a net negative charge approaching that for muscovite.

The (W.B.) illite is degraded, less crystalline and shows a comparatively lower net negative charge.

8) The structural formulae, calculated for smectite and illite compare well with the published formulae, reported in Table (7.1A5). These formulae may be considered semi-quantitative, as the abundances of clay minerals are also semi-quantitative.

7.2 Geochemistry of Clay Fraction (< 2μ) of the (W.K.B.) and (W.B.) Sediments

I. Introduction

The geochemical studies of the clay fraction (< 2μ) sediments of 12 representative samples from each borehole collection were carried out with the aim of observing the possible relationships between the chemical components and clay mineral species. Methods of separation of the clay fraction (< 2μ) and the preparation for chemical analysis of minor elements on X.R.F., and major elements on Betaprobe, were as described in Chapter Two.

II. Presentation of Data

The results of chemical and mineralogical analyses of the studied sediments of the (W.K.B.) and (W.B.) are tabulated respectively in Appendices (7.1B) and (7.2B). Summaries of statistics of the samples of the two boreholes are presented in Appendices (7.1C and 7.2C). The correlation coefficient summaries showing significant correlations are presented in Tables (7.2A4 & 7.2B4). Factor loadings, inter-factor correlations and factor scores of the (W.K.B.) and (W.B.) samples are shown in Tables (7.2A1, 7.2A2 & 7.2B1 and 7.2B2) respectively. Table (7.3) shows the average values of the chemical analyses of the studied samples and their comparison with the average values of chemical analyses reported by CHOWDHURY (1980) for the clay fraction (< 2μ) samples of the Lower Calcareous Grit Group from the Dorset area. Atomic ratios of some of the elements studied in the present sediments were calculated and are reported in Table (7.4), which also shows a comparison of these ratios with similar ratios determined for the Lower Calcareous Grit Group (CHOWDHURY, 1980), the Indian Ocean D.S.D.P. sediments (PAPAVASILIOU, 1979) and terrigenous material (BOSTRÖM et al., 1976).

III. Analyses of the Data

The chemical and mineralogical data of the studied samples were subjected to bivariant correlations and R-mode factor analysis to observe the relationships and specific trends, if any, between the chemical and mineralogical components in the studied samples. For

TABLE (7.2A1): Promax Factor Loadings for $K_{min} = 3$ and Correlations between the Promax Factors for $K_{min} = 3$ for the 12 clay fractions ($< 2\mu$) samples of the (W.K.B.) sediments.

COMPONENTS	F-1	F - 2	F - 3
Depth	0·88		
SiO_2	-0·87		
TiO_2		0·33	0·75
Al_2O_3	0·53		0·86
Fe_2O_3(T)	-0·66	-0·57	
MgO	-0·81		0·28
CaO			-0·77
Na_2O	0·33	0·54	-0·52
K_2O		0·29	0·88
S	0·39	-0·50	-0·55
P_2O_5	0·38	0·46	-0·60
V	-0·48	-0·40	0·56
Cr	0·71		0·29
Mn		0·46	0·63
Ni			0·77
Ba	0·42	0·72	0·37
Ce	0·31		-0·62
Th		0·54	-0·62
Pb	0·30	-0·92	
As	-0·82	0·43	
Zn		-0·89	
Cu	0·69	-0·47	
Rb			0·32
Sr	0·56	0·30	
Y	0·64		-0·41
Zr	0·25	0·81	
Nb	-0·39	-0·32	0·27
Mo	0·61	-0·75	
La		0·80	
C_{org}	0·93		

/contd.over

TABLE (7.2A1) contd.

COMPONENTS	F - 1	F - 2	F - 3
H_2O^+	0·83		0·49
Fe^{2+}	0·81		-0·25
Fe^{3+}	0·84		
Percentage of Total Explanation	35·02	21·93	16·22

Cumulative explanation = 73·17%

Correlations between Promax Factor for $K_{min} = 3$

(F-1)	1·0000		
(F-2)	0·0818	1·0000	
(F-3)	0·2227	0·0603	1·0000
	(F-1)	(F-2)	(F-3)

Note: Factor loadings < 0·25 (±) were omitted.

TABLE (7.2A2): Scores on Promax Factors for the 12 clay samples ($< 2\mu$) of the (W.K.B.) sediments.

(F-1)	(F-2)	(F-3)
-2·240	-1·034	-1·292
-1·198	0·412	0·957
-0·847	0·541	1·586
-0·928	0·416	1·288
0·460	-1·536	0·083
0·641	-2·213	0·388
0·951	-0·091	-1·314
0·820	0·976	-1·292
0·732	0·741	-1·109
0·668	0·737	0·013
0·727	0·597	0·332
0·213	0·455	0·360

TABLE (7.2A3): Summary of Promax Factor Loadings, showing the correlation coefficient for different levels of significance of the loaded components in the respective factors, clay fraction ($< 2\mu$) samples of the (W.K.B.).

	Significance Levels	(F-1)	(F-2)	(F-3)
+ve	10%	Al	Na, Th	H_2O^+
	5%	Sr, Y, Mo		V, Mn
	0.01%	Depth, Cr, Cu, C_{org}, H_2O^+, Fe^{2+}, Fe^{3+}	Ba, Zr, La	Ti, Al, K, Ni
-ve	0.01%	Si, Mg, As	Pb, Zn, Mo	Ca
	5%	Fe_2O_3(T)	Fe_2O_3(T)	Ce, Th
	10%	V	S	Na, S, P

Significance levels are: 10% ≥ 0.49
5% ≥ 0.57
0.01% ≥ 0.70

TABLE (7.2A4): Summary of the correlation coefficients, showing the various levels of significance between the chemical elements determined in clay fraction ($< 2\mu$) of 12 samples and the abundances of clay minerals, in the (W.K.B.) sediments.

Significance Levels		ILLITE	KAOLINITE	CHLORITE	SMECTITE	Corg
+ve	10%	P, Cr, Fe^{3+}	Na, P	Cr, Zr	V, As, Zn	S, P
	5%	Al, Na, Y, Zr, Fe^{2+}, Chlr.	Cu, Y, Mo, H_2O^+ Fe^{3+}	Depth, Ti, Sr, Ill.		
	0·01%	Depth, Ba, C_{org}, H_2O^+, Kaol.	Depth, C_{org}, Fe^{2+}, Ill.	Ba	Si, Fe(T), Mg	Depth, Cu, Y, Mo, H_2O^+, Fe^{2+}, Fe^{3+}, Ill, Kaol.
-ve	0·01%	Si, Fe(T), Mg, Smect.	Si, Mg, Smect.		Depth, C_{org}, Ill, Kaol.	Si, Mg, As, Smect.
	5%	Zn	Fe(T), As		Al, Ba, Y, Zr, H_2O^+, Fe^{2+}, Fe^{3+}, Chlr.	Fe(T)
	10%	V		Zn, Smect.	Na, P, Cr, Sr	V

For 10 degrees of freedom the correlation coefficient values for 10%, 5% and 0·01% levels of significance are as follows:

10% $>$ 0·49
5% $\geq$ 0·57
0·01% $\geq$ 0·70

TABLE (7.2B1): Promax Factor Loadings for K_{min} = 3 and Correlations between the Promax Factors for K_{min} = 3 for the 12 clay fraction samples of the (W.B.) sediments

COMPONENTS	FACTOR(F-1)	FACTOR(F-2)	FACTOR(F-3)
Depth in Borehole	0·91		
SiO_2	-0·245		0·67
TiO_2	0·47	0·49	0·28
Al_2O_3	0·62	0·58	
Fe_2O_3(T)	-0·86	0·25	
MgO	-0·39		0·57
CaO	-0·94		
Na_2O	0·32		-0·86
K_2O	-0·57	0·68	
P_2O_5	-0·64		-0·69
V	-0·39	0·81	
Cr	0·48		
Mn		0·87	
Ni		0·61	-0·35
Ba			-0·74
Ce	0·62	0·48	
Th			
Pb		0·55	
As	-0·565		
Zn		0·79	
Cu	0·62		-0·39
Rb		0·84	
Sr	0·57	0·32	-0·44
Y	0·39		-0·52
Zr	0·63	0·24	
Nb		-0·66	
Mo	0·60		
La	0·27		-0·40
Percentage Explanation	31·92	18·5	11·95

/contd.over

TABLE (7.2B1) contd.

Correlations between the Promax Factors for $K_{min} = 3$

F-1	1·0000		
F-2	0·0665	1·0000	
F-3	0·2379	0·0414	1·0000
	(F-1)	(F-2)	(F-3)

Note: Factor loadings < 0·24 were omitted.

TABLE (7.2B2): Scores on Promax Factors of 12 Clay Fraction Samples (W.B.)

FACTOR (F-1)	FACTOR (F-2)	FACTOR (F-3)
-2·069	-2·176	1·465
-0·698	0·414	-1·317
-1·073	1·032	0·769
-0·447	1·881	1·066
-0·388	0·116	0·137
-0·334	-0·619	-0·450
0·257	-0·062	-1·919
0·530	0·518	-0·670
0·615	0·237	0·695
0·952	-0·048	0·389
1·261	-0·873	0·044
1·393	-0·417	-0·209

TABLE (7.2B3): Summary of components loaded in the respective factors indicating 10%, 5% and 0·01% levels of significance in the (W.B.), samples.

	Significance levels	FACTOR(F-1)	FACTOR(F-2)	FACTOR(F-3)
+ve	10%	Cr	Ti, Ce, Pb	
	5%	Al, Ce, Cu, Sr, Zr, Mo	Al, K, Ni	Si, Mg
	0·01%	Depth, LOI	V, Mn, Zn, Rb	NONE
-ve	0·01%	Fe(Total), Ca	NONE	Na, Ba
	5%	K, P, As	Nb	P
	10%			Y
Percentage of Explanation		31·92%	18·5%	11·95%

Cumulative Explanation = 62·4%

Factor loadings indicate the significance levels for 10%, 5% and 0·01% levels. For 10 degrees of freedom these levels are:

10%	$\geq$ 0·49
5%	$\geq$ 0·57
0·01%	$\geq$ 0·70

TABLE (7.2B4): Summary of the Correlation Coefficient Matrix of Clay Minerals and Clay Fraction chemistry of the (W.B.) sediments

	Significance Levels	ILLITE	KAOLINITE	MIXED-LAYERS	CHLORITE
+ve	10%	Rb, M.L.	Ti, Sr, Chlr.	Mg	Sr, Kaol.
	5%	Mn	Ce, Cu	Nb	Al, Ce, Cu
	0·01%	NONE	Depth, Al, Zr		Pb, Zr
-ve	0·01%	NONE	Fe, Ca, M.L.	Al, Zr, Kaol.	
	5%	NONE	Mg	Rb, Chlr.	Mg, M.L.
	10%	NONE	NONE	Ti, Mn, Ce, Ill.	Si

n = 12

For 10 degrees of freedom the significance levels for 10%, 5% and 0·01% correlation coefficients are as under:

10%	⩾ 0·49
5%	⩾ 0·57
0·01%	⩾ 0·70

TABLE (7.3): Comparison of the clay fraction ($< 2\mu$) chemistry of the Oxford Clay and Kellaways Formations of the (W.K.B.) and (W.B.) samples with the clay fraction ($< 2\mu$) chemistry of the Lower Calcareous Grit Group sediments from Dorset.

Major Elements (%)	1		2		3	
	(a)	(b)	(a)	(b)	(a)	(b)
Si	24·32	3·191	21·90	3·086	23·940	3·175
Ti	0·50	-0·683	0·53	-0·635	0·306	-1·184
Al	11·97	2·482	12·49	2·525	10·107	2·313
Fe	3·94	1·371	3·66	1·297	4·168	1·427
Mg	1·14	0·131	1·28	0·247	1·592	0·465
Ca	0·65	-0·427	0·39	-0·942	0·572	-0·559
Na	0·50	-0·690	0·75	-0·288	0·163	-1·814
K	2·86	1·052	3·40	1·224	2·374	0·864
Minor Elements (%)						
V	0·0196	-3·932	0·0202	-3·902	0·0170	-4·074
Cr	0·0192	-3·953	0·0191	-3·958	0·0095	-4·656
Mn	0·0196	-3·932	0·0174	-4·051	0·0095	-4·656
Ni	0·0070	-4·962	0·0073	-4·920	0·0053	-5·240
Ba	0·0421	-3·168	0·0458	-3·083	0·0462	-3·075
Ce	0·0097	-4·630	0·0073	-4·920	0·0068	-4·990
Pb	0·0084	-4·779	0·0025	-5·991	0·0032	-5·745
Zn	0·0253	-3·677	0·0088	-4·733	0·0084	-4·779
Cu	0·0026	-5·952	0·0027	-5·914	0·0024	-6·032
Rb	0·0224	-3·800	0·0260	-3·650	0·0162	-4·122
Y	0·0032	-5·745	0·0027	-5·914	0·0028	-5·878
Zr	0·0154	-4·173	0·0158	-4·148	0·0050	-5·298
Nb	0·0020	-6·215	0·0018	-6·320	0·0021	-6·166

Explanation of Table (7.3)

1. Average values of the chemistry of clay fraction ($< 2\mu$) of the Oxford Clay and Kellaways Formations from the (W.K.B.)sediments.

2. Average values of the chemistry of clay fraction ($< 2\mu$) of the Oxford Clay and Kellaways Formations from the (W.B.) sediments.

3. Average values of the chemistry of clay fraction ($< 2\mu$) of the Lower Calcareous Grit Group from Dorset coast, reported by CHOWDHURY (1980).

(a) Average values of elements determined by Betaprobe and X.R.F. in the clay fraction ($< 2\mu$).

(b) Average values of elements represented in $\log_{10}$ (concentration %).

the correlation programme, both chemical and mineralogical data were used, but for R-mode factor analysis, only chemical data were processed. Atomic ratios of some of the elements were determined in order to gain some idea regarding the origin of the elements and the nature of the parent rocks which contributed to the formation of the clay minerals. Details of these studies are given as under.

(A) Study of some critical Atomic Ratios (A.R.):

The study of atomic ratios of the elements is considered a good measure for tracing the origin of the elements present in the sediments, and also for determining the nature of the source which contributed to the formation of clays. Some also reflect the physico-chemical conditions prevailing in the sediments and the basin of deposition.

The $Si/Al_{(A.R.)}$ of the (W.K.B.) is lowest when compared with the values of this ratio, shown in Table (7.4),for the (W.B.) and other terrigenous sediments. The higher value of this ratio for the (W.B.) sediments suggests a greater influence of the terrigenous material on these sediments as compared with the (W.K.B.) sediments. The Ti/Al (A.R.) for both the borehole sediments is close to the ratios shown in the columns 4 and 5 of Table (7.4). It confirms the detrital nature of titanium in the Oxford Clay sediments. Anatase was found to be present in some of the bulk samples, as previously mentioned in Chapter Four. Titanium in the (W.K.B.) sediments is present in significant proportions in the octahedral sheets of smectite and illite, as compared with the illites of the (W.B.) sediments, as shown in Table (7.1A5). $Ti/Al_{(A.R.)}$ for the Corallian clay fraction ($< 2\mu$) sediments is shown in column 3 in Table (7.4); these sediments contain zeolite and other recognisable volcanic debris, but show a much lower value of $Ti/Al_{(A.R.)}$.

Cr is known for its lithogenous character; the $Cr/Al_{(A.R.)}$ of both the borehole sediments is higher than for terrigenous material, and very close to that of the D.S.D.P. Indian Ocean sediments. It suggests that the detrital clays in the Oxford Clay sediments are the product of an original assemblage dominated by basic and intermediate igneous rocks. The $Ni/Al_{(A.R.)}$ for the (W.K.B.) is the highest in Table (7.4), and suggests the influence of basic to intermediate rocks on the detritus of the Oxford Clay. The $K/Al_{(A.R.)}$ for the Oxford Clay

TABLE (7. 4): Comparison of some critical atomic ratios of elements in the clay fraction ($< 2\mu$) sediments of the (W.K.B.) and (W.B.) with those of other workers.

ATOMIC RATIOS	1	2	3	4	5
Si/Al	1·95	2·35	2·27	3·69	2·96
Ti/Al	0·0238	0·0239	0·017	0·035	0·033
Fe/Al	0·159	0·141	0·199	0·380	0·29
K/Al	0·165	0·187	0·162	0·092	0·19
Na/Al	0·049	0·070	0·019	0·027	0·16
Cr/Al	0·00083	0·00086	0·00049	0·00089	0·00064
Ni/Al	0·049	0·00026	0·00024	0·001	0·00051
Zn/Al	0·00087	0·00028	0·00034	0·0012	0·0004
Mn/Al	0·0008	0·00065	0·00046	0·0035	0·0053
Fe/Mn	198·13	218·33	431·21	108·00	55·68

Note: (1) Atomic ratios of elements in clay fraction ($< 2\mu$) of the (W.K.B.) samples.
(2) " " " " " " " " " " (W.B.) samples.
(3) " " " " " " " " " " Lower Calcareous Grit Group samples from Dorset (CHOWDHURY, 1980).
(4) " " " " " " " " " " Indian Ocean Sediments (PAPAVASILIOU, 1979).
(5) " " " " " " " " " Terrigenous material (BOSTROM *et al.*, 1976).

sediments is higher than that for the D.S.D.P. sediments; it is highest in the (W.B.) sediments and is very close to the terrigenous material. The K/Al$_{(A.R.)}$ values of the Oxford Clay sediments reflect the variation of the abundance of illite. Appendices (7.1B & 7.2B) show the average values of illite and indicate a higher abundance of illite (66%) in the (W.B.) sediments as compared with the (W.K.B.) sediments (57·58%) and explains the reason for higher K/Al$_{(A.R.)}$ for the (W.B.) sediments.

PAPAVASILIOU (1979) reported a higher value of Na/Al$_{(A.R.)}$ for the > 2μ samples containing zeolites (clinoptilolite). The average value of Na/Al$_{(A.R.)}$ in the studied samples is much higher than that reported by PAPAVASILIOU (1979) and CHOWDHURY (1980), but lower than that for terrigenous material. The higher value of Na/Al$_{(A.R.)}$ in the Oxford Clay sediments may be either an indication of the presence of zeolites in minor amounts, or it may be due to the presence of Na-bearing feldspar, as mentioned in Chapter Four. The Fe/Mn$_{(A.R.)}$ value in the Oxford Clay sediments for both the boreholes is much higher than its value in the Indian Ocean sediments and terrigenous material, but it is lower than for the Corallian sediments. The higher iron content, as shown by the (W.K.B.) samples, is due to the presence of Fe^{+3} in significant amounts in the octahedral sheets of smectite and illite, as illustrated in Table (7.1A5). High iron contents may also be related to the presence of iron oxides, coating the surfaces of clay minerals. The Fe/Al$_{(A.R.)}$ of the (W.K.B.) is higher than that of the (W.B.), and supports the above suggestion.

The Zn/Al$_{(A.R.)}$ in the (W.K.B.) sediments is higher than its value in the (W.B.) sediments. Table (7.4) shows the highest value of Zn/Al$_{(A.R.)}$ in the D.S.D.P. sediments from the Indian Ocean, reported by PAPAVASILIOU (1979). He related the high value of Zn/Al$_{(A.R.)}$ to the basaltic influence on the studied sediments. The higher value of Zn/Al$_{(A.R.)}$ in the (W.K.B.) sediments, as compared to the (W.B.) sediments, also suggests the influence of basic and intermediate source in the detritus of the (W.K.B.) sediments.

Figure (7.5a) shows enrichment of Ni, Zn, Cr, Na, Ti, Zr, Pb, Ce and Rb elements in the (W.K.B.) sediments over the Corallian rocks (Mg-rich), postulated by CHOWDHURY (1980) to contain a significant volcanogenic component. This enrichment of elements, probably of direct igneous origin, would support a theory of substantial igneous provenance, dominated evidently (Zn, Ni, Cr) by basic material.

FIG.(7.5a): This figure shows a plot on 1:1 basis of the average values of chemistry, expressed as Log_{10} (per cent) of the clay fractions ($< 2\mu$) of the (W.K.B.) and Lower Calcareous Grit Group (i.e. L.C.G.G.) of the Corallian sediments from the Dorset coast, as reported by CHOWDHURY (1980). This plot clearly shows the enriched values of elements Mn, Zn, Cr, Ni, Pb, Na and Ti in the (W.K.B.) sediments over the (L.C.G.G.) sediments, and confirms the greater influence of igneous (basic) material over the (W.K.B.) detritus.

FIG.(7.5b): Shows a plot on 1:1 basis of the average values of chemistry, expressed as Log_{10} (per cent) of the clay fractions ($< 2\mu$) of the (W.K.B.) and (W.B.) sediments. This plot shows enrichment of elements Pb, Zn, Ce, Ca in the (W.K.B.) over the (W.B.) sediments, which show an enriched value of only one element, i.e. Na.

AVERAGE CHEMISTRY LOWER CALCARIOUS GRIT GROUP,DORSET COAST

CLAY FRACTION

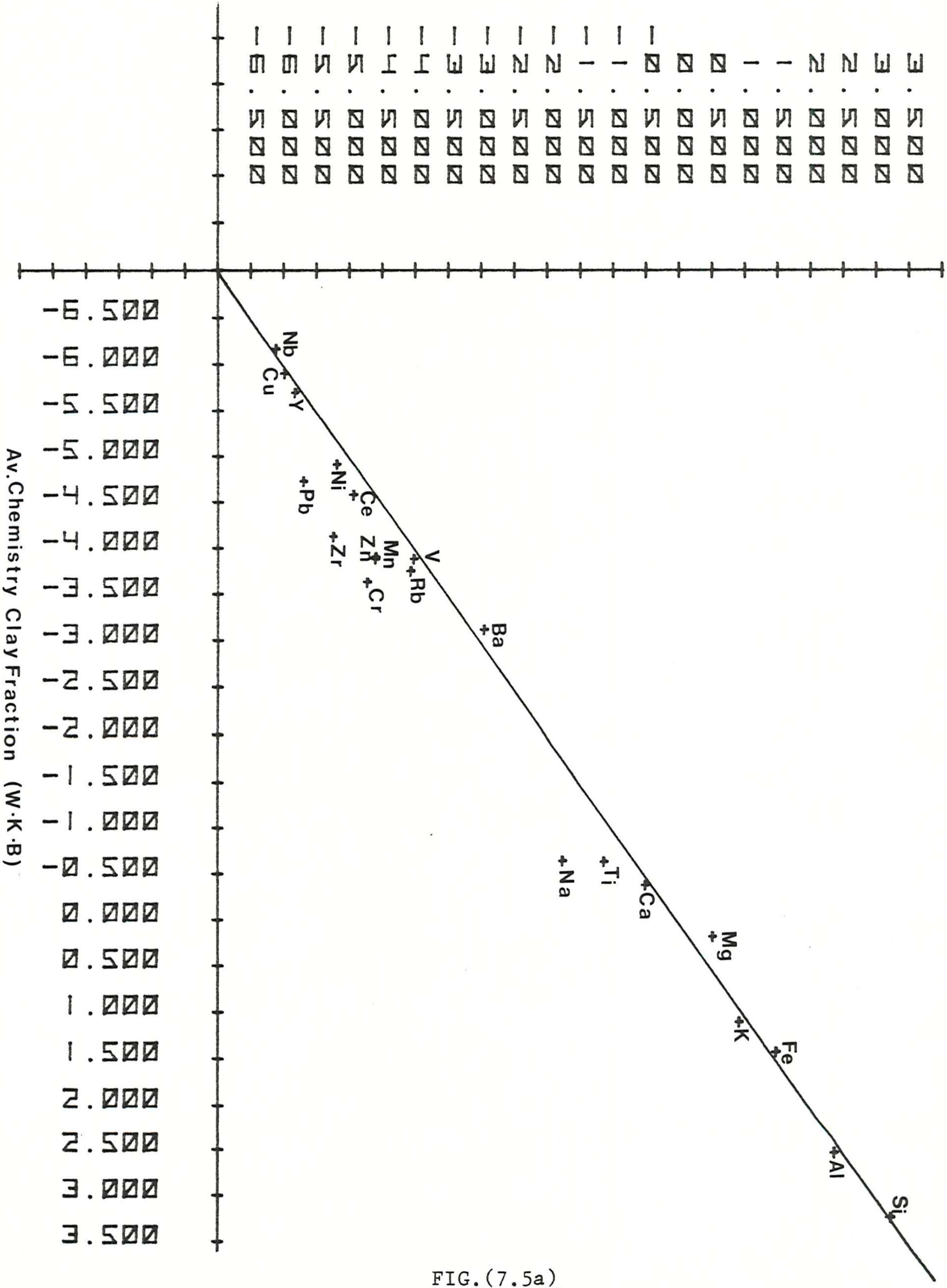


FIG.(7.5a)

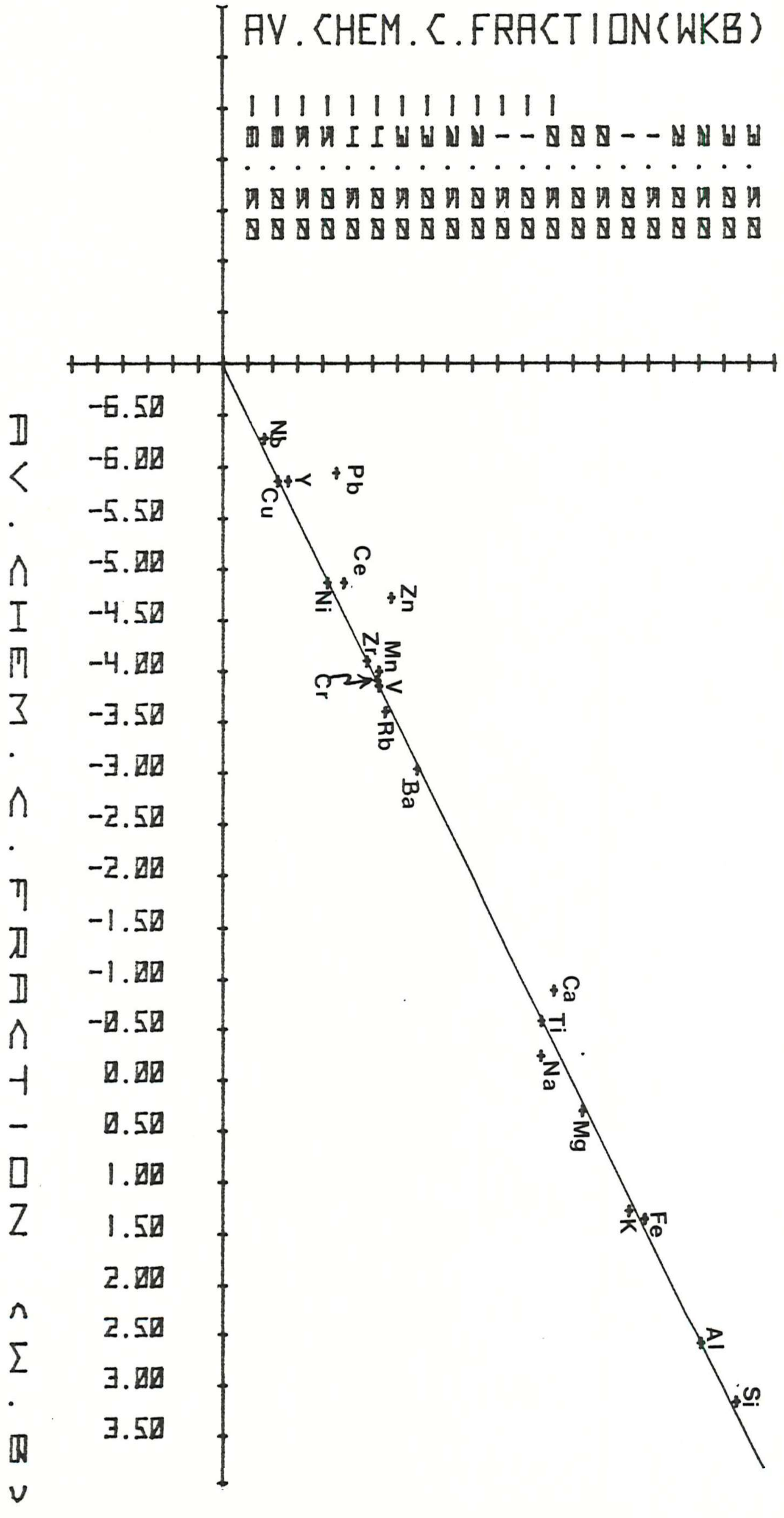

AV.CHEM.C.FRACTION(WKB)
AV.CHEM.C.FRACTION
-6.50
-6.00
-5.50
-5.00
-4.50
-4.00
-3.50
-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
Nb
Pb
Y
Cu
Ce
Ni
Zn
Zr
Mn
V
Cr
Rb
Ba
Ca
Ti
Na
Mg
Fe
K
Al
Si

FIG (7.5b)

Figure (7.5b) shows enrichment of elements Ca, Zn, Pb, Y and Ce in the (W.K.B.) sediments over the (W.B.) sediments, which have demonstrated an enriched value of Na, K and Rb; which supports a sedimentary provenance for the (W.B.) samples.

(B) Correlations

Data pertaining to chemical and mineralogical analyses of the studied sediments ($< 2\mu$) were run on the University Computer to observe the inter-relationships between the elements and clay minerals. The correlation coefficients shown by the clay minerals with elements are summarized in Tables (4.2A4 & 4.2B4) for the (W.K.B.) and (W.B.) samples respectively.

Clay mineral species, i.e. illite, kaolinite, chlorite and smectite of the (W.K.B.) sediments in Table (7.2A4) show stronger positive and negative correlations between themselves and also with chemical elements as compared with those of the (W.B.) sediments, shown in Table (7.2B4). The correlation of illite tends to indicate that it is detrital; its abundance increases with depth in the borehole, and it controls the abundance of elements such as Al, Fe^{+3} and Fe^{+2} in association with Cr in the octahedral sheet (WEAVER and POLLARD, 1973). The association of Y^{+3} (0·98Å) suggests that probably some amount of Y^{-3} was substituted for Al^{+3}(0·61Å) in the octahedral sheet. The association of Na with illite is quite obvious, being an inter-layer cation. The association of Zr may be due to the detrital nature of illite and Zr in true zircons, although some Zr may be associated as adsorbed onto the illite grains.

The correlations of kaolinite in the (W.K.B.) sediments clearly indicate that it is detrital and increases with the depth in the borehole. Higher average values of kaolinite are present in the sediments of the (L.O.C.) and (K.F.) as shown in Table (4.1B). The strong positive correlation of kaolinite with C_{org} and Fe^{+2} is also due to simultaneous increase of these components towards the deeper parts in the borehole. The very strong positive and negative correlations of kaolinite with illite and smectite respectively confirm its detrital nature. PERRIN (1971) stated that kaolinite, in contrast to mica, is not affected by prolonged transportation in water of low ionic strength. It implies that kaolinite entering a basin of deposition is essentially the same in type and amount as that leaving the terrain which is being eroded. The relationship of illite with C_{org} and chalcophile elements shown in Table (7.2A4) is due to relatively larger particle size of kaolinite, which settle rapidly. The rapid rate of sedimentation may cause the burial of the living organisms along with the freshly deposited sediments. The freshly buried organisms consume all the available oxygen present in the environment for their survival, and thus reducing conditions are created within the freshly deposited sediments and also at the water and sediment interface; thus the precipitation of sulphides is facilitated. The weaker positive association of kaolinite with Na and P_2O_5 may be due to the presence of Na-bearing feldspar in the studied sediments.

The correlations of chlorite also suggest that it is detrital in origin. The association of Cr^{+3}(0·70Å), Zr^{+4}(0·80Å) and Ti^{+3}(0·75Å) seems to be the result of the substitution of these elements either for Al^{+3}(0·61Å) or Mg^{+2}(0·80Å) in the octahedral sheet, on grounds of the close ionic radii of these elements. The larger elements Ba^{+2}(1·44Å) and Sr^{+2}(1·21Å) seem to be substituted for the larger cations K^{+}(1·46Å), Na^{+}(1·10Å) and Ca^{+2}(1·08Å) in the inter-layer position. In the (W.B.) sediments the very strong association of Pb and Zr with chlorite may be due to their adsorption onto the grains of chlorite.

The correlations of smectite most obviously suggest a non-detrital origin. A strong positive correlation of Si, Fe_2O_3 and Mg with smectite would seem to be obvious. According to ROSS and HENDRICKS (1945), Mg is essential for the formation of montmorillonite; it increases the size and the charge of the octahedral sheet and tends to decrease the layer strain. WEAVER and POLLARD (1973) mentioned that the major contribution of Mg in smectite is to enable Al to take six-fold co-ordination under basic conditions. Al tends to take six-fold co-ordination at low temperature only in acid environments. In the basic environments where montmorillonite and illite are formed, it is likely that Al tends to resist six-fold co-ordination; therefore Mg is necessary to nucleate the octahedral co-ordination.

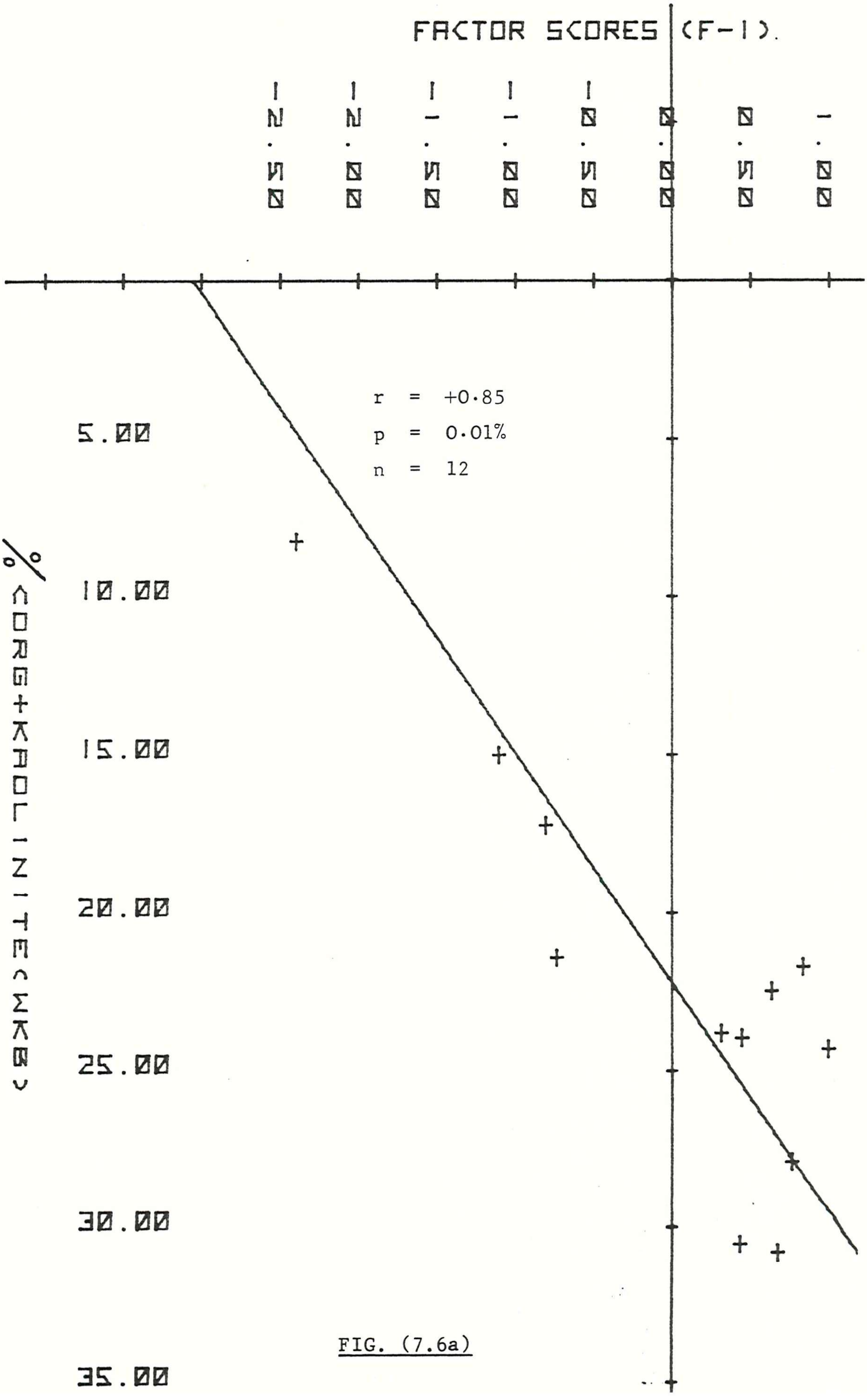

FACTOR SCORES (F-1).
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
r = +0.85
p = 0.01%
n = 12
5.00
10.00
15.00
20.00
25.00
30.00
35.00
% (ORG+KAOLINITE(WKB)

FIG. (7.6a)

C-1: R-mode Factor Analysis of Clay Fraction Chemical Data of the (W.K.B.) Samples

Introduction

Chemical data of the clay fraction ($<2\mu$) of the (W.K.B.) samples was analysed by R-mode factor analysis in the usual way, as described for the bulk rock samples in Chapter Four. Three factors were extracted, which explained 73·17% of the total variance. Factor loadings and inter-factor correlations for $K_{min} = 3$ are tabulated in Table (7.2A1). Factor scores are shown in Table (7.2A2) and a summary of loaded components in respective factors is shown in Table (7.2A3). A detailed description of each factor is as follows:

FACTOR (F-1):

This factor explains 35·02% variance, and is the most important factor in the studied samples. Considering the very strong loadings of C_{org}, H_2O^+, Fe^{+2}, Fe^{+3}, depth, Cr and a medium strong positive loading on Al_2O_3, this factor is being designated as the factor representing the 'Kaolinite + C_{org}' phases in the studied sediments. The strong relationship between C_{org}, kaolinite and chalcophile elements in these sediments has been explained earlier in the account of the correlations. The association of C_{org} with kaolinite suggests that a significant amount of terrestrial organic material is present with detrital kaolinite. The strong positive loading on depth reflects the higher average amounts of kaolinite and C_{org} in the sediments with depth in the borehole. Figure (7.6a) shows a plot of the combined abundances of kaolinite + C_{org} and the factor scores of (F-1) tabulated in Table (7.2A2). It shows a very strong positive correlation ($r = +0·85$) between the two variables, which is highly significant at the 99·99% level. It confirms that this factor is represented by kaolinite and C_{org}, and these two phases control the variance loaded in the positive phase of (F-1).

The negative phase of Factor (F-1) shows very strong loadings on Si, Fe_2O_3, MgO and As. Elements such as Mg (ROSS and HENDRICKS, 1945), Fe and Si are essentially present in montmorillonite or smectite, as has been mentioned in the study of correlations. WEAVER and POLLARD (1973) stated that Mg and Ca occupy the exchange position in montmorillonite, and Fe is mainly present in the octahedral sheet; some Fe^{+3} hydroxides

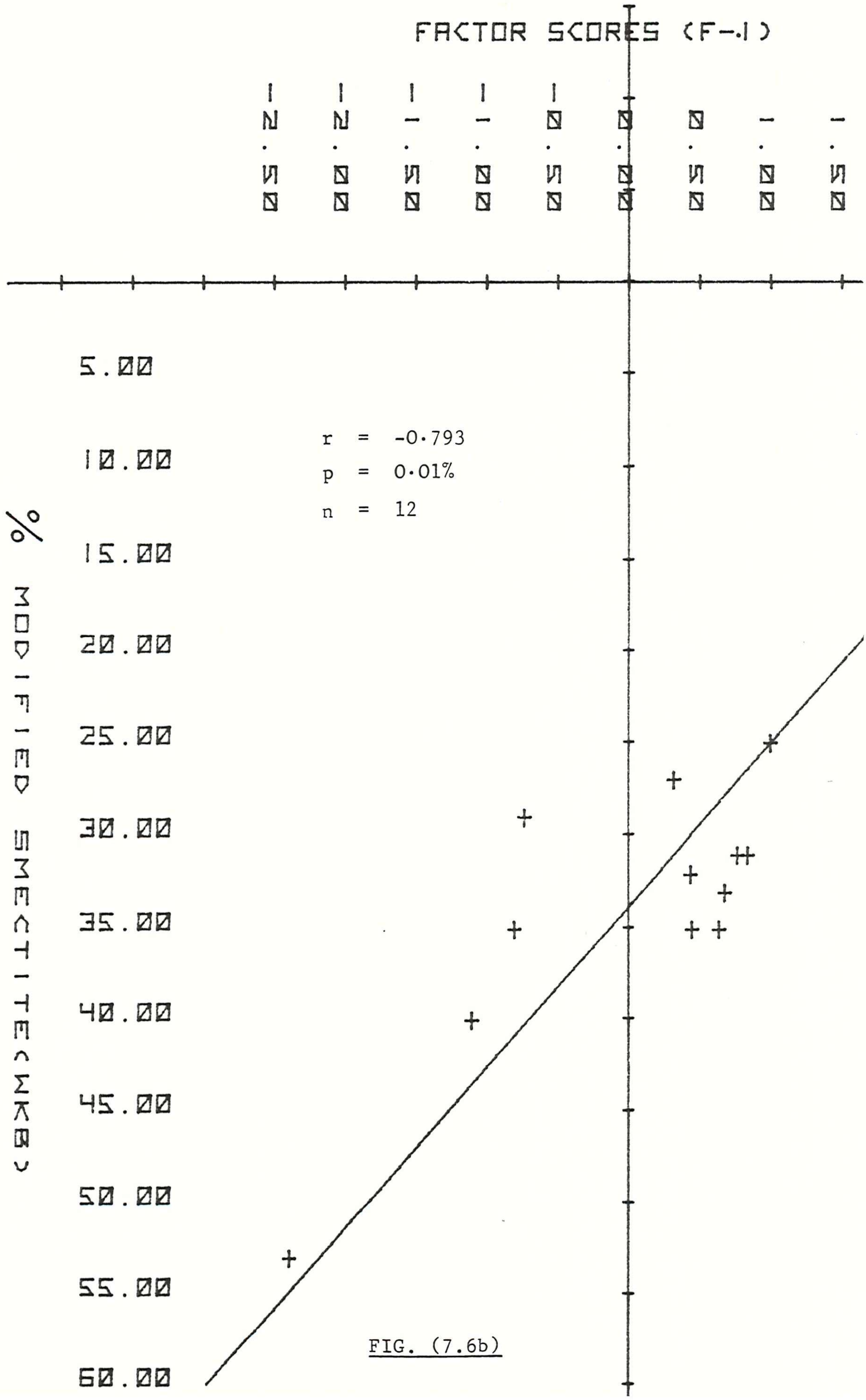

FACTOR SCORES (F-1)
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
% MODIFIED SMECTITE(WKB)
r = -0·793
p = 0·01%
n = 12

FIG. (7.6b)

may coat the grains of the clay minerals. Table (7.1A5), in column 1, shows the amounts of Fe^{+3} and Mg^{+2} present in the octahedral sheet of smectite in sample WBK-12. Taking into consideration these facts, the negative section of Factor (F-1) is interpreted as the phase of smectite. Figure (7.6b) shows a very strong negative correlation ($r = -0{\cdot}79$) between the abundances of smectite and the factor scores of (F-1), being highly significant at the 99·99% level. The whole factor thus representing the major detrital and non-detrial components.

FACTOR (F-2):

This factor explains 21·93% of the total variance. The elements Ba, Zr and La have their highest positive loadings in this factor, suggesting that the positive phase represents detrital components. There is a very weak positive correlation between factors (F-2) and (F-1) shown in Table (7.2A1), which supports this interpretation. The association of Na, K and Ba is common in feldspars, the presence of which has been mentioned in Chapter Four. Therefore, it is likely that very fine grains of feldspar, which are impossible to separate from the clay fraction, are present in the studied sediments and control the variance of Ba, Na and K. The association of P_2O_5 and La suggests the presence of monazite in the studied samples; Zr may be present as detrital grains of zircon. Mn may be associated as hydroxide.

The negative phase of Factor (F-2) is dominated by chalcophile elements along with sulphur, thus suggesting that this phase be designated the 'Sulphides phase'. The antipathetic relationship of this phase with the detrital phase in this factor indicates an authigenic origin for the 'sulphide phase'. Since the abundance of sulphur was known for each sample, the amount of pyrite was calculated for each sample. In order to confirm whether this phase really represents sulphide minerals, the abundances of pyrite were plotted against the factor scores of (F-2). Figure (7.7) shows a good negative correlation ($r = -0{\cdot}53$), significant at the 95% level, between the two variables and confirms the identification of the negative phase of (F-2). The weak positive correlation between Factors (F-2) and (F-1) further confirms this view. A much more detailed account of the relationship of components loaded in the negative phase of (F-2) with sulphide minerals has been given in Chapter Five.

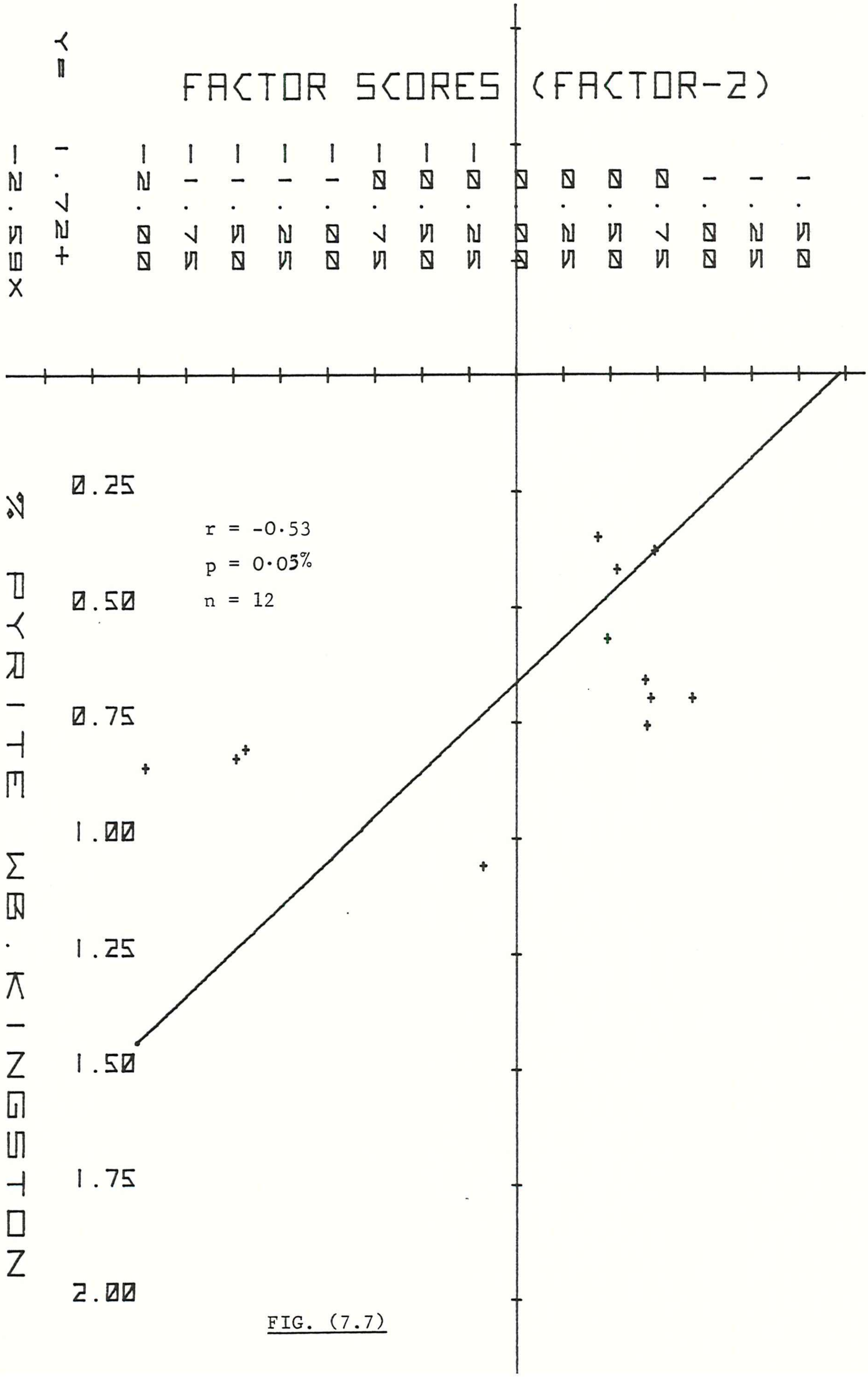

FACTOR SCORES (FACTOR-2)
Y=
1.72+
-2.59X
-2.00
-1.75
-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
1.25
1.50
% PYRITE W.KINGSTON
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
r = -0.53
p = 0.05%
n = 12

FIG. (7.7)

FACTOR (F-3):

This factor explains 16·22% of the total variance and shows its subordinate nature in the present study. The association of Ti, Al, K, Ni, V, Mn, Mg, Cr, Ba and Rb in the positive phase of this factor suggests a phase represented by illite and chlorite. VAN OLPHEN and FRIPIAT (1979) mentioned that most micas contain two or more cations in the octahedral sheet, i.e. Al, Mg and Fe, in association with other cations such as Mn, V, Cr, Li, Ti and a variety of other cations. WRIGHT (1972) (quoted by CALVERT, 1976) stated that elements like Ni, Zn and Cu may occur in the lattices of mica and chlorite. CHOWDHURY (1980) has reported the association of K, Rb, Ba, V, Cr, Pb, Zr, Nb, Si, Al, Fe, Ti, Cu, La and Ga in the illite phase present in the Corallian sediments from the Dorset coast. Factor (F-3) showed a strong negative correlation (r = -0·2227) with Factor (F-1), as shown in Table (7.2A1). This means that loadings of the positive phase of Factor (F-3) are related to the loadings of the negative phase of Factor (F-1) and vice versa. The positive phase of Factor (F-1) has been recognised as a phase of 'kaolinite + C_{org}'. Its correlation with the negative phase of Factor (F-3), showing loadings of CaO, Na_2O, P_2O_5, Ce, Th and Y, is explainable and will be described later. The negative phase of Factor (F-1) has been recognised as the phase of smectite, and its relationship with components loaded in the positive phase of Factor (F-3) is possible, since all these elements may be present in the lattices of clay minerals.

In order to test the above thesis, the abundances of illite (calculated from the amounts of K_2O for each sample, assuming that the entire K_2O resides in illite) were plotted against the factor scores of (F-3). The plot shows a very strong positive correlation (r = +0·77, significant at the 99·99% level) (Figure (7.8)) and confirms that this phase is represented by illite + chlorite minerals. First the X.R.D. determined abundances of illite + chlorite were plotted against the factor scores of Factor (F-3). This plot did not show a good relationship, possibly due to over-generous abundances of illite based on the X.R.D. results. The very strong loadings of K_2O, Al_2O_3, TiO and Ni, however, strongly suggest that this phase be recognised as the 'illite phase'. Allocation of the entire amount of K_2O to illite to produce possibly more reliable illite values seems to justify the identification of the phase

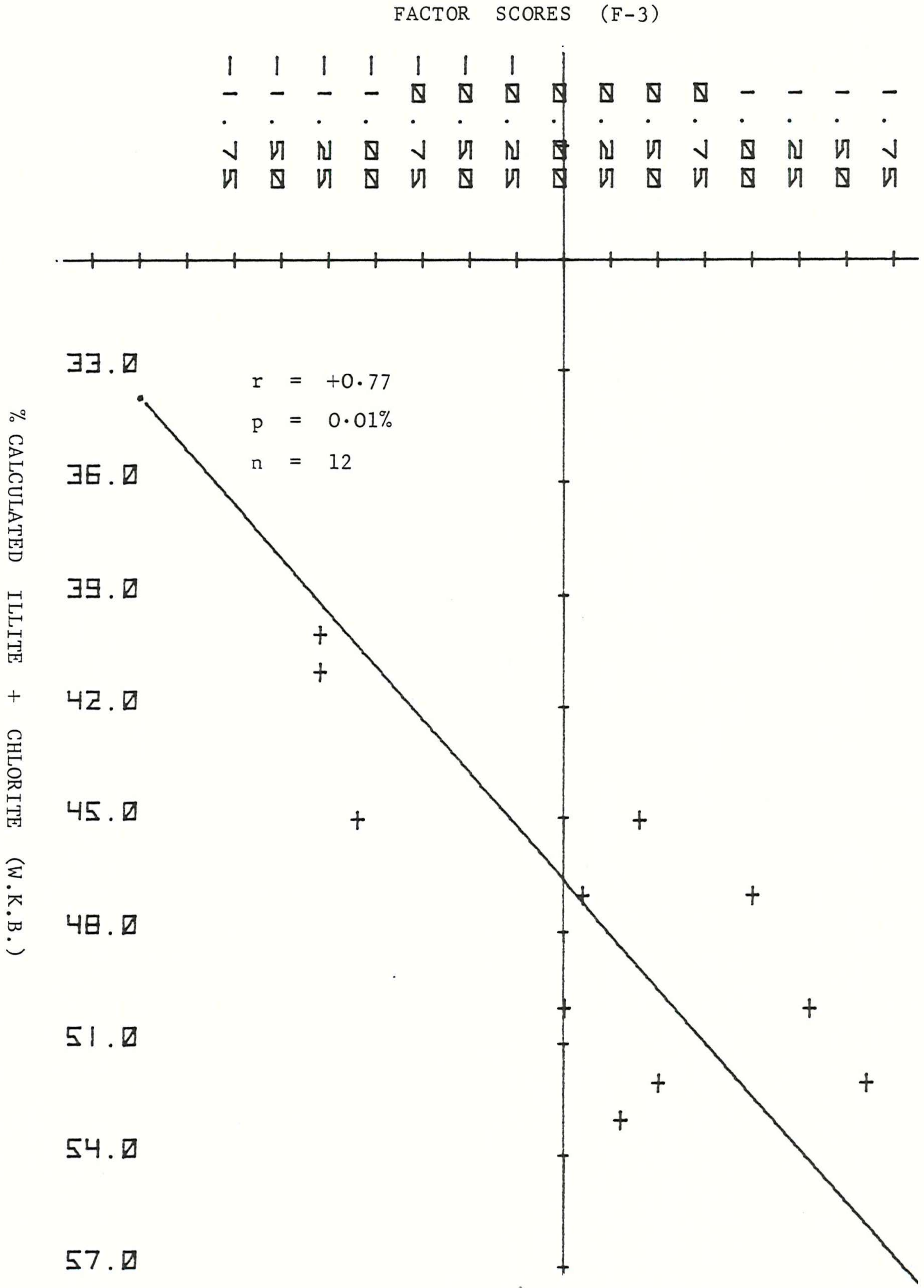

FACTOR SCORES (F-3)
-1.75
-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
% CALCULATED ILLITE + CHLORITE (W.K.B.)
33.0
36.0
39.0
42.0
45.0
48.0
51.0
54.0
57.0
r = +0·77
p = 0·01%
n = 12

FIG. (7.8)

from Figure (7.6).

The loadings in the negative phase of Factor (F-3) are typical and indicate the presence of such minerals as apatite (i.e.$CaO + P_2O_5$), monazite (i.e. P_2O_5 + Th + Ce) and feldspar (Na-bearing). The negative loading with Factor (F-1) relates this assemblage to the 'kaolinite + C_{org}' phase and its associated reducing environments (described earlier), a not unfamiliar association for phosphates. The detrital or authigenic origin of these minerals is not clear, although it is possible that both apatite and Na-bearing feldspar could (in part) be authigenic.

Summary

It may be summarized that Factor (F-1) in its positive phase is represented by 'kaolinite + C_{org}' and in its negative phase by non-detrital smectite. Factor (F-2), in its positive phase, shows the control of detrital components over the loaded variance and in its negative phase the control of the sulphide minerals, particularly pyrite. Factor (F-3), in its positive phase, indicates that the detrital clay minerals, i.e. illite and chlorite, control the variance, and in the negative phase the variance is explained by such minerals as phosphates + feldspar. The summaries given in Tables (7.2A3 & 7.2A4) support the above conclusions.

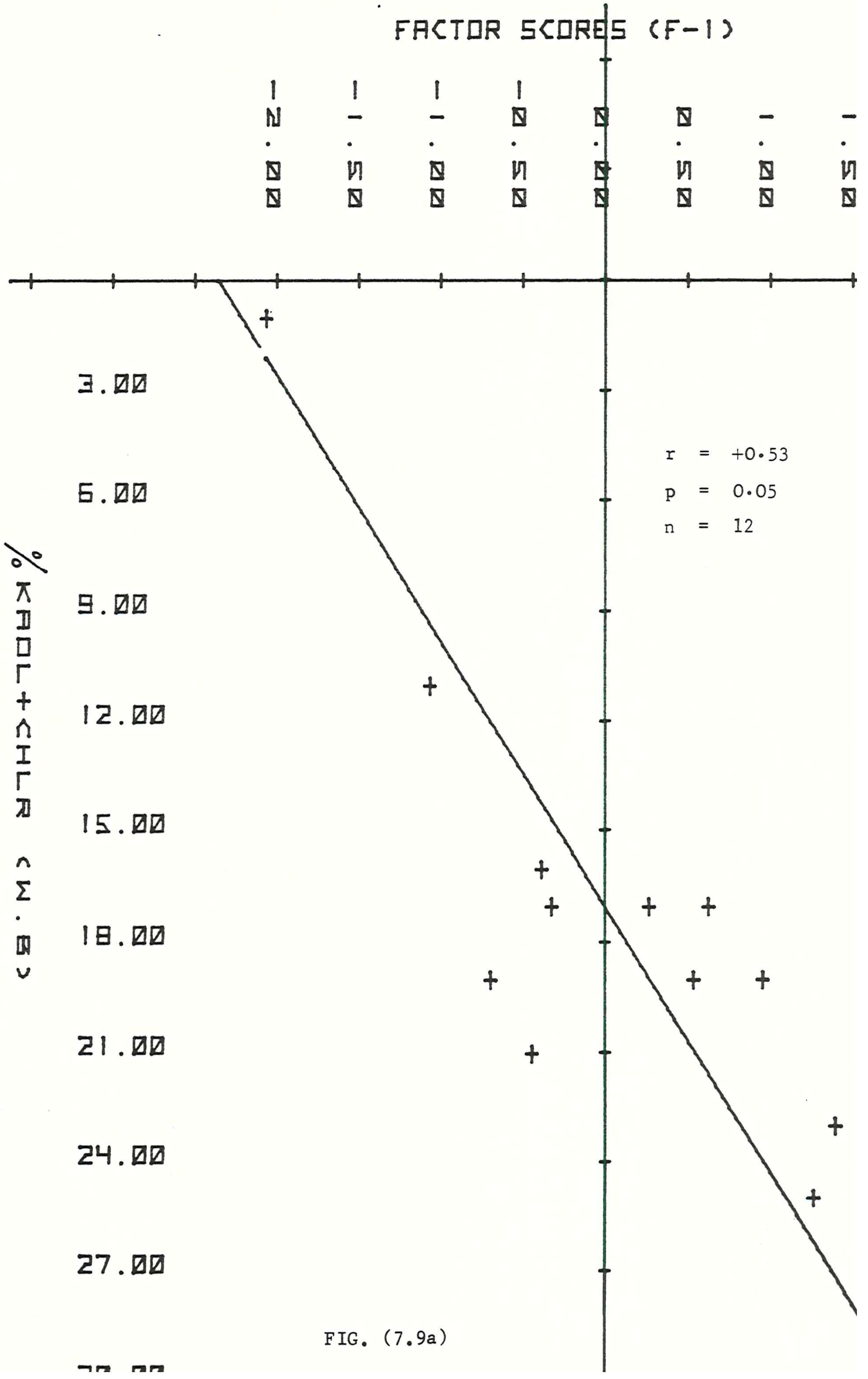
C.2: R-mode Factor Analysis of Clay Fraction Chemical Data of the (W.B.) Sediments

Three factors were extracted which explained 62·4% of the total variance. Factor loadings, inter-factor correlations and factor scores are shown in Tables (7.2B1 & 7.2B2) respectively. A summary of the components loaded in respective factors and indicating the levels of significance of loaded components is presented in Table (7.2B3). A detailed description of each factor is as follows:

FACTOR (F-1)

This factor explains 31·92% of the total variance. The nature of the strong association of elements such as Al, Zr, Ce along with Cu and Mo tends to suggest the occurrence of a kaolinite phase. According to WEAVER and POLLARD (1973), SCHULTZ (1964) and VAN OLPHEN and FRIPIAT (1979), kaolinites contain as much as ~40% weight percentage of Al_2O_3. Factor (F-1) in the (W.K.B.) clay fraction showed a similar nature of loadings and was recognised as 'Kaolinite + C_{org}' factor. Therefore the positive phase of Factor (F-1) of the (W.B.) is also designated as the 'Kaolinite factor'. The association of Cu and Mo may be due to the strong adsorptive ability of these elements onto the grains of clay minerals, as stated by KRAUSKOPF (1956). To confirm the present interpretation, abundances of kaolinite shown in Appendix (7.2B) and the factor scores of (F-1) tabulated in Table (7.2B2) were plotted. The resulting Figure (7.9a) shows a good positive correlation ($r = +0·89$), highly significant at the 99·99% level, between the two variables and confirms the identification.

The negative phase of Factor (F-1) shows an association of strongly loaded components, such as Fe_2O_3(T) and CaO, associated with moderate to low loadings of K_2O, As, MgO, Na_2O and V, suggesting the occurrence of a mixed-layer mineral. Elements Ca, Mg, Na and K may occur in the inter-layer position, and Fe_2O_3 in the octahedral sheet. It has already been mentioned in the earlier part of this chapter that mixed-layer minerals in the (W.B.) sediments do not expand on glycolation. BROWN (1954) noticed the occurrence of a similar clay mineral in samples of soil clays from Ireland, and called it 'degrading illite'. He stated that degrading illite fixes potash. The presence of K_2O in the negative phase of Factor (F-1) may be due to fixation of



r = +0·53

p = 0·05

n = 12

FIG. (7.9a)

potash as noticed by BROWN (op.cit.). This phase is thus designated as the mixed-layer (non-expanding) minerals phase. It is very difficult to determine the layer composition of such mixed-layer clays. WEAVER and POLLARD (1973) stated that, when expandable layers comprise > 60% and < 10%, it is difficult to determine accurately the number of illitic layers. To confirm this identification, abundances of mixed-layer minerals (modified values) shown in Appendix (7.2B) and factor scores of (F-1) shown in Table (7.2B2) were plotted. Figure (7.9b) shows a negative correlation ($r = -0{\cdot}53$, significant at 95% level), suggesting that the above identification is reasonable.

FACTOR (F-2)

This factor explains 18•5% of the total variance. The association of strongly loaded components such as K_2O, Rb, Al_2O_3, Ni, V, Mn and Zn points to the identification of the positive phase of Factor (F-2) as due to illite. The association of the loaded elements with illite has been explained in the study of the illite factor (F-3) in the (W.K.B.) clay fraction sediments. Factor (F-2) does not show any significant correlation with any other factor, which suggests that the illite present in this phase is not related strongly to other phases. Earlier, it has been mentioned (in this chapter) that illite abundances, calculated from the X.R.D. results, are over-generous due to the presence of a typical non-expanding mixed-layer mineral. K_2O showed its highest loading associated with the strongest and only loading of Rb in this positive phase, strongly indicating the existence of illite. Because the X.R.D.-determined values of illite are considered over-generous, it was decided to calculate the abundances of illite using the K_2O values determined for each sample, on the assumption that all K_2O resides in illite. Figure (7.10) shows a plot of the calculated illite abundances and the factor scores of (F-2). This plot shows a positive correlation ($r = +0{\cdot}65$), significant at the 99•99% level. It confirmed the identification of illite as the controlling phase here.

FACTOR (F-3)

This factor explains 11•95% of the total variance. The association of SiO_2, MgO and a low loading on TiO_2 is typical of mixed-layer clay minerals. This interpretation is further confirmed by the only strong negative correlation between Factors (F-1) and (F-3), as shown in

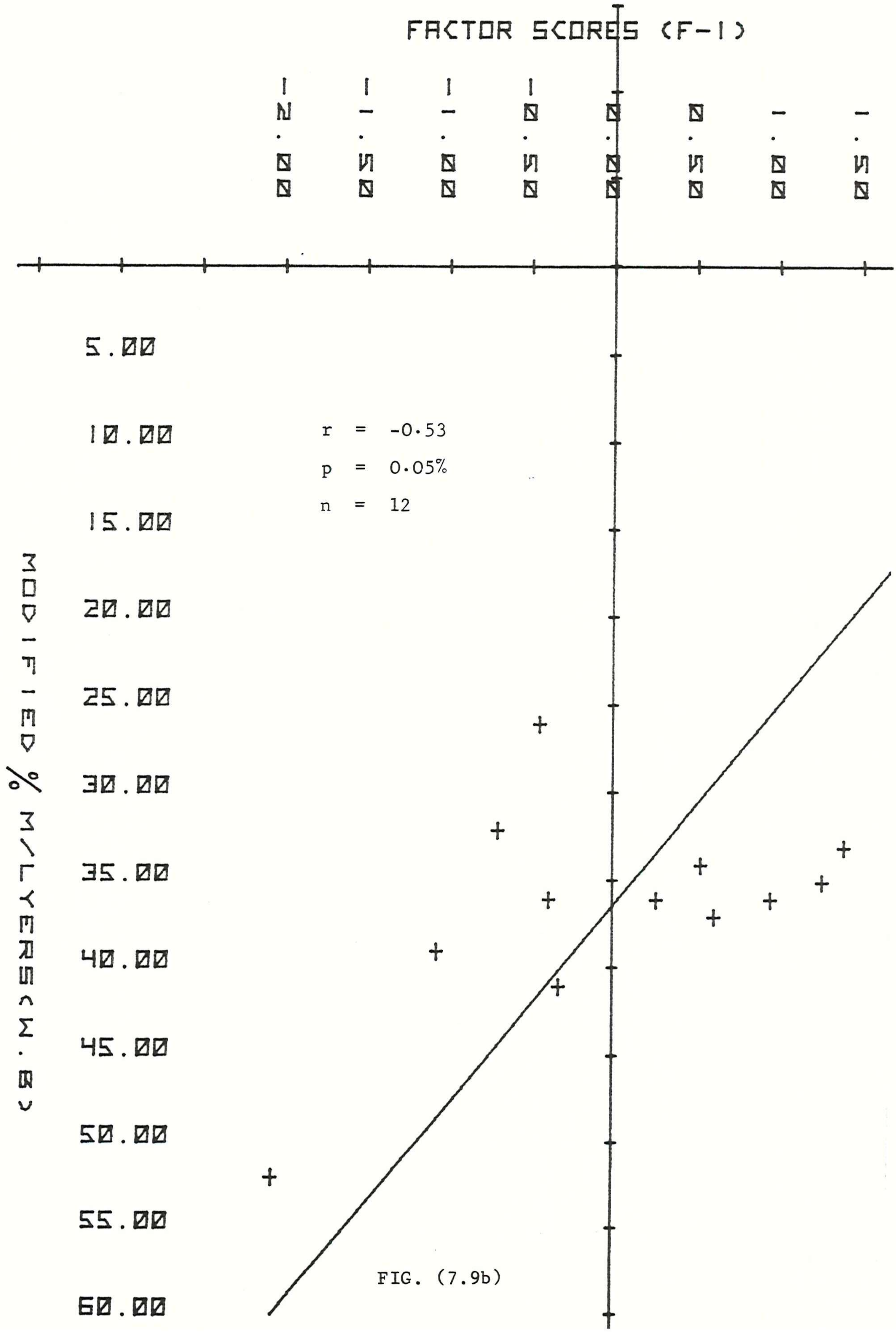

FACTOR SCORES (F-1)
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
MODIFIED % M/LYERS(W.B)
r = -0·53
p = 0·05%
n = 12

FIG. (7.9b)

Table (7.2B1). The negative phase of Factor (F-1) has already been recognised as the phase of mixed-layer minerals.

The negative phase of Factor (F-3) shows very strong loadings on Na_2O, Ba, P_2O_5, Y, and medium to low loadings on Sr, La, Ni and Cu. The strong association of Na_2O and Ba suggests the occurrence of Na-bearing feldspar and the associations of P_2O_5, Y and La suggest the presence of phosphate grains. Elements Cu and Ni have shown much stronger loadings in Factors (F-1) and (F-2) respectively, indicating their major role in the phases of these factors. The strong negative correlation between Factors (F-3) and (F-1) confirms the relationship of the positive phase of Factor (F-1),represented by detrital clay mineral kaolinite, with the detrital components, as suggested by the associations of the negative phase of Factor (F-3). Therefore the negative phase of Factor (F-3) is recognised as the phase of 'resistates' represented by Na-bearing feldspar and phosphate minerals. Clay fraction samples of the (W.K.B.) also contain 'detrital components' in the positive phase of (F-2) and show the association of TiO_2, Na_2O, P_2O_5, Ba, Th, La, etc. The great similarity of loaded components in the negative phase of Factor (F-3) of the (W.B.) and positive phase of Factor (F-2) of the (W.K.B.) samples confirms the occurrence of a detrital components phase in the clay fraction of the Oxford Clay sediments.

Summary:

It may be summarized that Factor (F-1) shows that kaolinite controls the variance in its positive phase and mixed-layer minerals its negative phase. Factor (F-2) is an independent factor, and the variance here is controlled by illite. Factor (F-3) shows the repetition of mixed-layer minerals antipathetically related to detrital components, probably containing Na-bearing feldspar and phosphate minerals. The results summarized in Tables (7.2B3 & 7.2B4) also confirm the identifications of the phases.

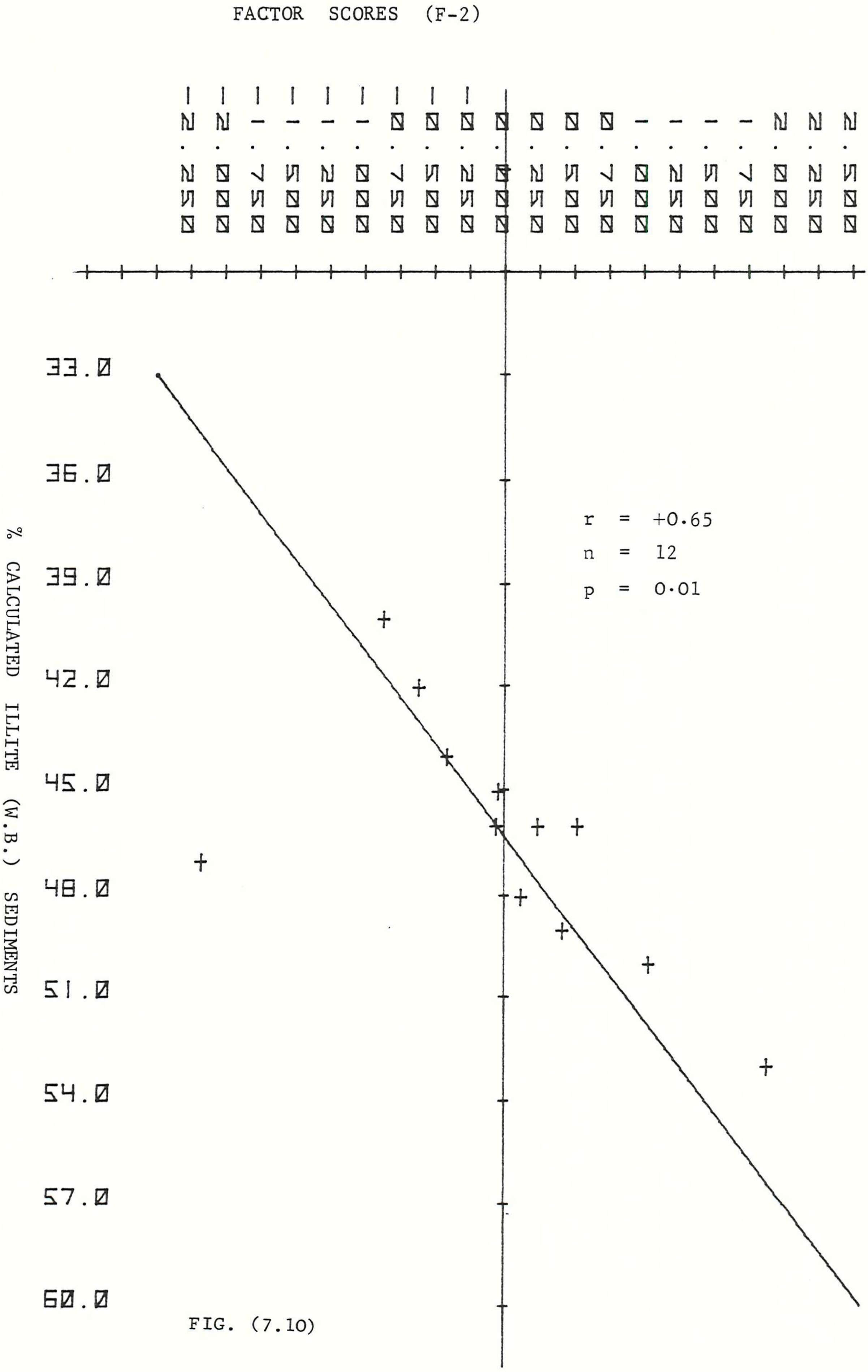

FACTOR SCORES (F-2)
-2.25
-2.00
-1.75
-1.50
-1.25
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
33.0
36.0
39.0
42.0
45.0
48.0
51.0
54.0
57.0
60.0
% CALCULATED ILLITE (W.B.) SEDIMENTS
r = +0·65
n = 12
p = 0·01

FIG. (7.10)

IV. Conclusions

The following broad conclusions may be derived on the basis of the foregoing pages:

(1) Kaolinite in the (W.K.B.) sediments, in association with C_{org}, controls the significant proportions of the abundances of Al, Na, P_2O_5, Cr, Ba, Ce, Pb, Cu, Sr, Y and Mo. Kaolinite in the (W.B.) sediments controls Al, Zr, Cu, Sr, Y and Mo. The relationship of depth with kaolinite in both the boreholes is sympathetic. The common relationship between the elements Cu and Mo and kaolinite in both the boreholes is due to reducing conditions caused by the rapid settlement of kaolinite in association with other detrital components in the basin of deposition.

(2) Smectite (montmorillonite-illite expanding mixed-layer) in the (W.K.B.) controls the abundance of SiO_2 in the tetrahedral and Fe_2O_3, MgO, As in the octahedral and inter-layer positions. In the (W.B.) the variance of Fe_2O_3, Mg and Ca, Na, K in association with V and As is associated with the octahedral and inter-layer positions respectively, and SiO_2 in the tetrahedral sheet in the mixed-layer minerals.

(3) Illite in the (W.K.B.) controls significant amounts of TiO_2, Al_2O_3, MgO, K_2O, V, Cr, Mn, Ni, Ba and H_2O, while in the (W.B.) it controls TiO_2, Al_2O_3, K_2O, V, Mn, Ni, Rb, Ce, Pb, Zn and Sr. The absence of MgO and Cr in tbe (W.B.) illite may suggest variation in the provenance for the two illites. It may suggest that the (W.K.B.) sediments contain illite produced by the weathering of intermediate to basic igneous rocks.

(4) Sulphide mineral pyrite in the (W.K.B.) sediments controls the variation of Pb, Zn, Mo and Cu. In the (W.B.) sediments, elements Pb and Zn seem to be adsorbed onto illite, and Mo and Cu onto kaolinite.

(5) The detrital phases in the (W.K.B.) show their control over TiO_2, Na_2O, P_2O_5, Mn, Ba, Th, Zr and La, while in the (W.B.) sediments they show their control over Na_2O, P_2O_5, Ba, La, Ni, Cu, Sr and Y. The association of Mn with the detrital components in the (W.K.B.) may suggest the presence of Mn-oxides/hydroxides adsorbed onto the detrital grains and suggests the contribution of intermediate-basic igneous material to the (W.K.B.) detritus.

CHAPTER EIGHT

SUMMARY AND CONCLUSION

8.1 Introduction

This chapter consolidates the inferences and conclusions derived in the previous chapters, on the basis of the study of certain associations and behaviours demonstrated by mineral phases and elements present in the sediments of the Oxford Clay and Kellaways Formations. The present study achieved, significantly, the aims and objectives as laid down in Chapter One. It provides an insight for the appreciation and reconstruction of the history of deposition and post-depositional events that took place in the southern England area during the Callovian-Lower Oxfordian times. Summary conclusions of the main components of the study are described in the following sections until a final synthesis of the geochemical environment of the Callovian-Lower Oxfordian Age is made.

8.2 Mineralogy of the Oxford Clay and Kellaways Formations

Minerals are the inseparable part of rocks and sediments; therefore their study unfolds the various episodes of the geological history the sediments have passed through. They help in the reconstruction of the palaeo-environments on the one hand, and may be used to predict the chemistry and geochemistry on the other hand, not only of the environments of deposition but also the areas of the source rocks. SCHULTZ (1964), REEVES (1971), MARSTON (1967) and BAQRI (1979) derived useful conclusions based on the observed relationships between the mineralogy and chemistry of the sediments studied by them. In the present study, an attempt has been made to derive conclusions in a similar way.

The sediments at present under study contain minerals of both detrital and non-detrital origin. The detrital minerals are present as major components, whereas the non-detrital (i.e. authigenic/diagenetic) minerals present are in a subordinate role. Nevertheless, they proved of great assistance in revealing the physico-chemical conditions that existed in the environments at the time of deposition. The detrital minerals provided clues regarding the provenance of the sediments and the palaeo-environments of the areas of source rocks.

Generally speaking, among detrital minerals these sediments contain quartz, kaolinite, illite, chlorite, mixed-layer (non-expanding) clay minerals and minor amounts of feldspars; mixed-layer (non-expanding) clays are confined only to the (W.B.) sediments. The non-detrital (authigenic/

TABLE (8.1): Carbonate corrected Average Chemistry of the Bulk Rock Samples of the (W.K.B.) and (W.B.) Sediments and the Comparison with the Average Chemistry of Average Shales, as reported by KRAUSKOPF (1979).
All values represent $\log_{10}$ (concentration %)

	(W.K.B.) Sediments	(W.B.) Sediments	Average Shale (KRAUSKOPF, 1979)
Si	3.2540	3.365	3.170
Ti	-0.868	-0.553	-0.798
Al	2.089	2.222	2.220
Fe	1.657	1.287	1.547
Mg	-0.045	-	0.336
Na	-0.600	-1.033	-0.105
K	0.861	1.043	0.916
S	0.760	0.231	-1.386
*P	-2.726	-3.036	-4.893
V	-4.240	-4.247	-4.343
Cr	-4.092	-4.167	-4.605
*Mn	-3.070	-4.150	-2.465
Ni	-4.893	-5.116	-4.828
Ba	-3.493	-3.289	-2.813
Ce	-4.948	-4.585	-4.962
La	-5.497	-5.067	-5.521
Th	-6.571	-6.502	-6.725
Pb	-4.920	-5.991	-6.215
As	-6.377	-6.320	-6.908
Zn	-2.795	-4.646	-2.408
Cu	-5.914	-5.952	-5.298
Rb	-4.261	-3.984	-4.269
Y	-5.521	-5.318	-5.655
Zr	-3.803	-3.612	-4.017
Nb	-6.320	-5.991	-6.502
Mo	-8.112	-8.112	-8.517
*Fe^{+2}	0.278	-0.248	-
*Fe^{+3}	0.642	0.875	-
*C_{org}	0.875	0.507	-2.302
*Sr	-3.249	-3.665	-3.219

* Absolute values

diagenetic) minerals, common in the sediments of both the boreholes, include calcite and pyrite. Besides these minerals, there are two other non-detrital minerals, namely smectite (expanding clay mineral), which is present only in the (W.K.B) sediments, and dolomite (ferroan), present only in the (W.B.) sediments. Both types of mineral in the sediments of the two boreholes demonstrated certain trends of specific enrichment and association with other components, either in the particular divisions or in the entire sequence of the studied sediments, and thus indicate the influence of various factors at various stages. For example, the sediments of the (W.K.B.) contain enriched abundances of kaolinite, pyrite, calcite, C_{org} and smectite over the (W.B.) sediments, which show higher abundances of detrital components, such as quartz, illite, chlorite, mixed-layer (non-expanding) clays, total clays and non-detrital dolomite. A summary of all the observed relationships demonstrated by the mineral phases is given here:

(a) Detrital minerals:

Illite is the most dominant detrital clay mineral in the sediments of both the boreholes; it showed enhanced concentration in the (W.B.) sediments, associated with mixed-layer (non-expanding) clay mineral. Illite in the (W.K.B.) sediments is more crystalline than that in the (W.B.), as indicated by the high C.I.W. value for the (W.K.B.) illite. Better crystallinity of illite in the (W.K.B.) is also indicated by comparatively higher net negative charge 0·81 per $(O_{10}(OH)_2)$ unit as compared with 0·71 per $(O_{10}(OH)_2)$ unit for the (W.B.) illite, as shown in Table (7.1A5). The variation of illite crystallinity in the two sediments clearly indicates different sources. Illite in the (W.K.B.) is associated with a comparatively higher amount of kaolinite and smectite, while in the (W.B.) its association with mixed-layer (non-expanding) clay mineral is of significant importance. These associations clearly suggest that the (W.K.B.) illite was part of detritus produced by the weathering of acid igneous rocks, and that of the (W.B.) by the weathering of sedimentary rocks, thus producing re-cycled detritus. It suggests that the 'Cornubian Massif', rich in acidic igneous rocks in the west, and the 'East Anglian Massif', rich in Palaeozoic sedimentary rocks in the east, contributed detritus to the depositional sites of the respective boreholes. Illite in both the boreholes is detrital, as suggested by its very strong positive correlations with typically known detrital components such as kaolinite, chlorite, Si, Ti, Zr and Nb, etc., as shown in Tables (8.3 and 8.4).

After illite, quartz is the second most abundant detrital mineral found in the studied sediments. It showed enriched abundance in the (W.B.) sediments, where the (K.F.) contains an exceptionally very high concentration. Quartz in the (W.K.B.) sediments is angular to sub-angular and coarser, as compared with that of the (W.B.) sediments, as shown in Plate (3.3). The variation of grain size and shapes of the (W.K.B.) quartz indicates less distance of transportation and less cycles of sedimentation, as compared with the (W.B.) quartz, which indicates more than one cycle of sedimentation. This study strongly suggests that the (W.K.B.) sediments received their quartz from the 'Cornubian Massif', and those of the (W.B.) from the 'East Anglian Massif' after weathering of the sedimentary rocks. The exceptionally very high concentration of quartz in the sediments of the (K.F.) of the (W.B.) may be related to more than one factor, such as near-shore type of deposition, more active role of the running waters and abundant availability of quartz in the source areas. The highest concentration of quartz in the (W.K.B.) sediments is in the (U.O.C.) and is associated with the highest abundance of calcite and lowest abundance of total clays; these associations strongly suggest a shallow depositional environment for these sediments.

Kaolinite is the third most abundant detrital mineral in the studied sediments. It showed slightly enhanced concentration in the (W.K.B.) sediments over the (W.B.) sediments. Concentration of kaolinite is considered an indication of the proximity of shore-lines. But its concentration in the (W.K.B.) sediments is due to a feldspar-rich provenance for these sediments; feldspar under humid climate weathers to produce kaolinite. Its exceptionally high concentration associated with the highest value of quartz in the (W.B.) sediments, however, is due to a near-shore environment of deposition. Kaolinite in the sediments of both boreholes is detrital, as indicated by its very strong positive correlations (significant at the 99·99% level) with illite, chlorite, Si, Ti, Nb in the (W.K.B.) and with quartz, Zr, Si, Ti, etc. in the (W.B.) sediments. Kaolinite in the (W.K.B.) sediments exhibited very strong positive correlations (significant at the 99·99% level) with depth, C_{org}, pyrite, S, Cr, Ni, Fe, and Mo, suggesting its role in causing the reducing conditions for the formation of sulphide phases, particularly pyrite. Kaolinite, being a coarser-grained detrital mineral, generally settles rapidly as compared with other components. Due to rapid deposition, kaolinite helps in promoting the reducing environments as a result of quick burial of the entrapped organisms. It is well established that organic matter on its deposition undergoes decomposition, and this helps in creating reducing conditions in the environments.

Chlorite showed a slightly enhanced value in the (W.K.B.) sediments as compared with the (W.B.) sediments. It is detrital in both the borehole sediments, as indicated by its very strong positive correlation (significant at the 99·99% level) with detrital components such as Zr, Nb, Si, Ti, illite and kaolinite, etc. Chlorite contains a significantly high amount of iron; it might have contributed some iron towards the formation of pyrite. Its presence indicates some contribution of low grade metamorphic rocks in the detritus of the Oxford Clay for the two sites.

Mixed-layer (non-expanding) clay minerals are present only in the (W.B.) sediments and bear a special significance in the present study. The abundant concentration of mixed-layer (non-expanding) clay minerals, associated with the highest amount of degraded illite in the (U.O.C.) sediments and its lowest amount associated with slightly more crystalline illite in the (K.F.), suggests that both minerals bear a genetic relationship, and it confirms a detrital origin for the mixed-layer (non-expanding) clays.

(b) Non-detrital minerals

Among non-detrital (authigenic/diagenetic) minerals, the dominant one is calcite in the sediments of both boreholes. The sediments of the (W.K.B.) showed an enhanced value of calcite as compared with the (W.B.) sediments. It is well established that calcite in sediments occurs as a pH dependent mineral. The sediments of both boreholes show the highest and lowest concentrations of calcite in the (U.O.C.) and (K.F.) respectively, which suggests that, comparatively, the pH was higher in the environment when the sediments of the (U.O.C.) were being deposited than those of the (K.F.). The antipathetic association of calcite with P_2O_5 in the sediments of the (U.O.C.) of both the boreholes, shown in Tables (4.1A & 4.2A), further confirms the views expressed earlier.

Smectite is present only in the (W.K.B.) sediments, and is the second most abundant non-detrital mineral. It showed the highest concentration in the (U.O.C.) sediments, and its abundance decreases with depth in the borehole. The smectite present in the (U.O.C.) sediments is well crystalline and contains $\gtrsim$60-80% expandable component. It is believed that smectite originated by the conversion of 'air-fall' volcanic ash from volcanoes of unknown location, as is suggested for the montmorillonite present in the Lower Calcareous Grit Group sediments of the Corallian rocks from Dorset, and reported by CHOWDHURY (1980). Smectite in the studied sediments is authigenic, as suggested by its very strong positive correlation (significant at the 99·99% level) with authigenically produced mineral phases, such as calcite, and also elements, e.g. Ca, Mn, Sr, etc. The presence of smectite in the (W.K.B.) and its complete absence in the (W.B.) sediments is of significance, and confirms two different provenances for the sediments of the two boreholes.

Dolomite (ferroan) is present as a diagenetically produced mineral only in the (W.B.) sediments. The source of Mg^{+2} was largely phreatic waters which flowed upward into the (W.B.) sediments, as a result of pressure caused by the thick sequence of sediments in the Wealden Trough. MATTES and MOUNTJOY (1980) have argued a similar theory of formation for the origin of dolomite in the Miette build-up in Alberta, Canada. Dolomite, presently under discussion, contains 52 mole % CaO, 40 mole % MgO and 8 mole % $FeCO_3$, and is thus very similar to the dolomite (ferroan) reported by BELLAMY (1980) in the Kimmeridgian sediments in southern England. Some of the Mg^{+2} for the Oxford Clay dolomite might have been contributed by clay minerals such as illite, chlorite and mixed-layer (non-expanding) clays, as mentioned by KAHLE (1965). BELLAMY (op.cit.) mentioned that organic carbon was the main source of Mg^{+2} for the Kimmeridgian dolomite. In the present sediments, it seems that organic carbon contributed Mg^{+2} only in a few cases where the content of C_{org} is very high.

Pyrite in the sediments of both boreholes occurs as the least abundant non-detrital mineral. The presence of pyrite in association with C_{org} in all the samples of the two boreholes indicates that reducing conditions existed during all the episodes of deposition and diagenesis of the studied sediments. Pyrite and C_{org} both show a higher concentration in the (W.K.B.) sediments over the (W.B.) sediments, which clearly indicates that much stronger reducing conditions existed in the

TABLE (8.2): Showing the Enriched and Depleted Concentrations of Elements in the Divisions of the Oxford Clay and Kellaways Formations of the (W.K.B.) Sediments with respect to the (W.B.) Sediments

Divisions of the Oxford Clay	Enriched abundances of Elements in the (W.K.B.) Sediments with respect to the (W.B.) Sediments	Depleted abundances of Elements in the (W.K.B.) Sediments with respect to the (W.B.) Sediments
(U.O.C.)	Fe(T), Ca, Na, S, P, Fe^{+2}, Mn, Pb, Zn, Sr and C_{org}	Si, Ti, Al, Mg, K, V, Cr, Ba, La, Ce, As, Cu, Ni, Rb, Y, Zr, Nb and Combined silica
(M.O.C.)	Fe(T), Ca, Na, S, P, Fe^{+2}, Fe^{+3}, V, Cr, Mn, La, Pb. As, Zn, Cu, Ni, Sr, H_2O^+ and C_{org}	Si, Ti, Al, Mg, K, Ba, La, Ce, Rb, Y, Zr, Nb and Combined silica
(L.O.C.)	Fe(T), Ca, Na, S, P, Fe^{+2}, Fe^{+3}, V, Mn, Pb, As, Zn, Cu, Ni, Sr, Mo, H_2O^+ and C_{org}	Si, Ti, Al, Mg, K, Cr, Ba, La, Ce, Th, Rb. Y. Zr. Nb and Combined silica
(K.F.)	Al, Fe(T), Mg, Ca, Na, K, H_2O^+, Fe^{+3} V, Cr, Mn, La, Th, Pb, Zn, Cu, Ni, Rb, Sr, C_{org} and Combined silica	Si, Ti, S, P, Fe^{+2}, Ba, La, Ce, As, Y, Zr, Nb, Mo and C_{org}

environment of deposition of the (W.K.B.) sediments. It seems true, as the sediments of the (W.K.B.) show a much thicker sequence of the Oxford Clay and Kellaways Formations and much deeper basin conditions that the (W.B.) sequence. It further indicates that the three factors described by BERNER (1971),as essential for the formation of pyrite, were abundantly available in the environments under which these sediments were laid down. The three factors are (i) concentration of reactivity of iron compounds; (ii) abundance of dissolved sulphate; and (iii) abundant availability of metabolizable organic matter.

Pyrite in the (W.B.) sediments showed its highest abundance in the sediments of the (K.F.) associated with the highest concentration of quartz, and kaolinite, and a significantly higher amount of C_{org}. It showed the lowest abundance in the sediments of the (U.O.C.) associated with the lowest amount of kaolinite. These relationships may be explained in the light of the explanations given earlier. Sediments of the (W.B.) contain pyrite in two forms, i.e. as perfect octahedral crystals and as framboidal concretions; both are shown in Plate (3.1). BERNER (1971) mentioned that, due to inhomogeneous solubilization, concentration gradients may occur and the dissolved ferrous iron may migrate to form concretions and other aggregations. The origin of the framboidal pyrite in the present sediments may be of this type.

It may be summarized that the mineral phases present in the studied sediments clearly reflect the history of deposition. The detrital minerals give clues regarding the provenance and palaeo-environment of the source rocks. Some of the detrital minerals, such as kaolinite and quartz helped in the creation of reducing conditions, and some other minerals like illite, chlorite and mixed-layer (non-expanding) mineral provided iron for the formation of pyrite, and some amount of Mg^{+2} for the formation of dolomite. The non-detrital phases gave valuable evidence of more exotic sources (volcanic), of particular post-depositional environments and possibly of later broad sedimentological and structural events.

8.3 Chemistry of the Oxford Clay and Kellaways Formations

The chemical analysis data of the samples (bulk rock and clay fraction) of both the boreholes was analysed by bi-variate and multi-variate correlation and R-mode factor analysis, through the University

FIG. (8.1): This figure shows a plot on a 1:1 ratio basis of the average values of chemistry corrected for carbonates, expressed as Log_{10} (per cent) of the Bulk rock samples of the (W.K.B.) and (W.B.) sediments. This plot clearly indicates the enriched abundances of elements such as Pb, Zn, Mn, Fe^{+2}, S, C_{org}, Sr and P in the (W.K.B.) sediments, as compared with the (W.B.) sediments which contain enhanced values of elements, e.g. Nb, Y, La, Ce, Rb, Zr, Ba, Ti, Fe^{+3} and K. These variations confirm the greater influence of basic igneous rocks over the (W.K.B.) detritus and the influence of detrital material over the (W.B.) sediments. It also indicates much stronger reducing environments for the (W.K.B.) sediments as compared with those for the (W.B.) sediments.

FIG. (8.2): This plot was prepared exactly on the same principles as were followed for Fig.(8.1), using the average values of chemistry of the (W.K.B.) sediments corrected for carbonates, and the average shales reported by KRAUSKOPF (1979). This plot shows enriched values of elements such as Mo, As, Pb, Cr, P, S, C_{org} in the (W.K.B.) sediments, which contain the depleted abundances of elements, e.g. Mg, Na, Zn, Mn, Ba and Cu. This variation suggests that sediments of the (W.K.B.) were deposited under much stronger reducing conditions than the average shales of KRAUSKOPF (op.cit.). The depletion of certain elements in these sediments, as mentioned above, may be related to the provenance.

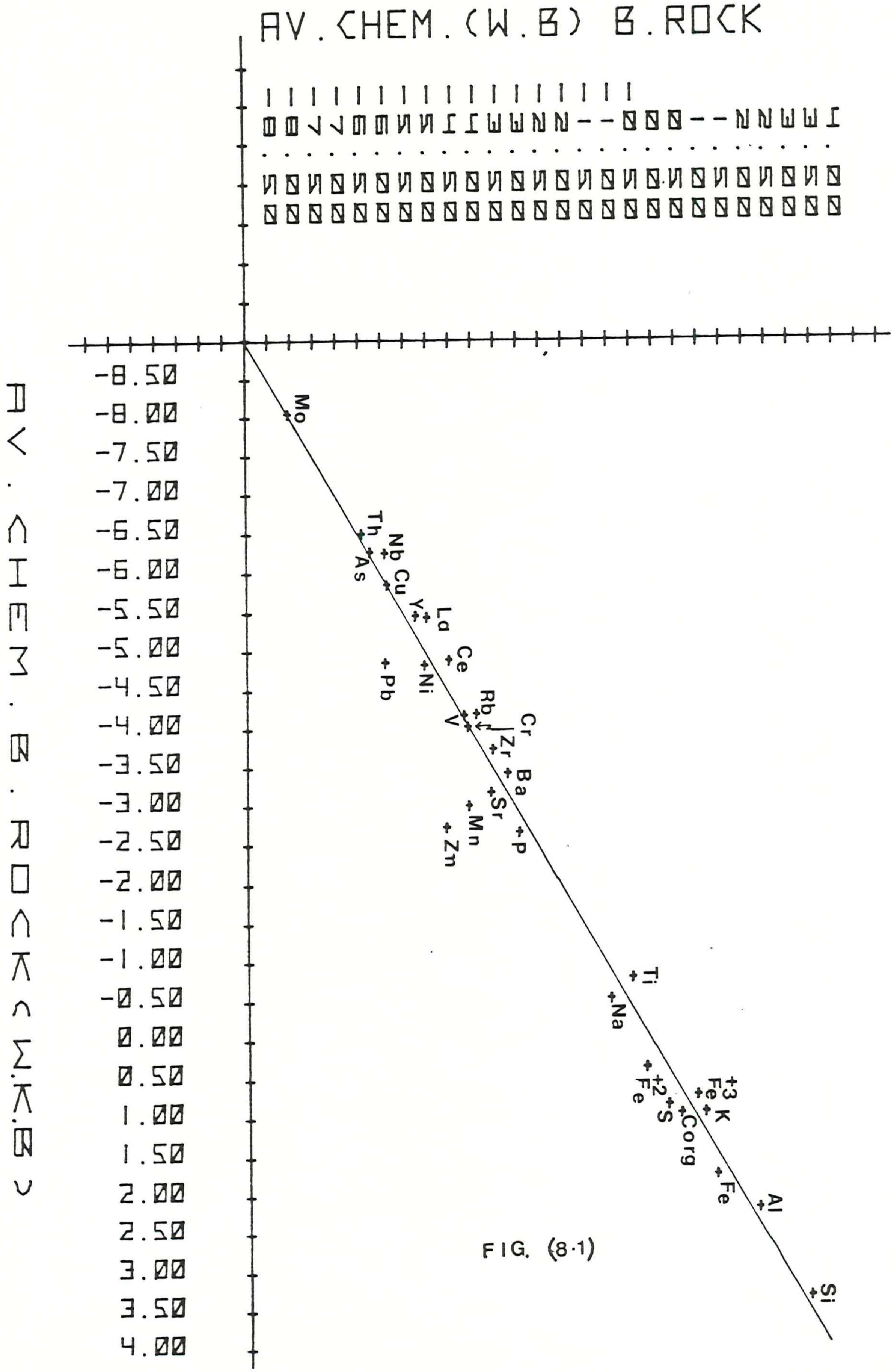

AV. CHEM. (W.B) B.ROCK
AV. CHEM. B. ROCK (Σ.K.B)
-8.50
-8.00
-7.50
-7.00
-6.50
-6.00
-5.50
-5.00
-4.50
-4.00
-3.50
-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
Mo
Th
As
Nb
Cu
Y
La
Ce
Ni
Pb
Rb
V
Cr
Zr
Ba
Sr
Mn
Zn
P
Ti
Na
Fe^{+2}
S
Fe^{+3}
K
Corg
Fe
Al
Si

FIG. (8·1)

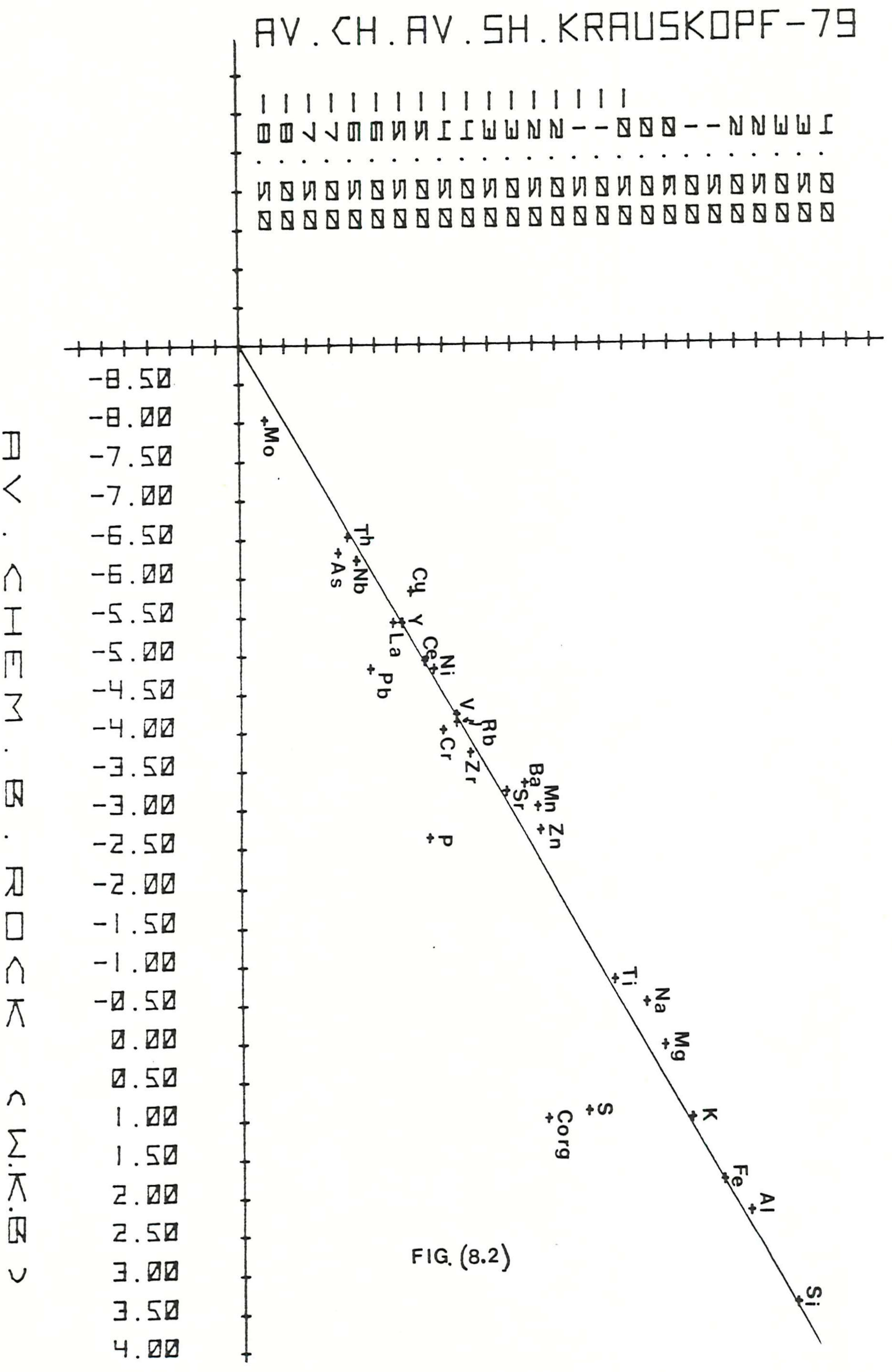

AV.CH.AV.SH.KRAUSKOPF-79
AV. CHEM. B. ROCK (Σ.K.B)
-8.50
-8.00
-7.50
-7.00
-6.50
-6.00
-5.50
-5.00
-4.50
-4.00
-3.50
-3.00
-2.50
-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
Mo
Th
Nb
As
Cu
Y
La
Ce
Ni
Pb
V
Rb
Cr
Zr
Ba
Sr
Mn
Zn
P
Ti
Na
Mg
S
Corg
K
Fe
Al
Si

FIG. (8.2)

Computer. Selected samples of the bulk rock of the two boreholes were subjected to a leaching technique proposed by CHESTER and HUGHES (1967) in order to observe the partitioning characteristics of the main major and minor elements. Average values of the chemistry of the bulk rock and clay fraction samples of the two boreholes were compared with the average chemistry of the average and bulk rock, and clay fraction samples of the Lower Calcareous Grit Group of the Corallian sediments from Dorset, respectively, reported by KRAUSKOPF (1979) and CHOWDHURY (1980). These investigations showed some very significant variations in the chemistry of the studied sediments, which are listed below.

(1) Bulk rock samples of the Oxford Clay and Kellaways Formations of the (W.K.B.) showed enriched concentration of elements such as Pb, Zn, Mn, Fe(T), S, C_{org}, P, Fe^{+2} and Mo, and depleted abundances of elements, e.g. Rb, Zr, Ba, K, Al, Si and Ce, as compared with their counterparts in the (W.B.). This variation is illustrated in Figure (8.1).

(2) Bulk rock samples of the (W. K.B.) showed depleted amounts of elements, e.g. Cu, Ba, Mn, Zn, Mg, Na and Al over the abundances of these elements in the average shales, reported by KRAUSKOPF (1979), as shown in Figure (8.2).

(3) Bulk rock samples of the (W.K.B.), on leaching with acetic acid hydroxylamine hydrochloride, as proposed by CHESTER and HUGHES (1967), exhibited enhanced contents of elements such as Zn, Mn, Ni, Fe(T) in the lattice-held fraction, over the lattice-held fraction of the (W.B.) sediments.

The chemical variations shown in Table (8.2) indicate the fluctuating 'physico-chemical' conditions that existed at the time of deposition of the sediments of the respective divisions of the Oxford Clay and Kellaways Formations at the depositional sites of the respective boreholes. According to VAN OLPHEN and FRIPIAT (1979) and WEAVER and POLLARD (1973) elements such as Fe, Al, Mg, Ca, Na, K, Fe^{+3}, V, Cr, Mn, La, Th, Pb, Zn, Cu, Ni, Rb and Sr are associated with clay minerals such as illite, chlorite, kaolinite, smectite, etc., mostly in their lattices. The sediments of the (K.F.) of the (W.K.B.)contain the highest abundance of total clays composed of dominating amounts of illite, chlorite and kaolinite, as shown in Table (4.1B). It implies that most of the elements concentrated in the (K.F.) of the (W.K.B.) sediments occur in the lattices of clays; this relationship will be elaborated further later in the description of the geochemistry of the studied sediments. Some of the elements such as Pb, Zn, Cu, Ni and Mn may be present adsorbed onto the surfaces of clay minerals (KRAUSKOPF, 1956). The variations also suggest that the reducing conditions during the time of deposition of the (K.F.) sediments at the (W.K.B.) site were not as strong as in the case of the (K.F.) of the (W.B.) sediments. This inference is derived on the basis of the enhanced concentration of certain elements, e.g. S, Fe^{+2} and Mo, which are typically known to concentrate in reducing conditions (CALVERT, 1976). These elements in the (K.F.) sediments of the (W.B.) are associated with higher abundances of detrital components such as Si, Zr, Nb, quartz and kaolinite. It is well known that the rapid accumulation of sediments brought about by high input of detritus helps to promote reducing conditions, as a consequence of the entrapment of organisms (including bacteria) in the sediments. This leads to the higher abundance of sulphur in the sediments of the (K.F.) of the (W.B.) due to the enhanced rate of reduction of the dissolved sulphates by the action of sulphate-reducing bacteria The enrichment of Fe^{+2} is obviously related to the stronger reducing conditions of the environment. It is very likely the Fe^{+3} present as Fe-oxides/hydroxides in the detritus reaching the site of deposition was reduced to Fe^{+2} due to the reducing conditions. The concentration of Mo in reducing environments is a well established fact (CALVERT, 1976); therefore its enrichment in the sediments of the (K.F.) of the (W.B.) is to be expected.

Similarly, the enriched and depleted concentrations of certain elements exhibited by the sediments of the Oxford Clay Formation of the (W.K.B.) over the corresponding sediments in the (W.B.), shown in Table (8.2), is explainable. These variations also reflect the variable 'physico-chemical' environments of the sediments of the two boreholes. The enriched abundances of elements such as Fe(T), S, P, Fe^{+2}, Pb, Zn, Cu, Ni, As, Mn, Ca, Na, Sr, Mo and C_{org}, and the depleted amounts of elements, e.g. Si, Ti, Al, Mg, K, V, Cr, Ba, La, Ce, Rb, Y, Zr, Nb and combined silica, as compared to their counterpart sediments in the (W.B.), strongly suggest that, generally speaking, the clays of the (W.K.B.) were deposited under comparatively much stronger reducing conditions than those

TABLE (8.3): Showing Relationships between the Main Mineral Phases, Chemical Elements and Depth in the (W.K.B.) Bulk Rock Samples

Elements	Depth	ILL	KAOL	CHLR	SMECT	TClays	C_{org}	Pyt	Cal.	QTZ
SiO_2	+2	+2	+2	+2	-2	+2		-1	-2	
TiO_2	+2	+2	+2	+2	-2	+2	+2		-2	-2
Al_2O_3	+2	+2	+2	+2	-2	+2	+2		-2	-2
Fe_2O_3(T)	+2	+2	+2	+2	-2	+2	+2	+2	-2	-2
MgO	+2	+2	+2	+2	-2	+2	+2		-2	-2
CaO	-2	-2	-2	-2	+1	-2	-2		+2	+2
Na_2O	+2	+2	+2	+2	-2	+2	+2		-2	-2
K_2O	+2	+2	+2	+2	-2	+2	+2		-2	-2
S	+2	+2	+2		-2		+2	+2		-2
P_2O_5		-1		-2		-2		+2	+2	
V	+2	+2	+2	+2	-2	+2	+2		-2	-2
Cr	+2	+2	+2	+2	-2	+2	+2		-2	-1
Mn	-2	-2	-2	-2	+	-2	-2		+2	+1
Ni	+2	+2	+2	+2	-2	+2	+2	+2	-2	-2
Ba	+2	+2	+2	+2	-2	+2	+2		-2	-2
Ce	+2	+2	+2	+2	-2	+2			-2	
La	+2	+2	+2	+2	-2	+2	+2		-2	-2
Th	+2	+2	+2	+2	-2	+2	+		-2	-2
Pb								+2		
As										
Zn							+1	+2		-2
Cu	+2	+2	+2	+2	-2	+2	+2	+2	-2	-2
Rb	+1	+2	+2	+2	-2	+2	+2		-2	-2
Sr		-1	-1	-2	+1	-2			+2	
Y	+1	+		+1	-1	+2			-2	
Zr				+1		+2		-2	-2	
Nb	+1	+2	+2	+2	+2	+2	+1		-2	
Mo	+1	+2	+2	+1	+2	+1	+2	+2	-1	-2
Fe^{+2}	+1	+2	+2		-2	+1	+2	+2		-2
Fe^{+3}		+2	+2			+1	+2	+2		-2
C_{org}	+1	+2	+2	+2	-2	+2	+2	+2	-2	-2
CO_2	-2	-2	-2	-2	+2	-2	-2		+2	+2
Depth	+2	+2	+2	+2	-2	+2	+2	+2	-2	-2

/contd.over

TABLE (8.3) contd.

Elements	Depth	ILL	KAOL	CHLR	SMECT	TClays	C_{org}	Pyt.	Cal.	QTZ
ILL	+2	+2	+2	+2	-2	+2		+2	-2	-2
KAOL	+2	+2	+2	+2	-2	+2		+2	-2	-2
CHLR	+2	+2	+2	+2	-2	+2			-2	-2
SMECT	-2	-2	-2	-2	+2	-2		-2	+2	+2
TClays	+2	+2	+2	+2	-2	+2			-2	-2
Pyt.	+2	+2	+2		-2					-2
Cal.	-2	-2	-2	-2	+2	-2			+2	+2
QTZ	-2	-2	-2	-2	+2	-2		-2	+2	+2

Note: n = 60

± 2 = ($r = \geqslant 0\cdot 32$) indicates 99·99% significance level.

± 1 = ($r = \geqslant 0\cdot 25$) indicates 95·00% significance level.

TABLE (8.4): Showing relationships between the Main Mineral Phases, Chemical Elements and Depth in the (W.B.) Bulk Rock Samples

Elements	Depth	ILL	KAOL	CHLR	M.L.	TClays	C_{org}	Pyt.	Cal.	Dol.	QTZ
SiO_2	+2	-1	+2		-2	+1			-2	-2	+2
TiO_2	+2		+2	+2	-2	+1	+1		-2	-2	
Al_2O_3	+2	+1	+1	+2	-2	+2	+2		-2	-2	-1
Fe_2O_3(T)						+2		+2	-1		-2
MgO	-2		-2		+2					+2	-2
CaO	-2		-2	-1	+2	-2	-2	-1	+2	+2	-2
Na_2O	+2		+2	+1	-2	+2		-1	-2	-2	+2
K_2O		+2		+2	-1	+2			-2	-2	
S	+2						+2	+2	-1		
P_2O_5	+2					+1	+2	+2		-1	
V			-1			+2			-2	+2	-2
Cr						+2	+2	+2	-2		
Mn	-2	+1	-2		+2	-1	-2	-2	+2	+2	-2
Ba	+2		+2		-2	+2	+1		-2	-2	+2
La	+2					+2	+2		-		
Ce	+2			+1	-1	+2	+2	+2	-2	-2	
Th	+2		+1	+1	-2	+2	+2		-2	-2	
Pb											
As	-2		-2	-1	+2	-1	-1			+2	
Ga											
Zn		+1									
Cu						+1	+2				
Ni						+1					
Rb	+2	+2		+2	-2	+2	+2		-2	-2	-2
Sr		+2	-2	+1					+2		-2
Y	+2		+2	+1	-2	+2	+1		-2	-2	
Zr	+2	-1	+2		-2				-2		+2
Nb						+1	+1		-2		
Mo	+2		+1				+1	+2			
C_{org}	+2	+1			-1	+1	+2	+2	-2	-1	
Fe^{+2}	+2					+1	+2	+2			
Fe^{+3}	-2	+1	+2				+2		-1	+1	-1
CO_2	-2		-2	-2	+2		-2	-1	+2	+1	-2
Depth		-1	+1		-2	+2	+2	+2	-2	-2	+1

/contd.over

TABLE (8.4) contd.

Elements	Depth	ILL	KAOL	CHLR	M.L.	TClays	C_{org}	Pyt.	Cal.	Dol.	QTZ
ILL	-1		-2		-1	+1					-2
KAOL	+2	-2			-2				-2	-2	+2
CHLR	+1				-2	+2				-2	
M.L.	-2	-1	-2	-2		-2			+1	+2	-2
TClays	+2	+1							-2	-2	-2
Pyt.	+2								-1		
Cal.	-2		-2		+1	-2		-1			-2
Dol.	-2		-2	-2	+2	-2					-1
QTZ	+1	-2	+2		-2	-2			-2	-1	+2

Note: n = 76

± 2 = ($r = \geqslant 0{\cdot}292$) indicates 99·99% level of significance.

± 1 = ($r = \geqslant 0{\cdot}22$) " 95·00% " " "

in the case of the (W.B.). This conclusion is derived on the basis of enriched abundances of elements in the (W.K.B.), such as S, Fe^{+2}, Mo, Cu, Zn, Mn, Pb and C_{org}. The association of S, P. Mo, Cu, Pb, Zn, Ni, and C_{org} suggests some genetic relationship (CALVERT, 1976, p.208). Sulphur seems to be derived largely by the action of sulphate-reducing bacteria from the dissolved sulphates, as explained earlier. Concentrations of Pb, Zn, Cu, Ni and Mn may be due to their presence in sulphide phases, particularly pyrite, which occurs abundantly in the (W.K.B.) sediments as compared with those of the (W.B.), and shown in Tables (4.1B & 4.2B). The elements Si, Ti, Al, Mg, K, V, Cr, Ba, La, Ce, Rb, Y, Zr, Nb and combined silica have shown depleted abundances due to the depleted contents of total clays (av. 32·67%) in the (W.K.B.) sediments, as compared with the higher contents of total clays (av.47·51%) in the (W.B.) sediments, which contain comparatively enriched abundance of clay minerals such as illite, kaolinite and chlorite; these minerals are well known to contain the above mentioned elements in their lattices (VAN OLPHEN & FRIPIAT, 1979; WEAVER & POLLARD, 1973). The enrichment of Zr and Nb in the (W.B.) sediments is due to the greater input of detrital components from the source areas.

It may be summarized that the enriched values of elements such as Mn, Zn, Pb, Fe(T) in the (W.K.B.) sediments as opposed to the (W.B.) sediments indicated the influence of basic igneous rocks on its detritus, while the enriched concentration of elements, e.g. Rb, Ba, K, Al, Si, Ce, Zr and combined silica, associated with higher abundances of degraded illite and non-expanding mixed-layer clays in the (W.B.) sediments, strongly indicated the influence of sedimentary and low-grade metamorphic rocks on its detritus. The enhanced concentration of S, Zn, Pb, Mn, Fe^{+2}, P, Mo and C_{org} in the (W.K.B.) sediments over the (W.B.) sediments indicated that much stronger reducing conditions existed at the (W.K.B.) in the basin of deposition.

8.4 Geochemistry of the Oxford Clay and Kellaways Formations

This section will elaborate certain relationships observed between the elements and mineral phases present in the studied sediments, as indicated by Factor Analysis and the bi-variate correlations. The The factor analysis in R-mode arranged the entire chemical data into groups of variables (factors), which can often be interpreted as the minerals found in sediments. Tables (8.5) and (8.6) summarize the

TABLE (8.5): Summary of the associations shown by elements and mineral phases present in the bulk rock samples of the respective boreholes, as suggested by the R-mode Factor Analysis of the chemical data of the sediments of the two boreholes.

Phases	Elements associated with phases in the (W.K.B.) sediments	Elements associated with phases in the (W.B.) sediments
Total Clays	Si, Ti, Al, Fe(T), Mg, Na, K, V, Cr, Ni, Ba, Ce, La, Th, Cu, Rb, Y, Zr, Nb, Fe^{+3}, H_2O^+, C_{org} and Depth in borehole.	Si, Ti, Al, Fe(T), Na, K, V, Cr, Ba, Ce, La, Th, Rb, Y, Nb, Fe^{+3}, H_2O^+, Corg, and Depth in borehole.
Sulphides, Phosphates, Corg	Fe(T), S, P, Ni, Pb, Zn, Cu, Mo, Fe^{+2}, H_2O^+ C_{org}, and Depth in borehole.	Fe(T), S, P, Cr, Ce, Y, Mo, Fe^{+2}, H_2O^+, Corg.
Calcite	Ca, Mn, Sr, CO_2, Pb, P	Ca, CO_2, As
Other Carbonates		Ca, CO , As, Fe(T), Mg, Fe^{+3}, Mn, Sr, V
Resistate Minerals	Si, Zr, Nb, Fe^{+3}, Ce	Si, Zr, Ba, Na, Y, Depth in borehole.
Fe-Mn Oxides/Hydroxides	Fe(T), Mn, Fe^{+3}, As, Mg	Fe^{+3} and Mn
Adsorbed Elements		Pb, Zn, Ga, Cu, Ni, As

Note: Underlined variables are those showing dissimilar behaviour as between (W.K.B.) and (W.B.) sediments.

mineral-chemical associations in the bulk rock and clay fraction components respectively. The detailed appraisals of the Factor Analysis of the two sets of data, which lead to the summaries given in these tables,are given in Chapters Five and Seven respectively. Table (8.5) shows the occurrence of phases such as total clays, sulphides, C_{org}, phosphates, calcite, resistates and Fe-Mn oxides/ hydroxides, being the commonly occurring components in the sediments of both the boreholes. The only exception is the occurrence of dolomite (ferroan) and a group of elements including Pb-Zn-Ga-Cu-Ni-As as adsorbed onto the clays in the (W.B.) sediments. The varying association of some of the phases with elements, as shown in Table (8.5), is interpreted as follows:

1. There is a great similarity of elements associated with total clays in the sediments of the two boreholes. The obvious exceptions are Mg, Ni, Cu and Zr, associated with the total clays in the (W.K.B.). This association indicates the origin of clays from basic igneous rocks (Mg, Ni and Cu). The presence of Zr may reflect the influence of granite in the source area on the clays.

2. The sulphide, phosphate and C_{org} phases in the (W.K.B.) reflect the greater availability of components such as Ni, Pb, Zn and Cu, as compared with (W.B.) sediments, which contain an additional association of elements such as Cr, Ce and Y, indicating, strongly, a greater influence of detrital phases.

3. The comparison of carbonate phases shows the occurrence of only one generation of carbonates, represented by calcite (low-Mg) in the (W.K.B.) sediments and two generations of carbonate, i.e. calcite (low-Mg) and dolomite (ferroan) in the (W.B.) sediments. The association of Fe - Mg - Mn in the (W.B.) sediments indicated the occurrence of dolomite (ferroan). In the (W.K.B.) sediments a strong influence of phosphate phase associated with calcite is apparent.

4. The resistate phases show typical association of elements such as Si, Zr, Nb, Ce, Y and Ba. The differences demonstrated by the resistate phases in the sediments of the two boreholes can be explained by the variations in the minerals present (e.g. feldspars) and the superficial mineral coatings by Fe-oxides in the case of the (W.K.B.). The occurrence of such phases (i.e. Fe-Mn oxides/

TABLE (8.6): Summary of the associations shown by clay mineral species and elements in the clay fraction ($< 2\mu$) samples of the respective boreholes, as suggested by R-mode Factor Analysis

Phases	Elements associated with clay minerals (W.K.B.)	Elements associated with clay minerals (W.B.)
Kaolinite	Depth, Al, Cr, Ce, Cu, Sr, Mo, Y, Na, S, Fe^{+2}, Fe^{+3}, Pb, Ba, P, H_2O^+, C_{org}	Depth, Al, Cr, Ce, Cu, Sr, Mo, Y, Zr, Ti, LOI Note: Sulphur and C_{org} were not determined due to fluxed samples.
Illite + Chlorite	Ti, Al, K, Rb, V, Mn, Ni, Ba, Mg, H_2O Cr	Ti, Al, K, Rb, V, Mn, Ni, Ce, Pb, Zn, Sr
Smectite	Si, Fe(T), Mg, As, Nb	
Mixed-layer Minerals		Fe(T), Mg, Ca, Na, K, P, V, As
Detrital Components	Ti, Na, Zr, Ba, Th, As, P, La, K	
Sulphides	Fe(T), S, Pb, Zn, Cu, Mo, V	
Phosphates	Ca, P, Na, Y, Ce, Th, S	P, Na, Y, Ni, Cu, Ba, Sr, La

Note: Underlined variables are those showing similar behaviour in the sediments of the two boreholes.

hydroxides) in the sediments of both the boreholes has been indicated by the R-mode Factor Analysis, described in Chapter Five. The presence of As in the Fe-Mn oxides/hydroxides phases in the (W.K.B.) again points to a Cornubian origin, whereas the association of As with carbonate phases in the (W.B.) is regarded as of essentially organic origin, derived from the organisms which participated in the precipitation of carbonate minerals.

5. The independent factor occurring in the (W.B.) sediments and represented by the association of elements such as 'Pb-Zn-Ga-Cu-Ni-As', compared with their association with total clays and sulphide factors in the (W.K.B.), emphasises the different sources for the two localities. The association of these elements in the (W.K.B.) sediments may be related to the igneous/metamorphic source terrain, whereas in the (W.B.) sediments they behave as a typical group of adsorbed elements, either originally held on the clays from the source area, or adsorbed onto the detrital clays during the course of deposition of the Oxford Clay sediments (KRAUSKOPF, 1956).

The description given in the foregoing pages elaborated the variations regarding the control over the chemical variance by the phases present in the bulk rock samples of the two boreholes. Similarly, Table (8.6) tends to highlight the differences in detail shown by the chemistry and minerals of the clay fraction ($< 2\mu$) of both the boreholes. This fraction was isolated physically, a process which allows the separation of non-clay minerals if the grain size is sufficiently fine (i.e. $< 2\mu$). It is evident from Table (8.6) that a phosphate phase was identified in the sediments of both the boreholes. A sulphide phase is confined to the (W.K.B.) sediments and emphasises the greater role played by sulphides (and hence Eh conditions) in the environments of the (W K.B.). A detrital phase is also unique in the (W.K.B.) sediments. The occurrence of an association of elements such as K-Ba-Na, P-Th-La, Zr and Ti, points strongly to a largely igneous source which provided fine-grained feldspar, phosphate and zircon, etc.

The associations of elements demonstrated by the clay minerals clearly reflect the variable sources of the material at the two depositional sites. As would be expected, the components Fe and Mg are associated with the smectite or the mixed-layer clays as appropriate, and K and Rb with the illite. The kaolinite phase shows association with elements such as Cu and Mo (and C_{org} in one borehole sediments only, due to analytical reasons). This association is obviously due to sedimentation rate; quick burial of organic matter leading to the formation of sulphide and related phases.

8.5 Depositional History of the Oxford Clay and Kellaways Formations

The depositional history of the studied sediments can be summarized from the mineralogy results produced in the foregoing pages. The detrital and non-detrital (authigenic/ diagenetic) minerals identified have shown variations of their concentration and association with elements in the various divisions of the Oxford Clay and Kellaways Formations, as shown in Tables (4.1A, 4.1B and 4.2A, 4.2B). A summary given in Table (8.2) also explains the varied abundances of elements in the various divisions of the studied sediments.

It is evident from the general mineralogy that sedimentation of the (K.F.) at the (W.B.) site took place in shallow water and near-shore conditions. The abundant presence of detrital components such as quartz, kaolinite, Zr, Si, Ti and Nb in the sediments of the (K.F.) confirms this view. On the other hand, the sediments of the (K.F.) in the case of the (W.K.B.) were deposited under comparatively deeper water conditions, as indicated by the highest abundances of combined SiO_2, Al_2O_3, K_2O, MgO, V, Cr, Rb and total clays dominantly composed of illite. The sediments of the (K.F.) of the (W.B.) were deposited at a higher rate of deposition, as inferred by the highest value (1·93) of the quartz/combined SiO_2 ratio shown in Table (4.2C). The highest rate of deposition in the case of the (W.K.B.) sediments was probably during the sedimentation of the (U.O.C.) sediments, which indicated the highest value (1·83) of the quartz/combined SiO_2 ratio, also shown in Table (4.1C). A higher rate of deposition may be related to the abundant supply of detritus, the role of running waters, tectonism and provenance.

During the entire depositional history, environments at both the sites never experienced complete anoxic conditions, as is revealed by the presence of fossils of plankton and benthonic animals throughout both the sequences. Reducing conditions were, on the whole, much stronger in the (W.K.B.) with respect to the (W.B.), as previously explained. The sediments of the (K.F.) of the (W.B.) experienced the existence of much stronger reducing conditions as compared with their counterparts in the (W.K.B.). This is indicated by the enriched abundances of certain elements, e.g. S, P. Mo, Fe^{+2} and C_{org}, shown by these sediments. The stronger reducing conditions in these sediments were created as a result of a greater input of detrital components, which caused rapid burial of the sediments leading to quick entrapment of marine organisms and probably desulphurizing bacteria.

Calcite is present in all the samples of the two boreholes. It showed enriched concentration in the sediments of the (U.O.C.) in both the boreholes, which may be related to the abundant availability of calcium and carbonate ions (increased biogenic activity), loss of CO_2 and an increase of pH in both the environments. The presence of calcite in all the samples in the studied sediments further indicates that, in the respective environments, the pH was never below 7 at all times.

The presence of smectite composed of 60-80% expandable components in the (W.K.B.) sediments, and its complete absence in the (W.B.) sediments, is a clear indication of different sources for the two boreholes. This variation strongly suggests a volcanogenic origin for part of the (W.K.B.) sediments. The abundant presence of well crystalline smectite in the (U.O.C.) sediments suggests either an increase in the supply of the source material or a local pulse of volcanism in a near-by locality.

8.6 Conclusions

Taking into consideration the information summarized in the foregoing pages, some broad conclusions may be derived as follows:

1. Sedimentation at the (W.B.) site started under shallow water near-shore and stronger reducing conditions, while at the (W.K.B.) it was, relatively, under deeper water conditions.
2. The pH in the environments of both the boreholes was never below pH 7.
3. Much stronger reducing conditions in general, as compared to those in the (W.B.), existed in the (W.K.B.) environments, due to a greater input of kaolinite, enriched abundance of C_{org}, and much deeper environments of the deposition.

4. Fe-Mn oxides/hydroxides occur in the sediments of both boreholes. They were probably transported to the sites of deposition with the detritus.

5. The higher abundance of total clays,dominated by degraded illite and non-expanding mixed-layer clays, in the (W.B.) sediments is probably due to the major contribution of detritus from pre-existing sedimentary rocks of Palaeozoic age from the 'East Anglian Massif', which acted as the provenance for the sediments of the Oxford Clay and Kellaways Formations at the (W.B.) site.

6. The higher abundances of better crystalline kaolinite and chlorite in the (W.K.B.) sediments with respect to those of the (W.B.) are due to a major contribution to the detritus by the acid igneous and low-grade metamorphic rocks of the 'Cornubian Massif', which acted as the provenance for the sediments of the Oxford Clay and Kellaways Formations at the (W.K.B.) site.

7. The enriched abundance of well crystalline smectite in the (U.O.C.) sediments of the (W.K.B.) is due either to the increased supply of 'air-fall' volcanic ash from the source area or a minor and local pulse of volcanism.

8. Organic carbon of detrital origin is more abundant in the (W.K.B.) sediments as compared with the (W.B.) sediments. This inference is derived from the very strong positive correlations shown by C_{org} with typically detrital components such as Al, Ti, Cr, illite, kaolinite and chlorite, etc.

9. The better crystallinity of illite and kaolinite in the (W.K.B.) sediments with respect to the (W.B.) indicates that these sediments did not undergo many cycles of sedimentation, as happened with the (W.B.) sediments.

10. The enriched abundances of certain elements such as Cr, Mn, Ni, Pb, Zn and Fe(T) in the bulk rock, and Mn-Ni-Zn in the lattice-held fraction of the (W.K.B.) samples clearly reflect the strong influence of basic igneous rocks over the (W.K.B.) sediments. The overall enrichment of elements, e.g. Fe(T), Ca, Na, S, P, Sr, Fe^{+2}, Fe^{+3}, Mn, Pb, Zn, Ni, H_2O^+ and C_{org} in the (W.K.B.) sediments, as compared to those in the (W.B.) sediments, strongly indicates the dominant control of non-detrital phases over the chemistry.

11. The enhanced abundances of elements such as S, P, Zn, Fe^{+2} and C_{org} in the (W.K.B.) sediments is due to the abundant biogenic activity and the existence of much stronger reducing conditions in the (W.K.B.) environments, as compared to those of the (W.B.).

12. The higher contents of Mg in the (W.B.) bulk rock samples is due to the presence of dolomite, which does not occur in the (W.K.B.) sediments.

13. The higher abundances of elements such as Si, Ti, Al, K, Ba, Rb, Zr and Y, etc. in the (W.B.) bulk rock sediments, as compared with those of the (W.K.B.), are due to the enriched contents of illite, total clays and other detrital components supplied by the pre-existing sedimentary rocks of Palaeozoic age from the 'East Anglian Massif'.

APPENDIX (2.1)

Appendix (2.1) shows the concentrations of components determined for each sample of the bulk rock of the Winterborne Kingston Borehole sediments. These components were determined independently and include the following:

1) Combined CO_2 in per cent, determined by Infra-red gas analyser.
2) Carbonate CO_2 in per cent, determined by Infra-red gas analyser.
3) Organic carbon CO_2, obtained as described in Chapter Two.
4) Organic carbon in per cent.
5) Calcite in per cent, calculated from CO_2, as described in Chapter Two.
6) Lattice-held water (H_2O^+) in per cent.
7) Ferrous iron (Fe^{+2}), independently determined in per cent.
8) Ferric iron (Fe^{+3}), independently determined in per cent.

Sample No.	1	2	3	4	5	6	7	8
WBK-1	23·55	19·15	4·40	1·20	43·50	2·00	0·70	2·56
WBK-2	21·82	18·08	3·74	1·02	41.10	3·50	0·62	2·64
WBK-3	22·86	18·97	3·89	1·06	43·10	3·40	0·72	2·60
WBK-4	23.22	18·08	5·13	1·40	41·10	2·80	0·70	2·77
WBK-5	26·32	22·73	3·59	0·98	50·00	3·80	0·70	2·86
WBK-6	22·11	18·44	3·67	1·00	41·90	3·50	0·78	2·90
WBK-7	21·08	18·44	2·64	0·72	41·90	3·20	0·73	3·11
WBK-8	25.76	21·25	4·51	1·23	48·30	3·80	0·81	2·93
WBK-9	29·77	24·34	5·43	1·48	55·30	3·80	1·03	2·70
WBK-10	23·21	18·44	4·77	1·30	41·90	3·20	0·84	3·14
WBK-11	20·32	15·92	4·40	1·20	36·20	3·60	0·83	3·23
WBK-12	28·00	20·22	7·77	2·12	45·90	3·00	1·02	3·13
WBK-13	24·80	16·84	7·96	2·17	38·30	3·60	1·14	2·94
WBK-14	25·36	17·73	7·63	2·08	40·30	2·80	1·05	3·09
WBK-15	21·80	14·53	7·26	1·98	33·00	3·80	1·03	3·33
WBK-16	18·63	17·02	1·61	0·44	38·70	3·20	0·80	3·11
WBK-17	25·32	21·25	4·07	1·11	48·30	3·80	2·13	3·03
WBK-18	24·38	18·44	5·94	1·62	41·90	3·70	1·13	3·29
WBK-19	19·00	14·53	4·47	1·22	33·00	3·60	1·37	3·24
WBK-21	19·34	13·47	5·87	1·60	28·30	3·80	1·18	3·28
WBK-22	19·56	12·41	7·15	1·95	28·20	4·60	1·13	3·62
WBK-23	22·96	13·94	9·02	2·46	31·70	3·80	1·15	3·22
WBK-24	22·50	14·18	8·32	2·27	33·00	3·80	1·95	2·99
WBK-25	24·43	14·53	9·90	2·70	28·60	5·20	1·75	3·04
WBK-26	19·91	12·61	7·30	1·99	24·10	5·90	0·92	3·93
WBK-27	17·93	10·63	7·30	1·99	24·10	5·90	0·77	3·94
WBK-28	18·65	10·99	7·66	2·09	25·00	5·60	0·77	4·13
WBK-29	20·40	12·76	7·63	2·08	29·00	5·40	1·31	3·89
WBK-30	24·60	13·93	10·67	2·91	31·60	5·00	1·28	3·59
WBK-32	20·74	12·05	8·69	2·37	27·40	5·20	0·89	4·00
WBK-33	18·27	15·08	3·19	0·87	34·30	4·80	1·75	3·34
WBK-34	18·64	12·41	6·23	1·70	28·20	5·00	1·12	3·79
WBK-35	17·60	12·05	5·54	1·51	27·40	5·00	1·25	3·57
WBK-36	18·27	11·34	6·93	1·89	25·80	5·60	1·65	3·36
WBK-37	20·00	14·18	5·87	1·60	32·20	3·60	2·11	3·63
WBK-38	16·54	10·64	5·90	1·61	24·20	5·00	0·97	4·05
WBK-39	17.92	10·99	6·93	1·89	25·00	4·70	1·21	3·92

/contd.over

APPENDIX (2.1) contd.

Sample No.	1	2	3	4	5	6	7	8
WBK-40	22·35	15·60	6·75	1·84	35·40	5·10	3·19	2·82
WBK-41	18·27	10·28	8·00	2·18	23·30	4·80	1·12	3·82
WBK-42	26·72	10·99	15·73	4·29	25·00	6·00	2·27	3·00
WBK-43	25·67	9·39	16·28	4·44	26·00	6·00	1·75	3·13
WBK-44	26·39	12·35	14·04	3·83	28·00	6·00	1·82	2·80
WBK-45	33·46	14·36	19·10	5·21	32·60	6·00	2·20	2·52
WBK-46	31·32	12·80	18·52	5·05	29·10	5·80	2·52	2·22
WBK-47	27·59	11·42	16·17	4·41	25·90	6·80	1·88	2·43
WBK-48	29·54	12·05	17·50	4·77	27·40	6·40	2·17	2·13
WBK-49	25·68	8·15	17·53	4·78	18·50	6·80	1·75	2·66
WBK-50	23·20	7·45	15·77	4·30	16·90	5·40	1·60	2·89
WBK-51	23·91	7·45	16·46	4·49	16·90	7·00	1·45	3·07
WBK-52	22·85	8·51	14·34	3·91	19·30	5·80	1·60	2·84
WBK-53	23·55	7·09	16·46	4·49	17·00	6·20	1·50	2·20
WBK-54	17·58	8·01	9·57	2·61	18·20	6·10	1·34	2·96
WBK-55	16·54	7·45	9·10	2·48	16·91	6·20	1·47	2·94
WBK-56	16·52	6·73	9·80	2·67	15·30	6·20	1·24	3·20
WBK-57	15·12	6·80	8·32	2·27	15·40	6·00	1·53	2·80
WBK-58	16·16	7·62	8·54	2·33	17·30	6·10	1·37	2·85
WBK-59	18·30	7·45	10·85	2·96	16·91	7·20	1·18	3·60
WBK-60	17·57	7·45	10·12	2·76	16·91	6·00	1·24	3·44
WBK-61	18·64	7·09	11·55	3·15	17·00	5·60	1·24	3·43
WBK-62	16·51	7·09	9·42	2·57	17·00	5·00	1·12	3·51
WBK-63	14·76	6·73	8·03	2·19	15·30	5·60	1·18	3·43
WBK-64	23·91	6·38	17·53	4·78	14·50	5·20	1·24	3·37
WBK-65	16·87	6·73	10·16	2·77	15·30	6·00	1·12	3·40

APPENDIX (2.2)

Appendix (2.2) shows the concentrations of components determined individually for each sample of the bulk rock of the Warlingham Borehole sediments. The components determined comprise the following:

1) Combined CO_2 in per cent, determined by Infra-red gas analyser.
2) Carbonate CO_2 in per cent, obtained from total carbonates determined by O·1N HCl.
3) Organic carbon CO_2 in per cent, obtained as described in Chapter Two.
4) Organic carbon in per cent.
5) Lattice-held water (H_2O^+) in per cent.
6) Ferrous iron (Fe^{+2}).
7) Ferric iron (Fe^{+3}).
8) Calcite/Dolomite peak height ratios, as obtained from X.R.D.
9) Calcite/Dolomite peak height ratios, corrected.
10) Total contents of carbonates, determined by O·1N HCl.

Sample No.	1	2	3	4	5	6	7	8	9	10
BR-115	22·50	21·51	0·99	0·27	1·72	0·82	3·06	0·3230	0·257	47·32
BR-123	21·73	19·68	2·05	0·56	2·26	0·79	3·51	0·1684	0·129	43·30
BR-129	31·86	31·82	0·04	0·01	0·70	0·21	1·68	5·9230	4·479	70·00
BR-131	27·60	25·84	1·76	0·48	1·68	0·37	2·33	1·1650	0·942	56·85
BR-134	27·65	26·00	1·65	0·45	1·91	0·42	2·22	1·3655	1·102	57·20
BR-145	28·91	26·23	2·77	0·73	2·24	0·24	2·70	2·6154	2·079	57·71
BR-154	19·92	17·28	2·64	0·72	3·00	0·80	2·47	0·5964	0·481	38·00
BR-167	19·22	16·69	2·53	0·69	2·37	0·99	2·00	1·0860	0·878	36·72
BR-180	24·80	23·00	1·80	0·49	1·64	0·61	2·90	5·2120	3·986	50·60
BR-199	12·99	11·89	1·10	0·30	1·71	0·72	2·90	1·0197	0·825	26·16
BR-211	23·00	21·53	1·47	0·40	2·53	1·71	1·54	8·8170	6·356	47·40
BR-236	22·20	19·89	2·31	0·63	1·48	0·44	2·15	6·9190	5·148	43·80
BR-246	21·00	19·42	1·58	0·43	1·68	0·34	2·11	9·8600	6·981	42·72
BR-278	23·96	19·56	4·40	1·20	3·65	0·37	2·72	10·1508	7·151	43·03
BR-303	15·00	12·72	2·27	0·62	2·65	0·40	2·61	4·4090	3·414	28·00
BR-320	14·50	12·26	2·24	0·61	2·62	0·64	2·54	7·2560	5·369	27·00
BR-356	14·50	12·22	2·27	0·62	2·65	0·49	3·00	3·7210	2·912	27·00
BR-405	19·72	18·88	0·84	0·23	1·38	0·30	2·50	8·3475	6·065	41·54
BR-444	17·53	15·37	2·16	0·59	3·04	0·36	3·40	3·5909	2·815	33·81
BR-468	14·87	13·40	1·47	6·40	2·69	0·34	3·86	4·6548	3·591	29·48

/contd.over

APPENDIX (2.2) contd.

Sample No.	1	2	3	4	5	6	7	8	9	10
BR-502	17·00	14·68	2·31	0·63	3·18	0·50	2·82	7·4167	5·474	32·30
BR-543	13·51	11·71	1·80	0·49	4·05	0·42	3·05	5·4319	4·140	25·76
BR-560	15·14	12·10	3·04	0·83	4·56	0·23	3·58	8·4468	6·127	26·62
BR-606	13·84	10·76	3·08	0·84	3·40	0·84	3·30	6·7618	5·044	23·67
BR-627	14·00	10·93	3·08	0·84	3·77	0·11	3·74	5·5815	4·243	24·00
BR-656	18·80	15·27	3·52	0·96	2·77	0·11	4·30	6·4293	4·822	33·60
BR-688	15·70	13·13	2·57	0·70	4·17	0·33	3·74	7·3580	5·435	28·89
BR-706	15·51	13·05	2·46	0·67	2·43	0·36	3·52	9·2948	6·646	28·71
BR-736	15·14	13·16	1·98	6·54	2·79	0·32	3·03	9·8625	6·982	28·95
BR-765	16·82	14·55	2·27	0·62	3·67	0·21	3·65	15·4133	9·857	32·00
BR-801	14·78	11·74	3·04	0·83	3·43	0·22	3·13	7·2994	5·397	25·83
BR-812	25·87	24·37	1·50	0·41	1·22	0·43	2·18	24·3600	13·074	53·61
BR-820	27·40	26·25	1·14	0·31	0·84	0·22	1·59	41·7919	12·882	57·75
BR-826	19·87	16·20	3·67	1·00	2·25	0·59	3·47	15·0364	9·686	35·64
BR-855	18·61	15·97	2·64	0·72	2·31	0·47	2·99	8·8219	6·359	35·13
BR-891	16·82	14·00	2·82	0·77	2·63	0·34	3·19	4·2781	3·319	30·80
BR-920	15·35	12·53	2·82	0·77	2·20	0·35	2·88	9·4668	6·749	27·57
BR-958	14·72	11·82	2·90	0·79	3·39	2·41	3·08	7·8539	5·754	26·00
BR-981	12·35	9·60	2·75	0·75	3·35	0·96	2·43	4·3251	3·354	21·12
BR-988	25·56	20·00	5·57	1·52	5·54	0·81	3·68	1·3877	1·120	44·00
BR-1008	24·65	19·34	5·28	1·44	3·22	0·62	2·27	4·2602	3·306	42·55
BR-1052	18·18	13·23	4·95	1·35	3·62	0·63	2·29	16·5897	10·369	29·10

/contd.over

APPENDIX (2.2) contd.

Sample No.	1	2	3	4	5	6	7	8	9	10
BR-1093	17.00	12.74	4.25	1.16	3.60	0.70	2.48	14.6705	9.517	28.00
BR-1123	13.60	9.20	4.40	1.12	3.91	0.81	2.74	11.7791	8.062	20.24
BR-1157	14.44	10.11	4.33	1.18	3.71	0.71	2.66	14.8841	9.616	22.24
BR-1194	19.22	11.34	7.88	2.15	5.00	1.01	1.81	16.7706	10.444	24.95
BR-1220	17.51	11.68	5.83	1.59	3.82	0.67	2.19	16.8513	10.477	25.70
BR-1257	16.16	11.94	4.22	1.15	4.61	1.17	2.31	6.8002	5.070	26.27
BR-1301	15.40	11.22	4.18	1.14	4.67	1.24	3.08	7.3009	5.398	24.68
BR-1339	16.65	11.74	4.91	1.34	4.22	1.12	2.28	9.2593	6.624	25.83
BR-1377	16.91	12.55	4.36	1.19	3.76	0.84	1.72	19.6529	11.538	27.61
BR-1386	20.61	13.90	6.71	1.83	3.71	0.84	1.38	21.9858	12.273	30.58
BR-1392	19.56	15.89	3.67	1.00	4.01	0.83	1.77	9.1940	6.585	34.96
BR-1424	26.34	14.54	11.81	3.22	4.51	0.82	1.76	2.8602	2.266	32.00
BR-1436	18.21	13.04	5.17	1.41	3.75	0.77	1.79	11.9143	8.134	28.69
BR-1467	20.96	8.46	12.50	3.41	5.13	0.75	1.77	12.1198	8.244	18.61
BR-1513	23.35	11.10	12.25	3.34	4.17	0.77	1.74	17.8039	10.860	24.42
BR-1544	25.75	9.62	16.13	4.40	5.98	0.88	1.63	16.1758	10.193	21.16
BR-1583	23.70	9.91	13.79	3.76	3.33	0.97	2.79	16.2039	10.205	21.80
BR-1636	21.97	9.36	12.61	3.44	5.30	0.83	1.94	17.4591	10.724	20.60
BR-1676	17.87	6.10	11.77	3.21	5.19	0.77	2.43	7.4630	5.503	13.42
BR-1683	26.46	8.86	17.60	4.80	6.34	0.80	2.20	10.9006	7.577	19.49

/contd.over

APPENDIX (2.2) contd.

Sample No.	1	2	3	4	5	6	7	8	9	10
BR-1691	24·74	10·11	14·63	3·99	5·40	0·74	2·25	5·1502	3·942	22·24
BR-1698	34·01	10·14	23·87	6·51	5·85	1·15	1·54	4·4901	3·473	22·31
BR-1713	16·12	8·57	7·55	2·06	5·12	0·76	2·59	2·3921	1·908	18·85
BR-1721	52·59	10·97	41·62	11·35	7·93	1·95	0·48	1·6161	1·301	24·13
BR-1734	23·38	2·44	20·94	5·71	6·85	0·94	3·16	3·9339	3·360	5·37
BR-1750	14·45	2·87	12·58	3·43	5·70	0·82	2·49	5·6593	4·297	6·31
BR-1755	12·70	4·45	8·25	2·25	3·90	1·11	2·86	10·7673	7·503	9·80
BR-1757	14·31	6·68	7·63	2·08	4·70	0·67	2·35	30·8345	13·833	14·70
BR-1762	27·83	8·10	19·73	5·38	6·52	5·91	0·00	38·9109	13·562	17·82
BR-1771	18·23	1·18	17·05	4·65	8·17	1·35	2·43	00·0000	00·000	2·60
BR-1781	5·48	2·36	3·12	0·85	2·29	0·58	0·75	6·6156	4·947	5·20
BR-1811	14·00	14·00	0·00	0·00	0·65	0·18	1·92	9·194	6·585	30·80
BR-1831	18·51	11·15	7·00	1·91	2·19	0·84	2·47	9·5813	6·817	24·53
BR-1852	7·52	0·00	7·52	2·05	1·80	0·26	0·60	0·0000	0·000	00·00
BR-1877	10·30	0·00	10·30	2·81	1·19	1·08	0·54	0·0000	0·000	00·00
BR-1890	5·43	2·28	3·15	0·86	4·36	2·11	1·75	32·2000	13·901	5·00

APPENDIX (3.1): Mineral abundances in the bulk-rock samples of the Winterborne Kingston Borehole sediments.

SR.NO.	S.NO.	CORG	QTZ	CAL	PYT	TCLAY	IL	KOL	CH	SMECT
1	WBK-1	1·20	22·70	43·50	1·50	31·10	12·13	0·93	0·31	17·73
2	WBK-2	1·02	25·40	41·10	1·30	31·18	10·91	0·62	0·62	19·02
3	WBK-3	1·06	21·80	43·10	1·60	32·44	14·60	0·97	1·30	15·57
4	WBK-4	1·40	24·50	41·10	1·50	31·50	14·17	0·95	1·26	15·12
5	WBK-5	1.00	21.00	50.00	1.50	26.50	6·36	0.80	0.26	19.08
6	WBK-6	1·00	28·00	41·90	1·70	27·40	10·41	0·82	0·82	15·34
7	WBK-7	0·72	25·20	41·90	1·60	30·58	14·68	1·53	1·22	13·15
8	WBK-8	1·23	20·80	48·30	1·70	27·97	10·63	1·40	1·12	14·82
9	WBK-9	1·48	19·80	55·30	2·20	21·22	7·43	0·85	0·64	12·31
10	WBK-10	1·30	28·10	41·90	1·80	26·90	8·07	1·08	0·54	17·22
11	WBK-11	1·13	25·10	36·20	1·80	35·77	13·23	2·50	1·07	18·96
12	WBK-12	1·20	25·40	45·90	2·20	25·30	9·87	1·77	1·01	12·65
13	WBK-13	2·12	25·20	40·30	2·50	29·88	9·56	1·49	0·90	17·93
14	WBK-14	2·17	27·40	33·00	2·30	35·13	13·35	1·40	1·05	19·32
15	WBK-15	2·08	22·90	48·30	2·20	24·52	13·73	3·43	1·72	5·64
16	WBK-16	1·98	25·20	41·90	1·70	29·22	11·98	1·75	0·58	14·90
17	WBK-17	0·44	22·40	33·00	4·60	39·56	17·01	3·16	1·58	17·80
18	WBK-18	1·11	19·50	28·30	2·40	48·69	27·27	8·76	3·89	8·76
19	WBK-19	1·62	22·30	28·20	3·00	44·88	22·44	6·28	1·80	14·36
20	WBK-21	1·22	23·00	31·70	2·60	41·48	20·74	4·98	1·66	14·10

/contd.over

APPENDIX (3.1) contd.

SR.NO.	S.NO.	CORG	QTZ	CAL	PYT	TCLAY	IL	KOL	CH	SMECT
21	WBK-22	1·60	24·00	32·20	2·40	39·80	19·90	5·57	1·59	12·74
22	WBK-23	1·95	22·80	33·00	2·40	39·85	21·52	5·18	2·39	10·76
23	WBK-24	2·46	23·10	28·60	4·20	41·64	19·15	7·50	2·91	12·08
24	WBK-25	2·27	24·50	33·00	3·70	36·53	18·26	5·11	1·10	12·05
25	WBK-26	2·70	20·80	28·60	1·90	46·00	24·84	9·66	3·22	8·28
26	WBK-27	1·99	19·70	24·10	1·60	52·61	28·93	8·42	5·79	9·47
27	WBK-28	2·09	22·00	25·00	1·60	49·31	28·11	8·75	5·92	6·41
28	WBK-29	2·08	19·60	29·00	2·80	46·52	28·38	8·84	4·65	4·65
29	WBK-30	2·91	21·60	31·60	2·80	41·10	25·89	5·75	2·05	7·40
30	WBK-32	2·37	21·10	27·40	1·90	47·23	28·34	8·97	4·72	5·19
31	WBK-33	0·87	17·40	34·30	3·70	43·73	24·50	7·43	3·50	8·31
32	WBK-34	1·70	17·90	28·20	2·40	49·80	26·39	7·97	2·99	12·45
33	WBK-35	1·51	19·00	27·40	2·60	49·49	28·70	7·92	2·97	9·90
34	WBK-36	1·89	18·10	25·80	2·90	51·31	32·84	10·77	2·56	5·13
35	WBK-37	1·60	17·90	32·20	4·50	43·80	27·16	7·00	3·50	6·13
36	WBK-38	1·61	17·70	24·20	2·10	54·39	29·91	9·25	4·35	10·88
37	WBK-39	1·89	18·50	25·00	2·60	52·00	31·72	10·92	2·08	7·28
38	WBK-40	1·84	16·70	35·40	6·80	39·26	20·81	7·85	1·18	9·42
39	WBK-41	2·18	19·00	23·30	2·30	53·22	29·80	7·98	4·79	10·64
40	WBK-42	4·29	17·00	25·00	4·90	48·81	27·33	9·27	5·86	6·34
41	WBK-43	4·44	16·60	26·00	3·60	49·36	27·15	8·88	4·44	8·88
42	WBK-44	3·83	13·60	28·00	3·90	50·67	30·40	12·16	3·55	4·56
43	WBK-45	5·21	17·70	32·60	4·80	39·69	23·81	7·94	4·37	3·57

/contd.over

APPENDIX (3.1) contd.

SR.NO.	S.NO.	CORG	QTZ	CAL	PYT	TCLAY	IL	KOL	CH	SMECT
44	WBK-46	5.05	17.50	29.10	5.40	42.95	24.05	10.74	3.86	4.29
45	WBK-47	4.41	17.40	25.90	4.00	48.29	28.00	12.07	2.90	5.31
46	WBK-48	4.77	18.50	27.40	4.70	44.63	27.22	11.60	2.23	3.57
47	WBK-49	4.78	17.00	18.50	3.70	56.02	35.85	12.32	2.24	5.60
48	WBK-50	4.30	19.60	16.90	3.50	55.70	37.32	12.25	2.78	3.34
49	WBK-51	4.49	18.70	16.90	3.10	56.80	36.35	14.77	2.84	2.84
50	WBK-52	3.91	18.90	19.30	3.50	54.40	34.82	10.88	4.35	4.35
51	WBK-53	4.49	19.20	20.00	3.20	53.11	33.99	11.15	5.84	2.12
52	WBK-54	2.61	19.60	18.20	2.90	56.69	37.41	10.77	6.23	2.27
53	WBK-55	2.48	19.50	20.00	3.10	54.92	34.60	11.53	5.49	3.29
54	WBK-56	2.67	18.70	15.30	2.70	60.63	38.80	11.52	6.67	3.64
55	WBK-57	2.27	19.00	15.40	3.30	60.03	36.62	13.21	7.20	3.00
56	WBK-58	2.33	17.70	17.30	3.00	59.67	36.40	13.72	5.97	3.58
57	WBK-59	2.96	22.20	16.90	2.50	54.44	34.30	11.43	6.54	2.18
58	WBK-60	2.76	18.60	16.90	2.60	59.14	37.26	12.42	7.10	2.36
59	WBK-61	3.15	21.90	20.00	2.60	52.35	34.03	12.04	6.28	4.19
60	WBK-62	2.57	22.20	16.10	2.40	56.73	35.74	11.91	6.24	2.84
61	WBK-63	2.19	24.50	15.30	2.50	55.51	33.86	12.77	6.11	2.77
62	WBK-64	4.78	22.10	19.00	2.70	51.42	33.42	12.34	3.10	2.57
63	WBK-65	2.77	23.20	15.30	2.40	56.33	36.05	12.39	4.51	3.38

Note: IL, KOL, CH, SMECT indicate the clay mineral abundances re-calculated in total clays.

APPENDIX (3.2): Mineral abundances in the bulk-rock samples of the Warlingham Borehole sediments.

SR.NO.	S.NO.	CORG	QTZ	DOL	CAL	PYT	TCLAY	IL	KOL	CH	MLYR
1	BR-115	0·27	16·00	36·39	9·35	1·76	36·23	21·01	0·00	0·00	15·21
2	BR-123	0·56	20·00	36·80	4·75	1·70	36·19	23·52	0·00	0·36	12·30
3	BR-129	0·01	10·00	12·99	58·20	0·45	18·34	11·92	0·00	0·37	6·05
4	BR-131	0·48	16·00	28·95	27·27	0·80	26·49	15·89	0·00	0·26	10·33
5	BR-134	0·45	16·00	27·00	29·76	0·90	25·89	16·83	0·00	0·26	8·80
6	BR-145	0·73	15·00	18·83	39·15	0·52	25·76	16·74	0·00	0·51	8·50
7	BR-154	0·72	22·00	25·06	12·05	1·72	38·45	25·38	0·00	0·38	12·69
8	BR-167	0·69	22·00	19·31	16·95	2·13	38·91	24·51	0·00	0·39	14·00
9	BR-180	0·49	19·00	10·30	41·08	1·31	27·82	16·97	0·00	0·56	10·29
10	BR-199	0·30	24·00	14·14	11·66	1·55	48·34	33·84	0·97	1·93	11·60
11	BR-211	0·40	16·00	6·57	41·79	3·68	31·55	20·82	3·15	1·58	5·99
12	BR-236	0·63	22·00	7·25	37·32	0·95	31·84	21·65	3·82	0·64	5·73
13	BR-246	0·43	26·00	5·47	38·19	0·73	29·18	18·96	3·50	1·75	4·96
14	BR-278	1·20	28·00	5·40	38·59	0·80	26·00	16·64	2·60	2·34	4·42
15	BR-303	0·62	25·00	6·42	21·93	0·86	45·16	31·16	4·97	2·71	6·32
16	BR-320	0·61	22·00	4·32	23·17	1·38	48·51	35·41	4·85	2·91	5·33
17	BR-356	0·62	21·00	6·95	20·23	1·05	50·16	33·10	6·52	5·01	5·01
18	BR-405	0·23	20·00	6·00	36·39	0·65	36·72	25·34	4·04	1·10	6·24
19	BR-444	0·59	14·00	8·95	25·20	0·78	50·46	38·81	4·04	2·02	5·55
20	BR-468	0·41	17·00	6·51	23·38	0·73	51·97	38·98	5·72	1·56	5·72
21	BR-502	0·63	23·00	5·08	27·84	1·07	42·38	30·94	3·81	2.12	4·66

/contd.over

APPENDIX (3.2) contd.

SR.NO.	S.NO.	CORG	QTZ	DOL	CAL	PYT	TCLAY	IL	KOL	CH	MLYR
22	BR-543	0.49	19.00	5.09	21.08	0.90	53.44	34.73	5.34	4.27	9.08
23	BR-560	0.83	19.00	3.81	23.36	0.49	52.51	33.61	4.20	4.20	10.50
24	BR-606	0.84	26.00	4.00	20.12	1.80	47.25	31.66	4.72	4.72	6.14
25	BR-627	0.84	23.00	4.66	19.78	0.24	51.48	33.97	6.17	5.15	6.18
26	BR-656	0.96	18.00	5.87	28.32	0.24	46.64	31.90	4.69	2.81	7.51
27	BR-688	0.70	14.00	4.57	24.87	0.71	55.14	38.05	4.41	3.31	9.37
28	BR-706	0.67	21.00	3.83	25.49	0.78	48.22	32.79	5.30	2.89	7.23
29	BR-736	0.54	28.00	3.71	25.88	0.69	41.18	27.18	5.76	2.47	5.76
30	BR-765	0.62	27.00	3.02	29.78	0.45	39.12	26.21	5.48	1.96	5.48
31	BR-801	0.83	28.00	4.11	22.21	0.47	44.37	28.84	4.88	3.99	6.66
32	BR-812	0.41	19.00	3.91	51.14	0.93	24.60	14.76	4.67	0.74	4.43
33	BR-820	0.31	20.00	4.27	55.02	0.47	19.93	13.15	2.59	0.80	3.19
34	BR-826	1.00	17.00	3.42	33.10	1.27	44.21	28.45	6.22	2.67	7.11
35	BR-855	0.72	23.00	4.87	31.00	1.01	39.39	24.42	4.73	3.94	6.30
36	BR-891	0.77	17.00	7.22	23.97	0.73	50.30	35.21	6.04	3.02	6.04
37	BR-920	0.77	23.00	3.63	24.53	0.75	47.32	33.12	5.68	3.31	5.20
38	BR-958	0.79	20.00	3.93	22.60	5.18	47.50	29.93	6.17	3.80	7.60
39	BR-981	0.75	22.00	4.91	16.48	2.06	53.80	37.12	5.92	5.38	5.38
40	BR-988	1.52	18.00	20.56	23.03	1.74	35.15	23.90	4.60	2.50	4.22
41	BR-1008	1.44	16.00	10.00	33.08	1.34	38.12	25.92	3.81	2.67	5.72
42	BR-1052	1.35	18.00	2.62	27.22	1.35	49.46	35.11	6.43	1.98	5.93
43	BR-1093	1.16	21.00	2.73	26.00	1.59	47.53	30.42	6.18	3.32	7.60
44	BR-1123	1.12	17.00	2.28	18.43	1.74	59.43	38.63	7.72	5.35	7.72

/contd.over

APPENDIX (3.2) contd.

SR.NO.	S.NO.	CORG	QTZ	DOL	CAL	PYT	TCLY	IL	KOL	CH	MLYR
45	BR-1157	1·18	17·00	2·15	20·64	1·53	57·49	36·22	6·32	5·17	9·77
46	BR-1194	2·15	17·00	2·23	23·34	2·17	53·10	35·04	5·84	3·72	8·49
47	BR-1220	1·59	19·00	2·29	24·05	1·44	51·62	34·07	5·68	3·10	8·77
48	BR-1257	1·15	17·00	4·41	22·35	2·52	52·57	36·27	6·31	2·63	7·36
49	BR-1301	1·14	19·00	3·93	21·23	2·66	52·04	32·27	6·24	2·60	10·93
50	BR-1339	1·34	14·00	3·46	22·92	2·41	55·86	38·54	6·14	3·35	7·82
51	BR-1377	1·19	19·00	2·26	26·07	1·81	49·67	31·79	7·95	1·99	7·95
52	BR-1386	1·83	25·00	2·36	29·02	1·81	39·97	24·38	4·80	4·40	6·39
53	BR-1392	1·00	19·00	4·70	31·00	1·78	42·51	27·63	6·80	2·12	5·95
54	BR-1424	3·22	20·00	8·36	23·92	1·76	42·74	26·07	5·13	4·24	7·26
55	BR-1436	1·41	22·00	3·21	26·14	1·66	45·57	30·98	6·83	1·82	5·92
56	BR-1467	3·41	21·00	2·06	17·00	1·61	54·93	35·16	7·69	6·04	6·04
57	BR-1513	3·34	21·00	2·11	22·93	1·66	48·95	31·82	7·83	1·96	7·34
58	BR-1544	4·40	17·00	1·94	19·76	1·89	55·01	36·86	7·70	4·95	5·50
59	BR-1583	3·76	17·00	2·00	20·35	2·08	54·81	36·18	7·67	2·74	8·22
60	BR-1636	3·44	18·00	1·80	19·31	1·78	55·66	38·96	7·24	2·78	6·70
61	BR-1676	3·21	15·00	2·10	11·58	1·66	66·44	43·19	11·96	3·99	7·31
62	BR-1683	4·80	15·00	2·32	17·61	1·72	58·54	38·64	8·20	3·51	8·20
63	BR-1691	3·99	15·00	4·57	18·01	1·57	56·85	40·94	6·82	1·70	7·39
64	BR-1698	6·51	13·00	5·05	17·55	2·47	55·41	37·68	7·20	1·66	8·31
65	BR-1713	2·06	14·00	6·50	12·41	1·63	63·40	41·21	8·87	3·17	10·14
66	BR-1721	11·35	12·00	10·44	13·59	4·19	48·43	31·48	8·23	0.48	8·23

/contd.over

APPENDIX (3.2) contd.

SR.NO.	S.NO.	CORG	QTZ	DOL	CAL	PYT	TCLY	IL	KOL	CH	MLYR
67	BR-1734	5·71	14·00	1·25	4·19	2·02	72·83	45·15	11·65	5·83	10·20
68	BR-1750	3·43	29·00	1·03	4·43	1·76	60·35	37·42	9·66	3·02	10·26
69	BR-1755	2·25	40·00	1·18	8·83	2·38	45·36	29·03	6·35	3·17	6·80
70	BR-1757	2·08	27·00	1·02	14·10	1·44	54·38	36·44	9·79	3·26	4·89
71	BR-1762	5·38	19·00	1·26	17·04	12·70	44·61	30·33	6·69	1·78	5·80
72	BR-1771	4·65	14·00	3·00	0·00	2·90	76·11	49·39	11·40	3·80	11·40
73	BR-1781	0·85	62·00	0·00	5·29	1·25	30·61	19·28	6·43	0·92	3·98
74	BR-1811	0·00	57·00	4·15	27·31	0·39	11·15	6·58	3·68	0·22	0·67
75	BR-1831	1·91	23·00	3·21	21·86	1·81	48·21	28·44	12·53	1·93	5·30
76	BR-1852	1·05	78·00	0·00	0·00	0·56	20·39	11·24	6·59	0·39	1·16
77	BR-1877	2·81	46·00	0·00	0·00	2·32	48·87	28·83	15·15	1·47	3·42
78	BR-1890	0·86	41·00	0·34	4·81	4·53	48·48	28·11	14·54	1·45	4·36

Note: IL, KOL, CH and MLYR indicate the clay mineral abundances re-calculated in Total Clays.

APPENDIX (4.1A)

Sample No.	WBK-1	WBK-2	WBK-3	WBK-4	WBK-5	WBK-6	WBK-7	WBK-8	WBK-9
Depth in B/H(metres)	468	471	474	477	480	483	486	489	492
Major Elements Oxides (%)									
SiO_2	39·39	38·27	35·79	38·36	29·57	36·10	36·89	31·56	25·79
TiO_2	0·32	0·33	0·32	0·33	0·26	0·35	0·34	0·29	0·22
Al_2O_3	6·07	6·37	6·60	6·42	5·34	7·08	7·04	6·05	4·55
Fe_2O_3(T)	3·68	3·63	3·75	3·89	3·68	4·15	4·28	4·16	4·22
MgO	0·89	0·92	0·90	0·89	0·77	0·95	0·94	0·83	0·70
CaO	24.17	23·93	24·46	23·76	28·54	23·46	23·35	26·57	30·05
Na_2O	0·56	0·61	0·40	0·39	0·39	0·49	0·29	0·37	0·30
K_2O	1·34	1·40	1·43	1·41	1·21	1·47	1·48	1·30	1·04
S	0·78	0·71	0·83	0·81	0·81	0·90	0·85	0·93	1·20
P_2O_5	0·16	0·16	0·14	0·14	0·20	0·15	0·13	0·16	0·18
C_{org}	1·20	1·02	1·06	1·40	0·98	1·00	0·72	1·23	1·48
H_2O^+	2·00	3·50	3·40	2·80	3·80	3·50	3·20	3·80	3·80
CO_2	19·15	18·08	18·9	18·08	22·73	18·44	18·44	21·25	24·34
FeO	1·00	0·89	1·03	1·00	1·00	1·12	1·05	1·16	1·48
Fe_2O_3	2·56	2·64	2·60	2·77	2·56	2·90	3·11	2·93	2·70
Minor Elements (p.p.m.)									
V	73	75	72	68	66	75	73	69	56
Cr	91	87	79	89	71	132	92	78	60
Mn	480	452	472	493	595	551	530	589	647
Ni	33	31	31	31	31	32	35	31	31
Ba	134	135	143	114	111	151	148	126	110
Ce	34	44	34	45	38	36	34	34	18

/contd.over

Appendix (4.1A) contd.

Sample No.	WBK-1	WBK-2	WBK-3	WBK-4	WBK-5	WBK-6	WBK-7	WBK-8	WBK-9
Minor Elements (p.p.m.)									
La	n.d.	22	n.d.	n.d.	43	n.d.	29	34	55
Th	7	7	10	7	5	5	6	6	n.d.
Pb	42	26	23	40	27	42	24	21	31
As	9	6	9	8	9	10	9	9	12
Zn	99	86	87	109	345	335	99	132	287
Cu	15	10	12	6	11	9	10	7	9
Rb	63	63	74	62	54	64	65	58	45
Sr	374	367	366	368	364	363	361	358	362
Y	23	22	25	20	25	24	22	19	18
Zr	154	164	158	158	129	146	148	134	111
Nb	11	9	7	9	11	9	14	10	5
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clay Minerals (%)									
ILLITE	39	35	45	37	24	38	48	38	35
KAOLINITE	3	2	3	3	3	3	5	5	4
SMECTITE	57	61	48	57	72	56	43	53	58
CHLORITE	1	2	4	3	1	3	4	4	3
Other Minerals (%)									
QUARTZ	22·70	25·40	21·80	24·50	21·00	28·00	25·20	20·80	19·80
CALCITE	43·50	41·10	43·10	41·10	50·00	41·90	41·90	48·30	55·30
PYRITE	1·50	1·30	1·60	1·50	1·50	1·70	1·60	1·70	2·20
T/CLAYS	31·10	31·20	32·40	31·50	26·50	27·40	30·60	28·00	21·20

APPENDIX (4.1A)

Sample No.	WBK-10	WBK-11	WBK-12	WBK-13	WBK-14	WBK-15	WBK-16	WBK-17	WBK-18
Depth in B/H(metres)	495	498	501	504	507	510	513	516	519
Major Elements									
Oxides (%)									
SiO_2	36·49	40·05	33·63	36·41	36·28	40·08	37·54	28·60	35·46
TiO_2	0·34	0·40	0·33	0·33	0·32	0·45	0·36	0·25	0·37
Al_2O_3	6·92	8·32	6·61	6·86	6·52	9·64	7·41	5·26	7·88
Fe_2O_3(T)	4·34	4·48	4·56	4·76	4·77	4·97	4·39	6·43	5·09
MgO	0·93	1·08	0·91	0·99	0·90	1·09	1·01	0·76	0·98
CaO	23·44	20·29	24·60	23·24	23·66	19·33	22·56	26·41	22·17
Na_2O	0·36	0·51	0·26	0·54	0·35	0·40	0·56	0·49	0·59
K_2O	1·45	1·68	1·41	1·44	1·37	1·84	1·54	1·15	1·56
S	0·96	0·95	1·85	1·32	1·22	1·19	0·91	2·46	1·30
P_2O_5	0·14	0·13	0·15	0·15	0·21	0·14	0·15	0·17	0·15
Corg	1·30	1·13	1·20	2·12	2·17	2·08	1·98	0·44	1·11
H_2O^+	3·20	3·60	3·00	3·60	2·80	3·80	3·20	3·80	3·70
CO_2	18·44	15·92	20·22	16·84	17·73	15·00	17·02	21·25	18·44
FeO	1·21	1·19	1·46	1·64	1·51	1·48	1·15	3·06	1·62
Fe_2O_3	3·14	3·23	3·13	2·94	3·09	3·33	3·11	3·03	3·29
Minor Elements (p.p.m.)									
V	76	84	75	74	72	96	80	65	90
Cr	87	100	82	144	79	102	88	62	82
Mn	554	514	550	558	520	502	530	617	627
Ni	35	38	37	40	35	48	39	46	42
Ba	143	172	163	143	143	183	149	119	161
Ce	33	43	43	41	39	49	46	26	48

/contd.over

Appendix (4.1A) contd.

Sample No.	WBK-10	WBK-11	WBK-12	WBK-13	WBK-14	WBK-15	WBK-16	WBK-17	WBK-18
Minor Elements (p.p.m.)									
La	23	40	22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Th	5	8	5	6	6	9	7	5	8
Pb	106	84	37	73	59	38	52	166	25
As	n.d.	12	11	10	8	17	10	13	14
Zn	367	572	805	600	240	325	395	465	160
Cu	14	17	15	15	15	14	10	15	10
Rb	64	79	62	62	61	94	70	49	75
Sr	371	364	372	351	369	360	353	330	341
Y	20	24	22	21	22	24	22	20	24
Zr	162	164	148	150	148	157	164	113	147
Nb	10	13	12	13	10	15	12	7	11
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clay Minerals (%)									
ILLITE	30	37	39	32	38	56	41	43	56
KAOLINITE	4	7	7	5	4	14	6	8	18
SMECTITE	64	53	50	60	55	23	51	45	18
CHLORITE	2	3	4	3	3	7	2	4	8
Other Minerals (%)									
QUARTZ	28·10	25·10	25·40	25·20	27·40	22·90	25·20	22·40	19·50
CALCITE	41·90	36·20	45·90	38·30	40·30	33·00	38·70	48·30	41·90
PYRITE	1·80	1·80	2·20	2·50	2·30	2·20	1·70	4·60	2·40
T/CLAYS	26·90	35·80	25·30	31·90	27·80	39·80	32·40	24·30	35·10

APPENDIX (4.1A)

Sample No.	WBK-19	WBK-21	WBK-22	WBK-23	WBK-24	WBK-25	WBK-26	WBK-27	WBK-28
Depth in B/H(metres)	522	528	531	534	540	543	546	549	552
Major Elements									
Oxides(%)									
SiO_2	39·43	40·81	40·50	40·63	37·90	37·42	38·88	40·89	42·26
TiO_2	0·41	0·45	0·48	0·47	0·39	0·40	0·52	0·59	0·58
Al_2O_3	8·46	9·61	10·34	10·12	8·15	8·44	12·13	13·31	13·66
Fe_2O_3(T)	5·43	5·16	5·42	5·06	6·10	5·83	5·40	5·17	5·36
MgO	1·00	1·09	1·13	1·13	0·95	0·99	1·48	1·40	1·44
CaO	19·61	18·11	17·33	17·77	19·83	20·07	16·07	14·42	14·01
Na_2O	0·52	0·61	0·47	0·53	0·46	0·49	0·50	0·56	0·66
K_2O	1·67	1·86	1·95	1·93	1·63	1·69	2·29	2·42	2·48
S	1·59	1·34	1·30	1·30	2·23	1·99	1·04	0·87	0·86
P_2O_5	0·15	0·14	0·13	0·13	0·15	0·16	0·13	0·13	0·12
C_{org}	1·62	1·22	1·60	1·95	2·46	2·27	2·70	1·99	2·09
H_2O^+	3·60	3·80	4·60	4·00	3·80	3·80	5·20	5·90	5·60
CO_2	14·53	13·47	12·41	13·94	14·18	14·53	12·61	10·63	10·99
FeO	1·97	1·69	1·62	1·65	2·80	2·51	1·32	1·10	1·10
Fe_2O_3	3·24	3·28	3·62	3·22	2·99	3·04	3·93	3·94	4·13
Minor Elements (p.p.m.)									
V	90	101	104	100	86	86	119	120	129
Cr	95	101	109	105	92	89	136	163	171
Mn	538	498	501	504	498	486	559	476	496
Ni	49	49	52	51	56	50	59	61	62
Ba	175	188	214	214	161	109	219	217	238
Ce	43	48	56	59	40	31	52	63	63

/contd.over

Appendix (4.1A) contd.

Sample No.	WBK-19	WBK-21	WBK-22	WBK-23	WBK-24	WBK-25	WBK-26	WBK-27	WBK-28
Minor Elements (p.p.m.)									
La	23	n.d.	24	32	27	n.d.	26	n.d.	38
Th	7	8	9	10	7	6	10	12	10
Pb	63	71	44	34	63	77	24	18	20
As	27	25	25	14	19	14	13	12	14
Zn	1304	483	500	196	795	652	213	271	138
Cu	13	13	14	18	17	17	13	19	18
Rb	72	84	94	73	52	48	128	147	147
Sr	344	349	342	323	291	273	336	354	390
Y	25	25	20	24	22	17	24	23	24
Zr	151	163	161	145	114	110	297	308	293
Nb	14	14	12	12	7	8	13	15	17
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clay Minerals (%)									
ILLITE	50	50	50	54	46	50	54	55	57
KAOLINITE	14	12	14	13	18	14	21	16	18
SMECTITE	32	34	32	27	29	33	18	18	13
CHLORITE	4	4	4	6	7	3	7	11	12
Other Minerals (%)									
QUARTZ	22·30	23·00	24·00	22·80	23·00	24·50	20·80	19·70	22·00
CALCITE	33·00	28·30	28·20	31·70	32·20	33·00	28·60	24·00	25·00
PYRITE	3·00	2·60	2·40	2·40	4·20	3·70	1·90	1·60	1·60
T/CLAYS	40.00	44.90	43.80	41.00	38.00	36.50	46.00	52.60	49.30

APPENDIX (4.1A)

Sample No.	WBK-29	WBK-30	WBK-32	WBK-33	WBK-34	WBK-35	WBK-36	WBK-37	WBK-38
Depth in B/H(metres)	555	558	564	567	579	582	585	588	591
Major Elements									
Oxides (%)									
SiO_2	36·24	38·23	40·59	36·73	38·12	39·59	38·95	36·78	40·74
TiO_2	0·52	0·50	0·55	0·43	0·52	0·53	0·56	0·49	0·59
Al_2O_3	11·61	10·95	12·24	9·14	11·63	11·34	12·14	10·14	13·04
Fe_2O_3(T)	5·98	5·63	5·43	6·13	5·58	5·57	5·99	7·00	5·60
MgO	1·28	1·25	1·37	1·07	1·33	1·24	1·29	1·15	1·38
CaO	17·65	17·72	15·70	19·22	16·92	17·17	16·35	18·32	15·14
Na_2O	0·52	0·43	0·62	0·48	0·52	0·56	0·45	0·49	0·54
K_2O	2·22	2·10	2·28	1·80	2·20	2·17	2·28	1·92	2·41
S	1·50	1·49	1·03	1·96	1·28	1·37	1·56	2·39	1·12
P_2O_5	0·15	0·14	0·13	0·13	0·14	0·15	0·15	0·20	0·13
Corg	2·08	2·91	2·37	0·87	1·70	1·51	1·89	1·60	1·61
H_2O^+	5·40	5·00	5·20	4·80	5·00	5·00	5·60	3·60	5·00
CO_2	12·76	13·93	12·05	15·08	12·41	12·05	11·34	14·18	10·64
FeO	1·88	1·84	1·28	2·51	1·61	1·79	2·37	3·03	1·39
Fe_2O_3	3·89	3·59	4·00	3·34	3·79	3·57	3·36	3·63	4·05
Minor Elements (p.p.m.)									
V	118	113	127	90	119	114	119	111	127
Cr	121	110	129	97	130	106	121	97	130
Mn	533	518	503	511	526	497	513	569	515
Ni	65	61	60	55	61	57	61	61	61
Ba	249	202	215	189	206	210	229	213	254
Ce	50	58	70	34	46	65	58	46	55

/contd.over

Appendix (4.1A)

Sample No.	WBK-29	WBK-30	WBK-32	WBK-33	WBK-34	WBK-35	WBK-36	WBK-37	WBK-38
Minor Elements (p.p.m.)									
La	44	n.d.	52	n.d.	51	38	n.d.	47	48
Th	9	9	10	7	11	11	10	10	9
Pb	47	61	44	92	53	20	47	52	26
As	18	13	13	14	15	17	12	13	17
Zn	748	310	234	462	290	402	232	488	163
Cu	20	20	22	25	17	20	21	16	14
Rb	109	101	118	77	109	102	106	88	119
Sr	361	358	370	339	376	369	365	357	361
Y	24	26	26	24	24	30	29	24	27
Zr	120	145	153	117	144	146	141	123	149
Nb	11	10	14	8	11	12	11	8	15
Mo	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clay Minerals (%)									
ILLITE	61	63	60	56	53	58	64	62	55
KAOLINITE	19	14	19	17	16	16	21	16	17
SMECTITE	10	18	11	19	25	20	10	14	20
CHLORITE	10	5	10	8	6	6	5	8	8
Other Minerals (%)									
QUARTZ	19·60	21·60	21·00	17·40	17·90	19·00	18·00	17·90	17·70
CALCITE	29·00	31·60	27·40	34·30	28·20	27·40	25·80	32·20	24·20
PYRITE	2·80	2·80	1·90	3·70	2·40	2·60	2·90	4·50	2·10
T/CLAYS	46·50	41·00	47·20	43·70	49·80	49·50	51·30	43·80	54·40

APPENDIX (4.1A)

Sample No.	WBK-39	WBK-40	WBK-41	WBK-42	WBK-43	WBK-44	WBK-45	WBK-46	WBK-47
Depth in B/H(metres)	594	597	600	603	606	609	612	615	618
Major Elements Oxides (%)									
SiO2	39·62	30·51	42·32	35·02	37·73	35·37	30·79	33·24	34·35
TiO_2	0·58	0·40	0·57	0·51	0·57	0·54	0·48	0·51	0·56
Al_2O_3	12·75	8·17	12·23	11·45	13·04	12·30	11·13	11·55	12·37
Fe_2O_3(T)	5·85	7·91	5·61	6·62	5·92	5·71	6·03	6·24	5·43
MgO	1·34	0·92	1·30	1·07	1·19	1·13	1·02	1·00	1·06
CaO	15·43	20·88	15·24	15·75	14·59	15·74	18·22	17·48	16·35
Na_2O	0·53	0·40	0·58	0·47	0·57	0·49	0·42	0·42	0·49
K_2O	2·32	1·59	2·29	2·00	2·25	2·11	1·90	1·96	2·08
S	1·40	3·66	1·24	2·62	1·94	2·07	2·55	2·87	2·15
P_2O_5	0·14	0·21	0·13	0·19	0·18	0·17	0·17	0·20	0·19
C_{org}	1·89	1·84	2·18	4·29	4·44	3·83	5·21	5·05	4·41
H_2O^+	4·70	5·10	4·80	6·00	6·00	6·00	6·00	5·80	6·80
CO2	10·99	15·60	10·28	10·99	9·39	12·35	14·36	12·80	11·42
FeO	1·74	4·58	1·61	3·26	2·51	2·61	3·16	3·62	2·70
Fe_2O_3	3·92	2·82	3·82	3·00	3·13	2·80	2·52	2·22	2·43
Minor Elements (p.p.m.)									
V	116	89	128	103	110	107	98	102	105
Cr	124	85	121	164	132	121	118	118	114
Mn	507	554	505	499	451	385	410	389	350
Ni	61	66	59	71	66	63	66	68	66
Ba	231	167	246	209	223	220	200	303	219
Ce	57	49	58	n.d.	n.d.	38	n.d.	18	37

/contd.over

Appendix (4.1A) contd.

Sample No.	WBK-39	WBK-40	WBK-41	WBK-42	WBK-43	WBK-44	WBK-45	WBK-46	WBK-47
Minor Elements (p.p.m.)									
La	41	n.d.	62	66	n.d.	45	n.d.	44	27
Th	21	18	22	11	7	11	8	9	12
Pb	46	59	27	155	135	130	106	82	95
As	15	19	19	11	12	7	13	10	7
Zn	282	573	142	1276	1914	1379	1584	671	372
Cu	17	19	17	32	27	27	36	28	29
Rb	114	69	119	102	116	112	99	101	102
Sr	350	342	362	362	354	362	360	377	363
Y	24	20	28	31	30	29	30	31	32
Zr	145	108	154	123	131	132	107	111	124
Nb	12	7	15	12	13	13	9	9	15
Mo	n.d.	n.d.	n.d.	12	8	11	16	9	9
Clay Minerals (%)									
ILLITE	61	53	56	56	55	60	60	56	58
KAOLINITE	21	20	15	19	18	24	20	25	25
SMECTITE	14	24	20	13	18	9	9	10	11
CHLORITE	4	3	9	12	9	7	11	9	6
Other Minerals (%)									
QUARTZ	18·50	16·70	19·00	17·00	16·60	13·60	17·70	17·50	17·40
CALCITE	25·00	35·40	23·30	25·00	26·00	28·00	32·60	29·00	25·90
PYRITE	2·60	6·80	2·30	4·90	3·60	3·90	4·80	5·40	4·00
T/CLAYS	52·00	39·30	53·20	48·80	49·40	50·70	39·70	42·90	48·30

APPENDIX (4.1A)

Sample No.	WBK-49	WBK-50	WBK-51	WBK-52	WBK-53	WBK-54	WBK-55	WBK-56	WBK-57
Depth in B/H(metres)	624	627	630	633	636	639	642	645	648
Major Elements									
Oxides (%)									
SiO_2	39·87	41·34	41·27	41·02	43·47	45·41	43·85	45·93	47·79
TiO_2	0·62	0·64	0·66	0·64	0·65	0·65	0·61	0·66	0·61
Al_2O_3	13·97	14·26	15·08	14·23	14·39	14·64	13·93	14·80	14·07
Fe_2O_3(T)	5·45	5·44	5·39	5·39	5·60	5·10	5·29	5·18	5·24
MgO	1·16	1·21	1·25	1·20	1·24	1·21	1·22	1·28	1·17
CaO	13·20	12·19	11·32	12·73	11·31	10·68	12·01	10·23	10·23
Na_2O	0·59	0·65	0·69	0·66	0·68	0·72	0·61	0·72	0·80
K_2O	2·33	2·38	2·48	2·36	2·42	2·59	2·54	2·68	2·72
S	1·97	1·85	1·67	1·85	1·72	1·53	1·67	1·43	1·78
P_2O_5	0·16	0·17	0·15	0·16	0·14	0·13	0·14	0·13	0·12
C_{org}	4·78	4·30	4·49	3·91	4·49	2·61	2·48	2·67	2·27
H_2O^+	6·80	5·40	7·00	5·80	6·20	6·10	6·20	6·20	6·00
CO_2	8·15	7·45	7·45	8·51	7·09	8·01	7·45	6·73	6·80
FeO	2·51	2·30	2·08	2·30	2·15	1·92	2·11	1·78	2·20
Fe_2O_3	2·66	2·89	3·07	2·84	2·20	2·96	2·94	3·20	2·80
Minor Elements (p.p.m.)									
V	117	115	115	116	121	112	110	118	108
Cr	134	132	139	136	146	138	158	149	154
Mn	337	326	330	319	340	321	363	354	324
Ni	64	61	59	60	65	60	58	61	57
Ba	271	270	261	257	268	287	285	294	289
Ce	68	69	61	67	75	71	56	74	83

/contd.over

Appendix (4.1A) contd.

Sample No.	WBK-49	WBK-50	WBK-51	WBK-52	WBK-53	WBK-54	WBK-55	WBK-56	WBK-57
Minor Elements (p.p.m.)									
La	40	47	50	51	42	43	39	n.d.	45
Th	12	13	11	12	11	14	21	26	13
Pb	30	29	29	39	44	9	45	28	34
As	13	11	10	7	6	9	9	10	11
Zn	357	239	243	460	709	116	499	126	228
Cu	27	25	27	29	25	23	21	15	25
Rb	133	127	135	129	138	146	136	149	139
Sr	361	366	349	357	339	337	349	347	353
Y	33	35	33	35	34	24	22	24	23
Zr	167	160	155	157	158	181	170	177	172
Nb	13	15	15	17	13	17	17	16	18
Mo	7	5	4	5	4	5	7	4	4
Clay Minerals (%)									
ILLITE	64	67	64	64	64	66	63	64	61
KAOLINITE	22	22	26	20	21	19	21	19	22
SMECTITE	10	6	5	8	4	4	6	6	5
CHLORITE	4	5	5	8	11	11	10	11	12
Other Minerals (%)									
QUARTZ	17·00	19·60	18·70	18·90	19·20	19·60	19·50	18·70	19·00
CALCITE	18·50	16·90	16·90	19·30	20·00	18·20	20·00	15·30	15·40
PYRITE	3·70	3·50	3·10	3·50	3·20	2·90	3·10	2·70	3·30
T/CLAYS	56·00	55·70	56·80	54·40	53·00	56·70	54·90	60·60	60·00

APPENDIX (4.1A)

Sample No.	WBK-58	WBK-59	WBK-60	WBK-61	WBK-62	WBK-63	WBK-64	WBK-65
Depth in B/H (metres)	651	654	657	660	663	666	669	672
Major Elements Oxides (%)								
SiO_2	47·26	44·80	45·61	47·22	46·58	46·78	46·80	47·33
TiO_2	0·63	0·63	0·63	0·64	0·67	0·67	0·66	0·65
Al_2O_3	14·45	13·99	13·90	13·91	14·58	14·45	14·24	13·62
Fe_2O_3(T)	5·04	5·48	5·42	5·41	5·30	5·31	5·35	5·20
MgO	1·19	1·29	1·27	1·24	1·29	1·22	1·21	1·18
CaO	10·24	11·85	11·60	11·19	10·47	10·29	10·63	11·37
Na_2O	0·74	0·49	0·48	0·48	0·59	0·51	0·52	0·51
K_2O	2·69	2·56	2·53	2·53	2·61	2·57	2·53	2·49
S	1·58	1·32	1·41	1·40	1·26	1·33	1·44	1·26
P_2O_5	0·13	0·14	0·13	0·13	0·13	0·13	0·12	0·13
C_{org}	2·33	2·96	2·76	3·15	2·57	2·19	4·78	2·77
H_2O^+	6·10	7·20	6·00	5·60	5·00	5·60	5·20	6·00
CO_2	7·62	7·45	7·45	7·09	7·09	6·73	6·38	6·73
FeO	1·97	1·69	1·78	1·78	1·61	1·69	1·78	1·61
Fe_2O_3	2·85	3·60	3·44	3·43	3·51	3·43	3·37	3·40
Minor Elements (p.p.m.)								
V	113	114	124	124	127	128	126	120
Cr	154	140	149	149	158	168	149	137
Mn	316	365	364	356	349	333	331	363

/contd.over

Appendix (4.1A) contd.

Sample No.	WBK-58	WBK-59	WBK-60	WBK-61	WBK-62	WBK-63	WBK-64	WBK-65
Minor Elements (p.p.m.)								
Ni	58	58	59	59	62	62	58	56
Ba	305	269	259	275	274	370	378	389
Ce	100	96	49	77	71	66	74	68
La	63	51	48	48	50	55	29	41
Th	12	9	15	12	12	11	12	14
Pb	46	50	38	37	33	29	33	26
As	10	11	9	8	10	8	9	6
Zn	631	263	219	181	198	163	291	167
Cu	23	24	23	24	27	24	26	26
Rb	139	129	125	125	129	133	134	133
Sr	325	303	305	299	281	291	295	324
Y	20	17	31	38	34	31	33	30
Zr	169	170	176	182	192	205	203	206
Nb	18	15	13	13	15	20	20	20
Mo	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clay Minerals (%)								
ILLITE	61	63	63	65	63	61	65	64
KAOLINITE	23	21	21	23	21	23	24	22
SMECTITE	6	4	4	8	5	5	5	6
CHLORITE	10	12	12	12	11	11	6	8
Other Minerals (%)								
QUARTZ	17·70	22·20	18·60	21·90	22·20	24·50	22·00	23·20
CALCITE	17·30	16·90	16·90	20·00	16·00	15·30	19·00	15·30
PYRITE	3·00	2·50	2·60	2·60	2·40	2·50	2·70	2·40
T/CLAYS	58·70	55·40	59·00	52·35	56·70	55·50	51·42	56·30

APPENDIX (4.1B)

Summary Statistics: Bulk Chemistry, Mineralogy and Clay Minerals of Oxford Clay, Winterborne Kingston

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness	Kurtosis
SiO2	38·967	24·716	4·9715	0·62635	-0·2097	-0·4524E-01
TiO_2	0·49254	0·16558E-01	0·12868	0·16212E-01	-0·3262	-1·128
Al_2O_3	10·731	9·7234	3·1182	0·39286	-0·3384	-1·276 *
Fe2O3(T)	5·2787	0·63728	0·79830	0·10058	0·1550	1·318 *
MgO	1·1162	0·31582E-01	0·17771	0·22390E-01	-0·2103	-0·6011
CaO	17·541	26·874	5·1840	0·65312	0·3528	-0·7146
Na_2O	0·52222	0·14863E-01	0·12191	0·15360E-01	0·7170 *	1·980 **
K_2O	2·0037	0·21721	0·46606	0·58717E-01	-0·2645	-1·193 *
S	1·5025	0·32412	0·56932	0·71727E-01	1·272 ***	2·386 ***
P_2O_5	0·15032	0.54506E-03	0·23346E-01	0·29414E-02	1·029 **	0,2775
V	101·24	417·06	20·422	2·5729	-0·4766	-1·066
Cr	117·62	815·66	28·560	3·5982	-0·4533E-01	-0·9808
Mn	463·60	8673·7	93·133	11·734	-0·2171	-1·162 *
Ni	53·079	144·49	12·021	1·5144	-0·7715 *	-0·8312
Ba	213·90	4392·6	66·277	8·3501	0·4835	0·3412E-01
Ce	50·095	408·70	20·216	2·5470	-0·2554	0·6910
La	28·698	485·34	22·031	2·7756	-0·2107	-1·414 *
Th	10·095	19·668	4·4349	0·55874	1·304 ****	2·983 ****
Pb	51·333	1100·5	33·174	4·1795	1·738 ****	2·956 ****

/contd.over

APPENDIX (4.1B) contd.

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness		Kurtosis	
As	11.937	22.189	4.7106	0.59348	1.025	**	2.203	***
Zn	429.95	0.13828E+06	371.86	46.850	2.141	****	4.974	****
Cu	19.127	45.371	6.7358	0.84863	0.1588		-0.6751	
Rb	99.206	975.91	31.240	3.9358	-0.1036		-1.358	*
Sr	346.71	849.79	29.151	3.6727	-1.561	****	2.459	***
Y	28.079	387.95	19.696	2.4815	7.182	****	54.93	****
Zr	156.94	1578.8	39.734	5.0060	2.152	****	6.187	****
Nb	12.905	23.797	4.8782	0.61460	2.786	****	14.47	****
Mo	1.9524	13.562	3.6827	0.46398	1.948	****	3.311	****
Corg	2.4044	1.5541	1.2466	0.15706	0.7838	**	-0.3878	
CO_2	12.943	21.643	4.6522	0.58612	0.3798		-0.6997	
$H_2\overset{+}{O}$	4.8476	1.5383	1.2403	0.15626	0.1593		-1.004	
Fe^{2+}	1.3235	0.26043	0.51033	0.63295E-01	1.181	***	1.821	**
FeO	1.8997	0.53797	0.73346	0.92408E-01	1.179	***	1.814	**
Fe_2O_3	3.1595	0.22412	0.47341	0.59644E-01	0.5265E-01		-0.3956	
Ill.	53.540	117.90	10.858	1.3680	-0.8703	**	-0.2726	
Kaol.	15.492	52.189	7.2242	0.91017	-0.6026	*	-0.9303	
Chlr.	6.6508	11.263	3.3561	0.42282	0.1922		-1.270	*
Smect.	24.444	399.12	19.978	2.5170	0.8265	**	-0.7151	
Qtz.	20.921	9.8852	3.1441	0.39612	0.3380		-0.4241	

/contd.over

APPENDIX (4.1B) contd.

	Mean	Variance	S.Deviation	S.E. of Mean	Skewness		Kurtosis	
Pyt.	2·8238	1·1947	1·0930	0·13771	1·206	***	1·837	**
Cal.	29·665	103·12	10·155	1·2794	0·4110		-0·6567	
TClay	44·181	116·12	10·776	1·3576	-0·3838		-1·047	

Number of Cases = 63

Significance Levels: * = 5%; ** = 1%; *** = 0·1%; **** = 0·01%.

(T) = Total iron as obtained from Betaprobe.

Ill = Illite
Kaol = Kaolinite
Chlr = Chlorite
Smect= Smectite
Qtz = Quartz
Pyt = Pyrite
Cal = Calcite
TClay= Total Clays.

APPENDIX
(4.1C)

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*******************************************************************************************************
CORRELATION COEFFICIENTS    BULK CHEMISTRY,MINERALOGY AND CLAY MINERALS OF OXFORD CLAY WINTERBORNE KINGSTON     OXCLBCM
*******************************************************************************************************


             DEPTH       SIO2       TIO2      AL2O3      FE2O3        MGO        CAO       NA2O        K2O          S

DEPTH      1.00000    0.59116    0.90521    0.89974    0.54562    0.51715   -0.89944    0.48577    0.86933    0.41975
SIO2       0.59116    1.00000    0.76104    0.72391   -0.01452    0.67788   -0.81547    0.57688    0.79320   -0.25545
TIO2       0.90521    0.76104    1.00000    0.99419    0.41089    0.84625   -0.98473    0.61241    0.98236    0.16094
AL2O3      0.89974    0.72391    0.99419    1.00000    0.42093    0.85185   -0.97940    0.62544    0.98435    0.17694
FE2O3      0.54562   -0.01452    0.41089    0.42093    1.00000    0.35970   -0.41343    0.11504    0.37823    0.81679
MGO        0.61715    0.67788    0.84625    0.35135    0.35970    1.00000   -0.82045    0.52077    0.88510   -0.08642
CAO       -0.89944   -0.81547   -0.98473   -0.97940   -0.41343   -0.82045    1.00000   -0.64311   -0.97838   -0.17997
NA2O       0.48577    0.57688    0.61241    0.62544    0.11504    0.52077   -0.64311    1.00000    0.62341   -0.00747
K2O        0.86933    0.79320    0.98236    0.98435    0.37823    0.88510   -0.97838    0.62341    1.00000    0.09340
S          0.41975   -0.25545    0.16094    0.17694    0.81679   -0.08642   -0.17997   -0.00747    0.09340    1.00000
P2O5      -0.14329   -0.70098   -0.37609   -0.35091    0.24597   -0.52451    0.42276   -0.31546   -0.46201    0.53047
V          0.80080    0.68527    0.93976    0.93539    0.48790    0.93282   -0.93878    0.52511    0.94037    0.11168
CR         0.73695    0.71242    0.85574    0.86515    0.25401    0.77898   -0.86699    0.56531    0.87134    0.02626
MN        -0.79836   -0.65598   -0.78653   -0.77780   -0.11903   -0.42488    0.80158   -0.55557   -0.73402   -0.17061
NI         0.82161    0.34168    0.81102    0.82712    0.60354    0.71078   -0.78948    0.40479    0.78172    0.57131
BA         0.88103    0.73409    0.90727    0.89181    0.33893    0.68603   -0.90145    0.48486    0.88962    0.16490
CE         0.49902    0.75875    0.62643    0.59320    0.00045    0.58170   -0.63611    0.53340    0.66333   -0.23286
LA         0.51267    0.28132    0.48059    0.48570    0.13539    0.35099   -0.44235    0.26389    0.46806    0.03333
I         -0.26266   -0.22726   -0.25834   -0.24211   -0.17931   -0.16942    0.25554    0.02053   -0.24696   -0.12471
U         -0.17516   -0.00558   -0.08008   -0.07416   -0.28769   -0.03744    0.03358   -0.01195   -0.06793   -0.18714
TH         0.64057    0.53179    0.67450    0.66123    0.35534    0.57737   -0.67124    0.45095    0.67663    0.19161
PB        -0.02995   -0.40640   -0.20666   -0.17355    0.39635   -0.27219    0.16549   -0.20155   -0.24169    0.53341
AS        -0.13592   -0.08139   -0.06093   -0.05641    0.38527    0.12860    0.04108    0.00839   -0.02979    0.17255
ZN         0.08635   -0.29428   -0.02752    0.00578    0.39654   -0.11704    0.00177   -0.10150   -0.06500    0.54222
CU         0.80078    0.27843    0.69596    0.71010    0.54262    0.41231   -0.68596    0.34357    0.62765    0.55342
RB         0.81734    0.72522    0.94935    0.95153    0.29064    0.85507   -0.93118    0.62975    0.96051    0.03756
SR        -0.42575   -0.48070   -0.34293   -0.31193   -0.18416   -0.17693    0.41210   -0.17532   -0.35150   -0.11008
Y          0.30074    0.25567    0.31958    0.31584    0.04551    0.21601   -0.31904    0.27895    0.31227    0.03617
ZR         0.14314    0.54518    0.38934    0.39412   -0.20972    0.55744   -0.40236    0.27802    0.44741   -0.47524
NB         0.50455    0.66716    0.61655    0.60797   -0.04311    0.49781   -0.63693    0.50236    0.63807   -0.15265
MO         0.40994   -0.17601    0.28276    0.33107    0.30908    0.03373   -0.25383    0.11520    0.21126    0.52202
CORG       0.67788    0.16767    0.60571    0.62971    0.38516    0.32777   -0.57696    0.30515    0.51219    0.45769
CO2       -0.90596   -0.80390   -0.97857   -0.96901   -0.41892   -0.79720    0.99014   -0.62885   -0.96252   -0.18963
H2O        0.85651    0.38749    0.83136    0.86233    0.48944    0.52919   -0.80068    0.50127    0.81099    0.36586
FE2        0.46068   -0.25594    0.19532    0.21271    0.83621   -0.05381   -0.20582    0.03656    0.12236    0.96207
FEO        0.46081   -0.25586    0.19522    0.21260    0.83612   -0.05389   -0.20575    0.03650    0.12228    0.96188
RFE2O3     0.05781    0.36033    0.28674    0.27565    0.21292    0.64362   -0.27215    0.05482    0.36872   -0.29626
ILL        0.86288    0.57633    0.88985    0.89065    0.58998    0.73623   -0.87623    0.50096    0.86810    0.35306
KAOL       0.88000    0.42326    0.84499    0.85791    0.67533    0.65992   -0.82740    0.46555    0.80603    0.49420
CHLR       0.70774    0.53689    0.72516    0.74531    0.41625    0.63622   -0.74517    0.37543    0.76072    0.20450
SMECT     -0.89692   -0.54576   -0.90360   -0.91308   -0.63372   -0.74115    0.89269   -0.50609   -0.88378   -0.40611
VH        -0.60298   -0.24648   -0.50985   -0.48305   -0.46686   -0.32091    0.48921   -0.21944   -0.45519   -0.39849
VP        -0.56931   -0.21911   -0.45649   -0.43392   -0.45242   -0.26860    0.44342   -0.16792   -0.40215   -0.39979
EL        -0.65260   -0.30338   -0.54683   -0.53053   -0.48096   -0.35459    0.54578   -0.23132   -0.49930   -0.41488
QTZ       -0.55986    0.03933   -0.47530   -0.51453   -0.57909   -0.36167    0.42148   -0.30343   -0.45566   -0.53029
ZCORG      0.67738    0.16767    0.60571    0.62971    0.38516    0.32777   -0.57696    0.30515    0.51219    0.45769
PYT        0.45537   -0.25978    0.18453    0.20272    0.82261   -0.07384   -0.19898    0.04184    0.11010    0.96367
CAL       -0.89758   -0.79751   -0.97657   -0.95749   -0.41768   -0.80300    0.98616   -0.63892   -0.96253   -0.18433
TCLAY      0.88419    0.74651    0.96976    0.95310    0.43463    0.83147   -0.95498    0.55119    0.96918    0.17803
```

APPENDIX (4.1C) contd.

	P2O5	V	CR	MN	NI	BA	CE	LA	I	U
DEPTH	-0.14329	0.80080	0.73695	-0.79836	0.82161	0.88103	0.49902	0.51267	-0.26266	-0.17516
SIO2	-0.70098	0.68527	0.71242	-0.65598	0.34168	0.73409	0.75875	0.28132	-0.22726	-0.00558
TIO2	-0.37609	0.93976	0.85574	-0.78553	0.81102	0.90727	0.62643	0.48059	-0.25834	-0.08008
AL2O3	-0.36091	0.93539	0.86615	-0.77730	0.82912	0.89181	0.59820	0.48570	-0.24211	-0.07416
FE2O3	0.24597	0.48790	0.25401	-0.11003	0.80354	0.33893	0.00045	0.13539	-0.17931	-0.28769
MGO	-0.52451	0.93282	0.77898	-0.42488	0.71078	0.68603	0.58170	0.35099	-0.16942	-0.03744
CAO	0.42276	-0.90878	-0.86699	0.80158	-0.78948	-0.90145	-0.63611	-0.44235	0.26554	0.08358
NA2O	-0.31646	0.52511	0.56531	-0.55557	0.40479	0.48486	0.53340	0.26389	0.02053	-0.01195
K2O	-0.46201	0.94037	0.87134	-0.73402	0.78172	0.88962	0.65333	0.46806	-0.24696	-0.06793
S	0.53047	0.11168	0.02626	-0.17061	0.57131	0.16490	-0.23286	0.03333	-0.12471	-0.18714
P2O5	1.00000	-0.39799	-0.42580	0.20798	-0.01906	-0.36273	-0.55094	-0.07382	0.12693	-0.02847
V	-0.39799	1.00000	0.80008	-0.57492	0.83816	0.83208	0.58056	0.46148	-0.19931	-0.08328
CR	-0.42580	0.80008	1.00000	-0.66515	0.66671	0.78286	0.49440	0.41451	-0.17041	-0.03134
MN	0.20798	-0.57492	-0.66515	1.00000	-0.52984	-0.75724	-0.51242	-0.39172	0.24976	-0.08891
NI	-0.01906	0.83816	0.66671	-0.52984	1.00000	0.69584	0.27063	0.38039	-0.22835	-0.16233
BA	-0.36273	0.83208	0.78286	-0.75724	0.69584	1.00000	0.59560	0.49639	-0.21918	-0.03835
CE	-0.55094	0.58056	0.49440	-0.51242	0.27063	0.59560	1.00000	0.35171	-0.16286	-0.06254
LA	-0.07382	0.46148	0.41451	-0.39172	0.38039	0.49639	0.35171	1.00000	-0.14005	-0.14574
I	0.12693	-0.19931	-0.17041	0.24976	-0.22835	-0.21918	-0.16286	-0.14005	1.00000	0.10925
U	-0.02847	-0.08328	-0.03134	-0.08891	-0.16233	-0.03835	-0.06254	-0.14574	0.10925	1.00000
TH	-0.23864	0.63355	0.54251	-0.49940	0.56503	0.60523	0.47500	0.25056	-0.26324	-0.06012
PB	0.41345	-0.21684	-0.14459	0.14008	0.16269	-0.22894	-0.60324	-0.18730	-0.17720	-0.02298
AS	-0.06531	0.11149	-0.15136	0.34373	0.18553	-0.11936	-0.02941	-0.11908	-0.04484	-0.35729
ZN	0.37337	-0.04447	0.01173	0.01152	0.29716	-0.06921	-0.51142	-0.07394	-0.06500	-0.17849
CU	0.09205	0.59425	0.59261	-0.71988	0.78513	0.64685	0.13506	0.38873	-0.20738	-0.04196
RB	-0.42027	0.89988	0.87497	-0.72774	0.73494	0.87064	0.62654	0.45470	-0.20303	0.01317
SR	0.32244	-0.25691	-0.26868	0.32529	-0.20430	-0.35902	-0.34310	0.02387	0.16804	0.24143
Y	-0.10493	0.24989	0.26089	-0.29593	0.21967	0.29644	0.13586	-0.07328	-0.07927	-0.05667
ZR	-0.55793	0.42394	0.53774	-0.21452	0.09852	0.36545	0.47127	0.06487	-0.04680	0.30564
NB	-0.44017	0.51653	0.59722	-0.52745	0.30682	0.63373	0.53358	0.15341	-0.21733	-0.06254
MO	0.39600	0.16293	0.26650	-0.45367	0.48868	0.21579	-0.29825	0.19345	-0.03007	0.02174
CORG	0.21608	0.49447	0.51208	-0.68791	0.67403	0.54830	0.05970	0.31581	-0.10104	0.00400
CO2	0.37491	-0.89523	-0.85751	0.81791	-0.78897	-0.89429	-0.62063	-0.44223	0.28836	0.09152
H2O	-0.08854	0.74406	0.72718	-0.71061	0.82637	0.74008	0.39252	0.46750	-0.22301	-0.09031
FE2	0.54899	0.14940	0.05352	-0.21733	0.62017	0.18107	-0.21055	0.07208	-0.12180	-0.17610
FEO	0.54895	0.14929	0.05354	-0.21779	0.62002	0.18117	-0.21044	0.07263	-0.12233	-0.17607
RFE2O3	-0.51191	0.50344	0.27551	0.25311	0.22451	0.21017	0.30441	0.08542	-0.11768	-0.15849
ILL	-0.25774	0.86048	0.66715	-0.67186	0.84974	0.79848	0.51521	0.36614	-0.16164	-0.14535
KAOL	-0.08605	0.81356	0.65180	-0.65358	0.91206	0.78095	0.40984	0.44351	-0.14150	-0.12436
CHLR	-0.32587	0.71358	0.73833	-0.50568	0.68717	0.67219	0.34568	0.40693	-0.02557	-0.15794
SMECT	0.22032	-0.87453	-0.71523	0.67915	-0.90390	-0.82334	-0.47769	-0.42208	0.14341	0.14729
VH	-0.06384	-0.46249	-0.26925	0.47451	-0.54573	-0.53790	-0.23136	-0.16912	0.10406	-0.01634
VP	-0.08018	-0.40605	-0.24182	0.45706	-0.50326	-0.48907	-0.22471	-0.18024	0.13098	-0.01276
EL	0.00873	-0.48988	-0.34456	0.53237	-0.58418	-0.55963	-0.28007	-0.22842	0.13637	0.07279
QTZ	-0.22839	-0.48072	-0.29658	0.29919	-0.69781	-0.36041	-0.02457	-0.33548	-0.03202	0.07620
ZCORG	0.21608	0.49447	0.51208	-0.68791	0.67403	0.54830	0.05970	0.31581	-0.10104	0.00400
PYT	0.55211	0.13161	0.04891	-0.22573	0.60775	0.17679	-0.21389	0.08155	-0.11131	-0.18687
CAL	0.37315	-0.89822	-0.85124	0.81052	-0.79108	-0.88698	-0.63272	-0.45581	0.30681	0.09678
TCLAY	-0.36566	0.91570	0.82426	-0.74808	0.80922	0.85916	0.61772	0.48220	-0.25681	-0.09507

APPENDIX (4.1C) contd.

	TH	PB	AS	ZN	CU	RB	SR	Y	ZR	NB
DEPTH	0.64057	-0.02995	-0.13592	0.08535	0.80073	0.81784	-0.42575	0.30074	0.14314	0.50455
SIO2	0.53179	-0.40640	-0.08139	-0.29428	0.27843	0.72522	-0.48070	0.25567	0.54518	0.66716
TIO2	0.67450	-0.20666	-0.06093	-0.02752	0.69596	0.94935	-0.34293	0.31958	0.38934	0.61655
AL2O3	0.66123	-0.17865	-0.05641	0.00578	0.71010	0.96163	-0.31193	0.31584	0.39412	0.60797
FE2O3	0.35534	0.39635	0.38527	0.39554	0.54262	0.29064	-0.18416	0.04551	-0.20972	-0.04311
MGO	0.57737	-0.27219	0.12860	-0.11704	0.41231	0.35507	-0.17693	0.21601	0.55744	0.49781
CAO	-0.67124	0.16549	0.04108	0.00177	-0.68596	-0.93118	0.41210	-0.31904	-0.40236	-0.63693
NA2O	0.45095	-0.20155	0.00839	-0.10150	0.34357	0.62975	-0.17532	0.27895	0.27602	0.50236
K2O	0.67663	-0.24169	-0.02979	-0.06500	0.62765	0.96051	-0.35150	0.31227	0.44741	0.63807
S	0.19161	0.53341	0.17255	0.54222	0.55342	0.28756	-0.11008	0.03617	-0.47524	-0.15265
P2O5	-0.23864	0.41345	-0.06581	0.37337	0.09205	-0.42027	0.32244	-0.10493	-0.55793	-0.44017
V	0.63355	-0.21684	0.11149	-0.04447	0.59425	0.89988	-0.25691	0.24989	0.42394	0.51653
CR	0.54251	-0.14459	-0.15136	0.01173	0.59261	0.87497	-0.26866	0.26089	0.53774	0.59722
MN	-0.49940	0.14008	0.34873	0.01152	-0.71988	-0.72774	0.32629	-0.29593	-0.21452	-0.52745
NI	0.56503	0.16269	0.18553	0.29716	0.78513	0.73494	-0.20430	0.21267	0.09852	0.30682
BA	0.60523	-0.22894	-0.11936	-0.06921	0.64685	0.87064	-0.35902	0.29544	0.36645	0.63373
CE	0.47500	-0.60324	-0.02941	-0.51142	0.13506	0.52654	-0.34310	0.18586	0.47127	0.53358
LA	0.25056	-0.18730	-0.11908	-0.07394	0.38873	0.45470	0.02387	-0.07328	0.06487	0.15341
I	-0.25324	-0.17720	-0.04484	-0.06500	-0.20738	-0.20303	0.15804	-0.07927	-0.04688	-0.21733
U	-0.06012	-0.02298	-0.35729	-0.17349	-0.04196	0.01317	0.24143	-0.05667	0.30564	-0.06254
TH	1.00000	-0.22990	0.03118	-0.17105	0.33435	0.66682	-0.31879	0.52449	0.20937	0.62070
PB	-0.22990	1.00000	-0.00729	0.69547	0.30355	-0.26768	0.07153	-0.09081	-0.45269	-0.27727
AS	0.03118	-0.00729	1.00000	0.21051	-0.18071	-0.11039	-0.00037	-0.09886	-0.12127	-0.12240
ZN	-0.17105	0.69647	0.21051	1.00000	0.38524	-0.08126	0.07913	-0.07341	-0.36503	-0.17204
CU	0.33435	0.30355	-0.18071	0.38524	1.00000	0.60840	-0.12040	0.09329	-0.02914	0.20408
RB	0.66682	-0.26768	-0.11039	-0.08126	0.60840	1.00000	-0.21651	0.33495	0.54384	0.66035
SR	-0.31879	0.07153	-0.00037	0.07913	-0.12040	-0.21651	1.00000	-0.46925	-0.09994	-0.46748
Y	0.52449	-0.09081	-0.09886	-0.07341	0.09329	0.33495	-0.45925	1.00000	0.03203	0.75497
ZR	0.20937	-0.45269	-0.12127	-0.36503	-0.02914	0.54384	-0.09994	0.03203	1.00000	0.40588
NB	0.62070	-0.27727	-0.12240	-0.17204	0.20408	0.66035	-0.46748	0.75497	0.40588	1.00000
MO	0.11089	0.46987	-0.19543	0.57368	0.70898	0.27263	-0.22163	0.03830	-0.24847	-0.01462
CORG	0.28174	0.19258	-0.21303	0.37754	0.81186	0.54389	-0.07637	0.19654	-0.00685	0.21710
CO2	-0.67522	0.15671	0.03609	-0.00350	-0.69420	-0.90987	0.40645	-0.31493	-0.36504	-0.61836
H2O	0.53606	0.01870	-0.10576	0.15095	0.78773	0.82450	-0.19675	0.26770	0.19414	0.42941
FE2	0.21172	0.52279	0.16783	0.50465	0.59460	0.06733	-0.08480	0.04132	-0.47311	-0.17071
FEO	0.21193	0.52306	0.16745	0.50436	0.59464	0.06714	-0.03455	0.04140	-0.47361	-0.17058
RFE2O3	0.20137	-0.21910	0.39098	-0.22055	-0.15541	0.30638	-0.14131	-0.01247	0.45165	0.20720
ILL	0.62995	-0.13260	0.07952	0.02248	0.70276	0.82033	-0.30764	0.26527	0.18544	0.43734
KAOL	0.55631	0.02044	0.08198	0.17737	0.78094	0.75889	-0.29242	0.20761	0.14143	0.36657
CHLR	0.45524	-0.03921	-0.04734	0.11525	0.58064	0.74806	-0.33736	0.25468	0.31165	0.44816
SMECT	-0.61725	0.06848	-0.07031	-0.10021	-0.75721	-0.84061	0.31905	-0.25877	-0.20020	-0.44541
VH	-0.25498	0.01191	0.07967	-0.04441	-0.57647	-0.37080	0.19777	-0.11225	0.06377	-0.16425
VP	-0.22164	-0.00287	0.10323	-0.00160	-0.54090	-0.31778	0.21091	-0.09431	0.04896	-0.14033
EL	-0.29402	0.01941	0.08365	-0.01158	-0.58987	-0.40765	0.31977	-0.15066	0.02061	-0.20531
QTZ	-0.44606	-0.14886	-0.12221	-0.30260	-0.55328	-0.47766	-0.07071	-0.18724	0.17548	-0.10314
ZCORG	0.28174	0.19258	-0.21303	0.37754	0.81186	0.54389	-0.07637	0.19654	-0.00685	0.21710
PYT	0.20648	0.52795	0.16664	0.51123	0.59304	0.05994	-0.08791	0.04599	-0.47785	-0.16352
CAL	-0.68288	0.17428	0.00832	0.01997	-0.68689	-0.90811	0.39775	-0.32147	-0.36837	-0.62701
TCLAY	0.72009	-0.19598	0.03572	-0.02532	0.65429	0.92588	-0.33576	0.32975	0.34498	0.61232

APPENDIX (4.1C) contd.

	MO	CORG	CO2	H2O	FE2	FEO	RFE203	ILL	KAOL	CHLP
DEPTH	0.40994	0.67788	-0.90596	0.85551	0.46068	0.46081	0.05781	0.86288	0.88000	0.70774
SIO2	-0.17601	0.16767	-0.80390	0.38749	-0.25594	-0.25586	0.36033	0.57633	0.42326	0.53689
TIO2	0.28276	0.60571	-0.97857	0.83136	0.19532	0.19522	0.23674	0.88985	0.84499	0.72516
AL2O3	0.33107	0.62971	-0.96901	0.86233	0.21271	0.21260	0.27565	0.89065	0.85791	0.74631
FE2O3	0.30908	0.38516	-0.41892	0.48944	0.83621	0.83612	0.21292	0.58998	0.67533	0.41625
MGO	0.03373	0.32777	-0.79720	0.62919	-0.05381	-0.05389	0.64862	0.73523	0.65992	0.63622
CAO	-0.26383	-0.57696	0.99014	-0.80068	-0.20582	-0.20575	-0.27215	-0.87523	-0.82740	-0.74517
NA2O	0.11520	0.30515	-0.62885	0.50127	0.03656	0.03650	0.05482	0.50096	0.46555	0.37643
K2O	0.21126	0.51219	-0.96252	0.81099	0.12236	0.12228	0.36872	0.86810	0.80603	0.76072
S	0.52202	0.45769	-0.18983	0.35536	0.96207	0.96188	-0.29626	0.35306	0.49420	0.20450
P2O5	0.39600	0.21608	0.37491	-0.08354	0.54899	0.54895	-0.51191	-0.25774	-0.08605	-0.32587
V	0.16293	0.49447	-0.89523	0.74406	0.14940	0.14929	0.50344	0.86048	0.81356	0.71358
CR	0.26650	0.51208	-0.85751	0.72718	0.05352	0.05354	0.27551	0.66715	0.65180	0.73833
MN	-0.45367	-0.68791	0.81791	-0.71061	-0.21783	-0.21779	0.25811	-0.67186	-0.65358	-0.50668
NI	0.43868	0.67403	-0.78897	0.82537	0.62017	0.62002	0.22451	0.84974	0.91206	0.68717
BA	0.21679	0.54830	-0.89429	0.74008	0.18107	0.18117	0.21017	0.79848	0.78095	0.67219
CE	-0.29825	0.05970	-0.62063	0.39252	-0.21055	-0.21044	0.30441	0.51521	0.40984	0.34568
LA	0.19345	0.31581	-0.44223	0.46750	0.07208	0.07263	0.03642	0.36614	0.44351	0.40693
I	-0.03007	-0.10104	0.28836	-0.22301	-0.12180	-0.12233	-0.11768	-0.16164	-0.14150	-0.02557
U	0.02174	0.00400	0.09152	-0.09031	-0.17610	-0.17507	-0.15849	-0.14535	-0.12436	-0.15794
TH	0.11089	0.28174	-0.67522	0.53506	0.21172	0.21193	0.20137	0.62995	0.55631	0.45524
PB	0.46987	0.19258	0.15671	0.01870	0.52279	0.52306	-0.21910	-0.13260	0.02044	-0.03921
AS	-0.19543	-0.21303	0.03609	-0.10576	0.16783	0.16745	0.39098	0.07952	0.08198	-0.04734
ZN	0.57068	0.37754	-0.00850	0.15095	0.50465	0.50436	-0.22055	0.02248	0.17737	0.11625
CU	0.70898	0.81186	-0.69420	0.78773	0.59460	0.59464	-0.15541	0.70276	0.78094	0.58064
RB	0.27263	0.54389	-0.90987	0.82450	0.06733	0.06714	0.30638	0.82033	0.75889	0.74806
SR	0.22163	-0.07637	0.40645	-0.19575	-0.08480	-0.08455	-0.14131	-0.30764	-0.29242	-0.33736
Y	0.03830	0.19654	-0.31493	0.25770	0.04132	0.04140	-0.01247	0.26527	0.20761	0.25468
ZR	-0.24847	-0.00685	-0.36504	0.19414	-0.47311	-0.47361	0.45165	0.18544	0.14143	0.31165
NB	-0.01462	0.21710	-0.61836	0.42941	-0.17071	-0.17058	0.20720	0.43734	0.36657	0.44816
MO	1.00000	0.76664	-0.27584	0.56443	0.56471	0.56458	-0.47877	0.34996	0.45134	0.29878
CORG	0.76664	1.00000	-0.61061	0.71960	0.51293	0.51312	-0.30753	0.58728	0.70605	0.40031
CO2	-0.27584	-0.61061	1.00000	-0.80513	-0.23096	-0.23097	-0.23421	-0.86061	-0.82384	-0.70470
H2O	0.56443	0.71960	-0.80513	1.00000	0.43015	0.42982	0.02449	0.78863	0.85526	0.63293
FE2	0.56471	0.51293	-0.23096	0.43015	1.00000	0.99999	-0.33559	0.40253	0.55663	0.20320
FEO	0.56458	0.51312	-0.23097	0.42982	0.99999	1.00000	-0.33557	0.40252	0.55653	0.20282
RFE2O3	-0.47877	-0.30753	-0.23421	0.02449	-0.33559	-0.33557	1.00000	0.23667	0.12787	0.28759
ILL	0.34996	0.58728	-0.86061	0.78863	0.40253	0.40252	0.23667	1.00000	0.88895	0.71386
KAOL	0.45134	0.70605	-0.82384	0.85526	0.55663	0.55653	0.12787	0.88895	1.00000	0.65050
CHLR	0.29878	0.40031	-0.70470	0.63293	0.20320	0.20282	0.28759	0.71328	0.65050	1.00000
SMECT	-0.40703	-0.63788	0.87590	-0.84369	-0.45525	-0.45514	-0.21949	-0.97806	-0.94732	-0.78091
VH	-0.27106	-0.43943	0.49751	-0.44116	-0.46453	-0.46506	0.03374	-0.62747	-0.63173	-0.28828
VP	-0.24290	-0.41580	0.45433	-0.40796	-0.46783	-0.46841	0.05792	-0.57229	-0.59582	-0.24714
EL	-0.28974	-0.47976	0.55006	-0.49793	-0.47372	-0.47425	0.05649	-0.64139	-0.65821	-0.35003
QTZ	-0.52131	-0.48585	0.41021	-0.56273	-0.57809	-0.57746	0.05803	-0.60224	-0.65901	-0.44213
ZCORG	0.76664	1.00000	-0.61061	0.71960	0.51293	0.51312	-0.30753	0.58728	0.70605	0.40031
PYT	0.57527	0.51863	-0.22273	0.41805	0.99643	0.99647	-0.35213	0.39029	0.54468	0.20016
CAL	-0.25952	-0.58784	0.99384	-0.80723	-0.22710	-0.22712	-0.24850	-0.85794	-0.82272	-0.69632
TCLAY	0.25940	0.52700	-0.96258	0.82321	0.22247	0.22227	0.28832	0.87627	0.83030	0.71603

APPENDIX (4.1C) contd

	SMECT	VH	VP	EL	QTZ	ZCORG	PYT	CAL	TCLAY
DEPTH	-0.89692	-0.60298	-0.56931	-0.65260	-0.55986	0.67788	0.45537	-0.89758	0.88419
SIO2	-0.54576	-0.24648	-0.21911	-0.30338	0.03933	0.16767	-0.25978	-0.79751	0.74651
TIO2	-0.90360	-0.50985	-0.45649	-0.54583	-0.47530	0.60571	0.18453	-0.97657	0.96976
AL2O3	-0.91308	-0.48805	-0.43392	-0.53053	-0.51463	0.62971	0.20272	-0.96749	0.96810
FE2O3	-0.63372	-0.46686	-0.45242	-0.48096	-0.57909	0.38516	0.82261	-0.41768	0.43463
MGO	-0.74115	-0.32091	-0.26860	-0.35459	-0.36167	0.32777	-0.07384	-0.80300	0.83147
CAO	0.89269	0.48921	0.44342	0.54578	0.42148	-0.57696	-0.19898	0.98616	-0.96498
NA2O	-0.50609	-0.21944	-0.16792	-0.23132	-0.30343	0.30515	0.04184	-0.63892	0.65119
K2O	-0.88378	-0.45519	-0.40215	-0.49930	-0.45566	0.51219	0.11010	-0.96253	0.96915
S	-0.40611	-0.39849	-0.39979	-0.41488	-0.53029	0.45769	0.95367	-0.18433	0.17803
P2O5	0.22032	-0.06384	-0.08018	0.00373	-0.22839	0.21608	0.55211	0.37315	-0.36566
V	-0.87453	-0.46249	-0.40605	-0.48938	-0.48072	0.49447	0.13161	-0.89822	0.91570
CR	-0.71523	-0.26925	-0.24182	-0.34456	-0.29658	0.51208	0.04891	-0.85124	0.82426
MN	0.67915	0.47461	0.45706	0.53237	0.29919	-0.68791	-0.22673	0.81052	-0.74808
NI	-0.90390	-0.54573	-0.50326	-0.58418	-0.69781	0.67403	0.60775	-0.79108	0.80922
BA	-0.82334	-0.53790	-0.48907	-0.55963	-0.36041	0.54830	0.17679	-0.88698	0.85916
CE	-0.47769	-0.23136	-0.22471	-0.28007	-0.02457	0.05970	-0.21389	-0.63272	0.61772
LA	-0.42208	-0.16912	-0.18024	-0.22342	-0.33548	0.31581	0.08155	-0.45581	0.48220
I	0.14341	0.10406	0.13098	0.13537	-0.03202	-0.10104	-0.11131	0.30681	-0.25681
U	0.14729	-0.01634	-0.01276	0.07279	0.07620	0.00400	-0.13687	0.09678	-0.09507
TH	-0.61725	-0.25498	-0.22164	-0.29402	-0.44606	0.28174	0.20648	-0.68288	0.72009
PB	0.06848	0.01191	-0.00287	0.01941	-0.14886	0.19258	0.52795	0.17428	-0.19598
AS	-0.07031	0.07967	0.10323	0.08365	-0.12221	-0.21303	0.15664	0.00832	0.03572
ZN	-0.10021	-0.04441	-0.00160	-0.01168	-0.30260	0.37754	0.51123	0.01997	-0.02532
CU	-0.75721	-0.57647	-0.54090	-0.58987	-0.55328	0.31186	0.59304	-0.68689	0.65429
RB	-0.84061	-0.37080	-0.31778	-0.40765	-0.47766	0.54389	0.05994	-0.90811	0.92588
SR	0.31905	0.19777	0.21091	0.31977	-0.07071	-0.07637	-0.08791	0.39775	-0.33576
Y	-0.25877	-0.11225	-0.09431	-0.15066	-0.18724	0.19654	0.04599	-0.32147	0.32975
ZR	-0.20020	0.06377	0.04896	0.02061	0.17548	-0.00685	-0.47785	-0.36833	0.34498
NB	-0.44541	-0.16425	-0.14033	-0.20531	-0.10314	0.21710	-0.15352	-0.62701	0.61232
MO	-0.40703	-0.27106	-0.24290	-0.28974	-0.52131	0.76664	0.57527	-0.26952	0.25940
CORG	-0.63788	-0.43943	-0.41580	-0.47976	-0.48585	1.00000	0.51863	-0.58784	0.52700
CO2	0.87590	0.49751	0.45433	0.55006	0.41021	-0.61061	-0.22273	0.99384	-0.96258
H2O	-0.84869	-0.44116	-0.40796	-0.49793	-0.66273	0.71960	0.41805	-0.80723	0.82821
FE2	-0.45525	-0.46453	-0.46783	-0.47372	-0.57809	0.51293	0.99643	-0.22710	0.22247
FEO	-0.45514	-0.46506	-0.46841	-0.47425	-0.57746	0.51312	0.99647	-0.22712	0.22227
RFE2O3	-0.21949	0.03374	0.06792	0.05549	0.05803	-0.30753	-0.35213	-0.24850	0.28832
ILL	-0.97806	-0.62747	-0.57229	-0.64139	-0.60224	0.58728	0.39029	-0.85794	0.87627
KAOL	-0.94732	-0.63173	-0.59582	-0.65321	-0.65901	0.70605	0.54468	-0.82272	0.83030
CHLR	-0.78091	-0.28828	-0.24714	-0.35003	-0.44213	0.40031	0.20016	-0.69632	0.71893
SMECT	1.00000	0.61746	0.56746	0.64342	0.64191	-0.63788	-0.44403	0.87462	-0.89225
VH	0.61746	1.00000	0.97599	0.93300	0.32823	-0.43943	-0.45127	0.49802	-0.46808
VP	0.56746	0.97599	1.00000	0.95478	0.27419	-0.41580	-0.45724	0.45815	-0.41682
EL	0.64342	0.93300	0.95478	1.00000	0.29897	-0.47976	-0.47030	0.55374	-0.50541
QTZ	0.64191	0.32823	0.27419	0.29897	1.00000	-0.48585	-0.56273	0.41458	-0.56938
ZCORG	-0.63788	-0.43943	-0.41580	-0.47976	-0.48585	1.00000	0.51863	-0.58784	0.52700
PYT	-0.44403	-0.45127	-0.45724	-0.47030	-0.56273	0.51863	1.00000	-0.21973	0.21003
CAL	0.87462	0.49802	0.45815	0.55374	0.41458	-0.58784	-0.21973	1.00000	-0.97255
TCLAY	-0.89225	-0.46808	-0.41682	-0.50541	-0.56938	0.52700	0.21003	-0.97255	1.00000

APPENDIX (4.2A)

Sample No.	BR-115	BR-123	BR-129	BR-131	BR-134	BR-145	BR-154	BR-167	BR-180	BR-199	BR-211
Depth in metres	959·20	959·5	959·7	959·8	959·9	960·5	961·3	962·1	962·9	964·1	
In per cent											
SiO_2	32·99	38·20	17·11	26·74	30·10	25·63	40·56	41·34	30·11	49·94	29·87
TiO_2	0·51	0·49	0·25	0·36	0·17	0·35	0·56	0·56	0·43	0·72	0·49
Al_2O_3	7·71	8·02	4·95	6·76	2·95	6·44	9·66	9·88	7·98	12·37	8·50
Fe_2O_3(T)	4·37	4·77	2·01	2·92	2·89	2·36	3·98	4·05	2·94	4·05	4·27
MgO	5·43	7·04	2·08	3·37	2·26	3·07	3·79	3·33	2·47	3·31	2·30
CaO	21·58	16·90	39·40	30·04	31·62	30·91	18·31	18·32	27·89	12·37	26·04
Na_2O	0·26	0·40	0·05	0·19	0·14	0·22	0·42	0·47	0·27	0·43	0·15
K_2O	2·04	2·08	1·09	1·64	0·99	1·47	2·32	2·43	1·97	3·03	1·89
S	0·94	0·91	0·24	0·43	0·48	0·28	0·92	1·14	0·70	0·83	1·97
P_2O_5	0·02	0·02	0·17	0·03	0·04	0·20	0·06	0·04	0·03	0·04	0·06
H_2O^+	1·72	2·26	0·70	1·68	1·91	2·24	3·00	2·37	1·64	1·71	2·53
CO_2	21·51	19·68	31·82	25·84	26·00	26·23	17·28	16·69	23·00	11·89	21·36
C_{org}	0·27	0·56	0·01	0·48	0·45	0·73	0·72	0·69	0·49	0·30	0·40
FeO	1·18	1·13	0·30	0·53	0·60	0·34	1·15	1·42	0·88	1·04	2·46
Fe_2O_3	3·06	3·51	1·68	2·33	2·22	1·97	2·70	2·47	2·00	2·90	1·54
In p.p.m.											
V	200	190	60	78	75	69	90	81	77	120	95
Cr	194	145	56	73	71	70	208	94	88	100	100
Mn	244	193	249	193	192	168	163	155	188	163	197
Ba	88	122	75	128	94	152	137	176	144	254	115

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APPENDIX (4.2A) contd.

Sample No.	BR-115	BR-123	BR-129	BR-131	BR-134	BR-145	BR-154	BR-167	BR-180	BR-199	BR-211
La	42	81	50	3	13	32	19	26	33	54	55
Ce	65	77	57	43	48	47	61	48	55	67	84
Th	12	11	n.d.	4	6	4	9	9	7	10	6
Pb	11	11	4	6	6	6	14	13	14	15	18
As	57	63	13	21	27	23	21	20	16	14	27
Ga	10	11	6	9	8	7	11	9	9	16	11
Zn	20	21	8	9	14	12	72	66	36	49	36
Cu	9	11	14	8	9	7	9	12	7	9	16
Ni	59	34	13	21	28	23	36	35	28	88	62
Rb	85	113	51	72	66	67	108	102	94	144	88
Sr	226	191	261	229	239	293	254	261	307	230	244
Y	17	18	14	12	9	26	28	23	28	37	18
Zr	118	132	46	69	63	75	146	133	97	207	132
Nb	37	29	10	14	13	19	18	16	14	22	15
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6
In per cent											
Illite	58	65	65	60	65	65	66	63	61	70	66
Kaolinite	0	0	0	0	0	0	0	0	0	2	10
Chlorite	0	1	2	1	1	2	1	1	2	4	5
M/Layer	42	33	39	34	34	33	33	36	37	24	19

APPENDIX (4.2A) contd.

Sample No.	BR-236	BR-246	BR-278	BR-303	BR 320	BR-356	BR-405	BR-444	BR-468	BR-502	BR-543
Depth in Metres	966·14	966·82	967·9	969·0	970·3	972·3	975·0	977·7	980·9	983·7	986·5
In per cent											
SiO_2	35·99	34·48	35·18	47·79	47·74	45·06	37·02	39·87	42·36	43·71	46·07
TiO_2	0·57	0·56	0·49	0·74	0·72	0·74	0·60	0·66	0·72	0·73	0·78
Al_2O_3	10·17	8·80	7·40	12·34	13·08	13·61	10·61	13·37	14·48	11·91	13·63
Fe_2O_3(T)	2·86	2·65	3·32	3·25	3·57	3·78	2·98	3·98	4·40	3·62	3·72
MgO	2·49	2·16	1·91	2·62	2·58	2·76	2·30	3·15	3·02	2·53	2·82
CaO	23·03	23·67	24·83	14·39	13·74	14·23	22·17	16·48	13·95	16·67	13·37
Na_2O	0·25	0·26	0·18	0·36	0·44	0·36	0·30	0·32	0·40	0·31	0·42
K_2O	2·16	1·84	1·78	2·59	2·81	2·85	2·25	3·19	3·31	2·44	2·96
S	0·51	0·39	0·43	0·46	0·74	0·56	0·35	0·42	0·39	0·57	0·48
P_2O_5	0·05	0·04	0·06	0·05	0·06	0·08	0·05	0·09	0·09	0·07	0·09
H_2O^+	1·48	1·68	3·65	2·65	2·62	2·65	1·38	3·04	2·69	3·18	4·05
CO_2	19·89	19·42	19·56	12·72	12·26	12·22	18·88	15·37	13·40	14·68	11·71
C_{org}	0·63	0·43	1·20	0·62	0·61	0·62	0·23	0·59	0·40	0·63	0·49
FeO	0·63	0·45	0·53	0·57	0·92	0·71	0·43	0·52	0·49	0·71	0·60
Fe_2O_3	2·15	2·11	2·72	2·61	2·54	3·00	2·50	3·40	3·86	2·82	3·05
In p.p.m.											
V	90	72	73	106	124	119	90	134	123	96	129
Cr	94	81	79	101	101	104	91	130	113	103	98
Mn	204	205	208	152	181	218	215	391	212	175	208
Ba	244	194	187	280	271	245	226	231	241	238	268

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APPENDIX (4.2A) contd.

Sample No.	BR-236	BR-246	BR-278	BR-303	BR-320	BR-356	BR-405	BR-444	BR-468	BR-502	BR-543
La	53	31	29	28	21	21	48	35	37	51	46
Ce	51	59	64	60	75	72	74	76	77	70	120
Th	9	8	7	9	11	12	8	12	12	11	11
Pb	11	11	9	14	16	15	13	18	14	15	21
As	14	7	7	8	14	14	8	19	14	15	12
Ga	6	11	11	16	15	17	13	17	16	14	16
Zn	27	39	38	50	622	44	55	61	72	60	70
Cu	10	10	12	12	10	14	12	22	17	18	12
Ni	35	25	25	31	46	43	33	46	50	44	44
Rb	105	95	85	137	152	147	111	148	167	132	160
Sr	261	244	246	215	249	249	255	341	255	239	248
Y	32	27	31	37	30	30	29	31	30	34	35
Zr	169	215	218	228	192	187	183	129	139	190	191
Nb	15	15	13	14	21	14	16	18	18	16	24
Mo	n.d.	n.d.	n.d.	n.d.	3.72	n.d.	n.d.	4.41	n.d.	n.d.	n.d.
In per cent											
Illite	68	65	64	69	73	66	69	77	75	73	65
Kaolinite	12	12	10	11	10	13	11	8	11	9	10
Chlorite	2	6	9	6	6	10	3	4	3	5	8
M/Layer	18	17	17	14	11	10	17	11	11	11	17

APPENDIX (4.2A) contd.

Sample No.	BR-560	BR-606	BR-627	BR-656	BR-688	BR-706	BR-736	BR-765	BR-801	BR-812	BR-820
Depth in Metres	989·7	993·0	995·8	999·4	1002·5	1006·1	1009·0	1012·0	1014·9	1015·3	1015·6
In per cent											
SiO_2	43·06	47·73	46·14	39·40	43·31	45·02	45·73	42·66	46·80	29·29	27·37
TiO_2	0·77	0·82	0·84	0·68	0·73	0·78	0·76	0·73	0·77	0·46	0·42
Al_2O_3	14·47	13·46	14·60	12·97	13·72	13·07	12·38	11·63	13·11	7·75	6·96
Fe_2O_3(T)	3·95	4·64	3·92	4·48	4·27	4·10	3·55	3·99	3·48	2·87	1·94
MgO	2·73	2·71	2·82	3·00	3·02	2·70	2·50	2·52	2·62	2·05	1·85
CaO	14·11	12·56	12·58	17·19	14·47	14·73	15·12	16·65	13·81	29·55	32·35
Na_2O	0·32	0·39	0·43	0·32	0·34	0·31	0·34	0·30	0·27	0·17	0·15
K_2O	2·96	2·79	3·06	2·76	3·08	2·68	2·47	2·33	2·70	1·46	1·26
S	0·26	0·96	0·13	0·13	0·38	0·42	0·37	0·24	0·25	0·50	0·25
P_2O_5	0·10	0·11	0·08	0·09	0·12	0·10	0·08	0·11	0·05	0·15	0·04
H_2O^+	4·56	3·40	3·77	2·77	4·17	2·43	2·79	3·67	3·43	1·22	0·84
CO_2	12·10	10·76	10·93	15·27	13·13	13·05	13·16	14·55	11·74	24·37	26·25
C_{org}	0·83	0·84	0·84	0·96	0·70	0·67	0·54	0·62	0·83	0·41	0·31
FeO	0·33	1·20	0·16	0·16	0·47	0·52	0·46	0·30	0·31	0·62	0·31
Fe_2O_3	3·58	3·30	3·74	4·30	3·74	3·52	3·03	3·65	3·13	2·18	1·59
In p.p.m.											
V	131	126	133	119	128	121	105	99	114	62	59
Cr	103	113	105	95	110	106	102	94	103	134	63
Mn	269	192	192	258	197	174	150	169	164	267	185
Ba	248	292	313	261	255	286	265	256	261	136	147

/contd.over

APPENDIX (4.2A) contd.

Sample No.	BR-560	BR-606	BR-627	BR-656	BR-688	BR-706	BR-736	BR-765	BR-801	BR-812	BR-820
La	44	54	51	40	59	56	55	40	28	22	23
Ce	78	69	68	65	73	58	67	65	74	56	49
Th	12	12	13	11	12	12	12	12	13	6	5
Pb	23	18	22	19	21	17	16	15	20	15	13
As	19	16	9	12	10	13	9	8	13	20	5
Ga	18	16	14	15	19	19	15	12	15	9	12
Zn	78	112	93	62	59	68	59	56	60	27	41
Cu	15	16	18	19	18	19	15	16	17	10	10
Ni	53	47	51	38	32	30	27	27	38	31	19
Rb	166	157	174	138	167	142	126	120	139	76	72
Sr	248	225	256	297	275	246	240	244	238	309	341
Y	37	30	34	29	31	37	34	35	34	18	25
Zr	170	182	199	142	153	193	227	224	248	134	158
Nb	20	20	21	15	17	16	18	13	19	13	11
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
In per cent											
Illite	64	67	66	68	69	68	66	67	65	60	67
Kaolinite	8	10	12	10	8	11	14	14	11	19	13
Chlorite	8	10	10	6	6	6	6	5	9	3	4
M/Layer	20	13	12	16	17	15	14	14	15	18	16

APPENDIX (4.2A) contd.

Sample No.	BR-826	BR-855	BR-891	BR-920	BR-958	BR-981	BR-988	BR-1008	BR-1052	BR-1093	BR-1123
Depth in metres	1016·25	1017·50	1019·0	1020·32	1022·60	1025·65	1026·60	1027·83	1029·60	1031·10	1032·51
In per cent											
SiO_2	37·12	42·54	43·89	47·36	40·01	50·18	30·76	32·96	42·66	43·17	47·78
TiO_2	0·60	0·67	0·79	0·79	0·75	0·83	0·53	0·55	0·75	0·74	0·82
Al_2O_3	11·71	9·44	12·83	12·76	14·00	13·36	10·80	10·59	14·19	13·65	15·78
Fe_2O_3(T)	4·41	3·74	3·73	3·44	6·93	3·97	4·97	3·27	3·29	3·66	4·03
MgO	2·33	2·37	2·69	2·41	2·63	2·53	2·90	2·60	2·38	2·37	2·48
CaO	19·30	19·78	15·84	14·52	13·73	11·21	21·15	23·09	14·87	15·06	10·68
Na_2O	0·22	0·27	0·32	0·43	0·36	0·43	0·21	0·23	0·31	0·34	0·36
K_2O	2·48	1·82	2·44	2·44	2·64	2·56	2·23	2·02	2·65	2·55	2·98
S	0·68	0·54	0·39	0·40	2·77	1·10	0·93	0·72	0·72	0·85	0·93
P_2O_5	0·08	0·06	0·11	0·05	0·09	0·11	0·15	0·09	0·05	0·07	0·05
H_2O^+	2·25	2·31	2·63	2·20	3·39	3·35	3·85	3·22	3·62	3·60	3·91
CO_2	16·20	15·97	14·00	12·53	11·82	9·60	20·00	19·34	13·23	12·70	9·20
C_{org}	1·00	0·72	0·77	0·77	0·79	0·75	1·52	1·44	1·35	1·16	1·12
FeO	0·85	0·67	0·49	0·55	3·10	1·38	1·16	0·89	0·90	1·06	1·16
Fe_2O_3	3·47	2·99	3·19	2·88	3·83	2·43	3·68	2·27	2·29	2·48	2·70
In p.p.m.											
V	102	83	114	111	124	106	87	75	104	98	119
Cr	107	88	129	86	101	9	53	52	73	117	121
Mn	166	156	165	133	160	115	181	147	106	270	114
Ba	215	206	263	267	262	287	183	240	254	239	309

/contd.over

APPENDIX (4.2A) contd.

Sample No.	BR-826	BR-855	BR-891	BR-920	BR-958	BR-981	BR-988	BR-1008	BR-1052	BR-1093	BR-1123
La	77	33	45	47	50	56	36	35	43	37	41
Ce	60	56	65	69	84	71	76	81	71	98	77
Th	10	8	10	9	12	11	8	9	12	12	13
Pb	16	12	17	15	28	22	19	17	22	14	22
As	16	7	10	7	21	7	9	5	7	6	8
Ga	21	13	16	16	18	17	13	15	18	17	20
Zn	52	44	41	67	103	45	28	29	46	42	53
Cu	19	14	13	16	24	15	15	15	15	17	20
Ni	32	23	30	30	51	24	25	22	45	42	58
Rb	129	96	127	134	134	138	106	111	141	138	173
Sr	270	243	251	221	214	215	342	314	266	309	293
Y	32	35	37	36	25	36	30	33	34	38	31
Zr	162	233	191	217	128	241	116	119	165	172	173
Nb	15	14	19	17	11	18	13	16	19	20	17
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
In per cent											
Illite	64	62	70	70	63	69	68	68	71	64	65
Kaolinite	14	12	12	12	13	11	13	10	13	13	13
Chlorite	6	10	6	7	8	10	7	7	4	7	9
M/Layer	16	16	12	11	16	10	12	15	12	16	13

APPENDIX (4.2A) contd.

Sample No.	BR-1157	BR-1194	BR-1220	BR-1257	BR-1301	BR-1339	BR-1377	BR-1386	BR-1392	BR-1424	BR-1436
Depth in metres	1034·00	1035·61	1037·00	1038·60	1040·00	1042·00	1044·00	1044·22	1044·40	1045·31	1045·64
In per cent											
SiO_2	46·36	43·57	44·99	43·27	42·34	43·68	44·37	43·08	38·96	39·12	44·03
TiO_2	0·79	0·76	0·76	0·75	0·74	0·75	0·75	0·66	0·68	0·70	0·73
Al_2O_3	15·15	14·61	14·12	14·22	14·68	14·66	13·42	10·82	11·87	13·34	13·21
Fe_2O_3(T)	3·80	3·42	3·26	4·18	5·06	4·07	3·07	2·72	3·09	3·07	3·02
MgO	2·50	2·40	2·45	2·67	2·40	2·64	2·26	2·05	2·33	2·77	2·30
CaO	11·98	13·22	13·42	13·11	12·87	13·11	14·34	17·80	18·62	15·84	14·78
Na_2O	0·40	0·38	0·41	0·35	0·42	0·44	0·37	0·37	0·30	0·53	0·41
K_2O	2·93	2·78	2·71	2·88	2·89	2·93	2·42	1·94	2·16	2·42	2·38
S	0·82	1·16	0·77	1·35	1·42	1·29	0·97	0·97	0·95	0·94	0·89
P_2O_5	0·07	0·12	0·08	0·08	0·15	0·10	0·10	0·15	0·15	0·19	0·13
H_2O^+	3·71	5·00	3·82	4·61	4·67	4·22	3·76	3·71	4·01	4·51	3·75
CO_2	10·11	11·34	11·68	11·94	11·22	11·74	12·55	13·90	15·89	13·27	13·04
C_{org}	1·18	2·15	1·59	1·15	1·14	1·34	1·19	1·83	1·00	3·22	1·41
FeO	1·02	1·45	0·96	1·68	1·78	1·61	1·21	1·21	1·19	1·18	1·11
Fe_2O_3	2·66	2·81	2·19	2·31	3·08	2·28	1·72	1·38	1·77	1·76	1·79
In p.p.m.											
V	109	103	102	108	112	113	95	75	84	89	93
Cr	119	117	113	118	126	89	108	98	84	102	110
Mn	131	112	113	147	148	151	116	107	128	148	110
Ba	289	331	333	268	281	263	250	214	244	259	267

/contd.over

APPENDIX (4.2A) contd.

Sample No.	BR-1157	BR-1194	BR-1220	BR-1257	BR-1301	BR-1339	BR-1377	BR-1386	BR-1392	BR-1424	BR-1436
La	47	43	55	37	42	39	57	51	65	81	37
Ce	74	62	67	72	99	96	80	78	61	65	76
Th	11	11	11	12	12	11	12	10	12	12	12
Pb	16	17	14	17	18	21	15	14	15	19	16
As	7	5	6	12	12	9	6	5	7	4	6
Ga	20	16	17	17	19	14	18	10	16	16	16
Zn	46	430	49	47	47	77	47	34	48	33	93
Cu	21	17	12	18	19	19	20	16	13	21	16
Ni	39	37	37	55	41	39	29	24	21	36	50
Rb	163	156	155	161	158	161	141	113	128	140	126
Sr	307	325	304	286	271	326	282	284	261	271	305
Y	27	36	46	39	44	38	36	35	32	33	44
Nb	23	17	16	18	25	24	17	18	16	13	13
Zr	167	160	184	179	180	143	181	218	172	147	201
Mo	n.d.	4	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
In per cent											
Illite	63	66	66	69	62	69	64	61	65	61	68
Kaolinite	11	11	11	12	12	11	16	12	16	12	15
Chlorite	9	7	6	5	7	6	4	11	5	10	4
M/Layer	17	16	17	14	18	14	16	16	14	17	13

APPENDIX (4.2A) contd.

Sample No.	BR-1467	BR-1513	BR-1544	BR-1583	BR-1636	BR-1676	BR-1683	BR-1691	BR-1698	BR-1713	BR-1721
Depth in metres	1047·00	1048·60	1050·21	1051·61	1053·20	1054·45	1054·71	1055·04	1055·30	1055·67	1055·88
In per cent											
SiO_2	48·83	45·00	43·50	43·13	45·83	49·44	45·37	44·49	41.17	46·69	34·72
TiO_2	0·83	0·77	0·75	0·75	0·80	0·88	0·81	0·78	0·69	0·82	0·58
Al_2O_3	14·68	14·10	14·92	15·31	15·49	18·53	15·60	15·81	15·07	16·87	12·83
Fe_2O_3(T)	2·97	2·97	3·04	4·34	3·26	3·66	3·48	3·44	3·38	3·80	3·59
MgO	2·33	2·24	2·34	1·43	2·40	2·60	2·64	2·76	2·63	2·96	2·95
CaO	10·28	12·47	11·29	12·30	10·12	5·87	9·44	10·20	10·50	8·51	10·78
Na_2O	0·44	0·42	0·42	0·30	0·37	0·43	0·38	0·37	0·20	0·41	0·28
K_2O	2·61	2·48	2·59	2·83	2·77	3·03	2·94	3·05	2·80	3·09	2·35
S	0·86	0·89	1·01	1·11	0·95	0·89	0·92	0·84	1·32	0·87	2·24
P_2O_5	0·11	0·24	0·07	0·13	0·16	0·17	0·13	0·08	0·14	0·09	0·34
H_2O^+	5·13	4·17	5·98	3·33	5·30	5·19	6·34	5·40	5·85	5·12	7·93
CO_2	8·46	11·10	9·62	9·91	9·36	6·10	8·86	10·11	10·14	8·57	10·97
C_{org}	3·41	3·34	4·40	3·76	3·44	3·21	4·80	3·99	6·51	2·06	11·35
FeO	1·08	1·11	1·26	1·39	1·19	1·11	1·15	1·07	1·65	1·09	2·80
Fe_2O_3	1·77	1·74	1·63	2·79	1·94	2·43	2·20	2·25	1·54	2·59	0·48
In p.p.m.											
V	101	93	105	105	106	118	112	108	100	110	86
Cr	132	176	132	132	172	158	133	125	128	176	96
Mn	97	99	86	105	90	90	111	117	114	131	152
Ba	317	257	257	297	297	319	301	313	273	306	212

/contd.over

APPENDIX (4.2A) contd.

Sample No.	BR-1467	BR-1513	BR-1544	BR-1583	BR-1636	BR-1676	BR-1683	BR-1691	BR-1698	BR-1713	BR-1721
La	42	40	38	46	42	51	72	50	52	76	82
Ce	57	78	78	69	69	77	66	71	77	86	90
Th	11	10	11	12	12	17	13	14	12	12	9
Pb	16	19	18	17	15	22	18	16	19	17	23
As	3	5	5	6	5	6	7	6	6	8	5
Ga	18	17	18	18	22	27	18	19	19	19	14
Zn	47	46	45	43	71	48	47	45	41	68	80
Cu	16	20	20	18	21	24	28	26	35	22	48
Ni	44	51	45	48	46	49	58	60	63	44	58
Rb	151	129	152	167	165	185	163	181	181	173	134
Sr	337	329	391	321	307	250	284	273	255	237	262
Y	37	49	37	48	48	46	37	42	44	36	61
Zr	202	185	178	167	184	181	178	165	154	163	121
Nb	17	16	15	15	12	19	15	15	16	19	14
Mo	n.d.	n.d.	7	n.d.	n.d.	n.d.	6	5	13	8	26
In per cent											
Illite	64	65	67	66	70	65	66	72	68	65	65
Kaolinite	14	16	14	14	13	18	14	12	13	14	17
Chlorite	11	4	9	5	5	7	6	3	3	5	1
M/Layer	11	15	10	15	12	10	14	13	15	16	17

APPENDIX (4.2A) contd.

Sample No.	BR-1734	BR-1750	BR-1755	BR-1757	BR-1762	BR-1771	BR-1781	BR-1811	BR-1831	BR-1852	BR-1877	BR-1890
Depth in metres	1056·20	1056·54	1056·61	1056·66	1056·82	1057·05	1057·15	1058·14	1059·20	1060·40	1061·18	1061·72
In per cent												
SiO_2	49·67	56·73	59·55	53·89	39·35	52·66	78·53	58·08	49·42	84·83	78·56	63·32
TiO_2	0·87	0·78	0·67	0·68	0·54	0·88	0·65	0·39	0·71	0·65	0·81	0·90
Al_2O_3	20·14	17·74	12·90	14·35	10·47	20·81	10·02	5·28	12·63	8·31	10·90	13·59
Fe_2O_3(T)	4·66	3·80	4·63	3·42	9·29	4·59	1·68	2·21	3·82	1·02	2·26	5·11
MgO	1·91	1·45	0·92	1·00	0·49	1·66	0·00	3·27	2·39	0·00	0·00	0·61
CaO	2·71	3·39	6·47	8·74	11·00	0·87	1·69	15·59	12·17	0·24	0·65	3·06
Na_2O	0·40	0·44	0·38	0·39	0·32	0·47	0·48	0·21	0·32	0·50	0·60	0·50
K_2O	3·68	3·25	2·55	2·74	2·06	3·63	2·00	1·13	2·36	1·71	2·09	2·70
S	1·08	0·94	1·27	0·77	6·79	1·55	0·67	0·21	0·97	0·30	1·24	2·42
P_2O_5	0·16	0·20	0·35	0·35	0·39	0·13	0·25	0·02	0·10	0·02	0·05	0·08
H_2O^+	6·85	5·70	3·90	4·74	6·52	8·17	2·29	0·65	2·19	1·80	1·19	4·36
CO_2	2·44	2·87	4·45	6·68	8·10	1·18	2·36	14·00	11·15	0·00	0·00	2·28
Corg	5·71	3·43	2·25	2·08	5·38	4·65	0·85	0·00	1·91	2·05	2·81	0·86
FeO	1·35	1·18	1·58	0·96	8·49	1·94	0·84	0·26	1·21	0·37	1·55	3·03
Fe_2O_3	3·16	2·49	2·86	2·35	0·00	2·43	0·75	1·92	2·47	0·60	0·54	1·75
In p.p.m.												
V	127	106	89	89	78	120	69	34	101	58	78	135
Cr	219	73	119	118	199	141	122	42	88	88	104	135
Mn	106	89	83	88	62	104	66	139	121	65	68	45
Ba	326	321	351	352	319	364	332	310	844	428	421	350

/contd.over

APPENDIX (4.2A) contd.

Sample No.	BR-1734	BR-1750	BR-1755	BR-1757	BR-1762	BR-1771	BR-1781	BR-1811	BR-1831	BR-1852	BR-1877	BR-1890
La	54	51	56	69	47	53	62	12	40	23	54	52
Ce	85	97	95	105	93	94	104	55	59	39	60	68
Th	17	18	15	13	8	18	13	4	10	9	10	14
Pb	23	15	15	13	26	24	14	8	20	16	13	19
As	6	6	9	6	33	7	2	3	10	3	9	28
Ga	25	22	18	18	11	23	10	4	16	8	12	18
Zn	54	44	62	43	83	58	33	1	74	12	11	20
Cu	38	24	19	17	39	35	10	3	23	3	12	20
Ni	55	41	38	37	62	66	28	12	47	16	33	28
Rb	228	179	131	149	81	240	104	40	138	73	95	118
Sr	213	193	195	225	219	183	137	101	293	89	108	164
Y	57	48	63	67	41	45	48	27	39	25	29	35
Nb	23	16	14	36	24	37	23	18	21	27	25	23
Zr	189	252	257	266	189	216	672	271	218	504	496	386
Mo	6	n.d.	8	6	38	n.d.	n.d.	n.d.	4	n.d.	n.d.	n.d.
In per cent												
Illite	62	62	64	67	68	65	63	59	59	58	59	58
Kaolinite	16	16	16	18	15	15	21	33	26	34	31	30
Chlorite	8	5	7	6	4	5	3	2	4	2	3	3
M/Layer	14	17	13	9	13	15	13	6	11	6	7	9

APPENDIX (4.2B)

Summary Statistics: Bulk Chemistry, Mineralogy and Clay Minerals of Oxford Clay, Warlingham

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness		Kurtosis	
SiO_2	43.889	115.72	10.757	1.2180	1.251	****	4.234	****
TiO_2	0.67769	0.22405E-01	0.14968	0.16948E-01	-1.212	****	1.298	*
Al_2O_3	12.365	11.092	3.3305	0.37710	-0.3590		0.5373	
Fe_2O_3(T)	3.6738	1.1695	1.0814	0.12245	1.850	****	9.441	****
MgO	2.4455	0.94255	0.97085	0.10993	0.9198	**	7.585	****
CaO	15.124	57.562	7.5870	0.85906	0.6443	*	1.059	*
Na_2O	0.34397	0.10157E-01	0.10078	0.11411E-01	-0.3995		0.2373	
K_2O	2.4278	0.38291	0.61879	0.70065E-01	-1.055	***	2.228	***
S	0.89359	0.70149	0.83755	0.94834E-01	4.873	****	32.10	****
P_2O_5	0.10859	0.59369E-02	0.77052E-01	0.87244E-02	1.841	****	3.829	****
V	101.56	668.46	25.855	2.9274	0.8147	**	3.251	****
Cr	109.62	1309.5	36.186	4.0973	0.6526	*	1.689	**
Mn	157.15	3858.5	62.117	7.0333	0.9888	***	1.952	***
Ba	264.59	10619.	103.05	11.668	2.352	****	12.66	****
La	45.000	258.58	16.112	1.8243	0.7492E-01		0.3076	
Ce	72.128	251.02	15.844	1.7939	0.5887	*	0.4833	
Th	10.474	11.032	3.3214	0.37608	-0.7152	**	1.852	***
Pb	18.077	285.55	16.898	1.9134	7.867	****	66.76	****
As	13.013	182.19	13.498	1.5283	3.635	****	16.15	****
Ga	16.859	253.06	15.908	1.8012	7.783	****	65.80	****

/contd.over

APPENDIX (4.2B) contd.

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness	Kurtosis
Zn	68.000	10059.	100.29	11.356	4.721 ****	22.65 ****
Cu	18.769	286.44	16.925	1.9163	6.287 ****	47.88 ****
Ni	42.359	875.22	29.584	3.3497	6.060 ****	46.28 ****
Rb	131.95	1412.6	37.584	4.2556	-0.3897E-01	0.3814
Sr	256.18	2959.7	54.403	6.1599	-0.6833 *	1.536 **
Y	34.692	111.41	10.555	1.1951	0.4553	1.387 **
Zr	191.44	8270.1	90.940	10.297	2.941 ****	12.17 ****
Nb	18.115	28.909	5.3767	0.60879	1.696 ****	3.709 ****
Mo	1.8077	31.534	5.6155	0.63583	4.784 ****	26.24 ****
C_{org}	1.6659	3.3047	1.8179	0.20583	2.686 ****	9.999 ****
CO_2	13.163	39.520	6.2865	0.71180	0.3918	0.6921
H_2O	3.5099	2.6142	1.6169	0.18307	0.6017 *	0.2893
Fe^{2+}	0.77679	0.53192	0.72933	0.82580E-01	4.871 ****	32.07 ****
FeO	1.1344	1.1338	1.0648	0.12057	4.638 ****	29.61 ****
Fe_2O_3	2.3994	0.73001	0.85441	0.96743E-01	-0.4547	0.4146
LOI	18.314	28.112	5.3021	0.60034	-0.2836E-01	1.273 *
Ill.	65.628	14.704	3.8346	0.43418	0.2444	0.4896
Kaol.	12.333	47.628	6.9013	0.78142	0.6872 *	2.381 ****
Chlr.	5.3590	7.5578	2.7491	0.31128	0.1910	-0.6721
Mix.Lyr	16.615	58.759	7.6655	0.86794	1.781 ****	2.738 ****
Qtz.	22.064	116.11	10.776	1.2201	3.173 ****	11.96 ****

/contd.over

APPENDIX (4.2B) contd.

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness		Kurtosis	
Dol.	6·5724	57·846	7·6057	0·86117	2·521	****	6·368	****
Cal.	22·517	128·54	11·338	1·2837	0·5586	*	1·438	**
Pyt.	1·6719	2·4530	1·5662	0·17734	4·876	****	32·13	****
TClay	45·514	146·42	12·100	1·3701	-0·4772		0·6405	
TDolCal	29·089	191·85	13·851	1·5683	0·4125		0·8633	
TCarb	29·850	185·27	13·611	1·5412	0·3434		0·8594	

Number of Cases = 78

Significance Levels: * = 5%; ** = 1%; *** = 0·1%; **** = 0·01%.

(T) = Total iron as obtained from Betaprobe.

APPENDIX
(4.2C)

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CORRELATION COEFFICIENTS    BULK CHEMISTRY,MINERALOGY AND CLAY MINERALS OF OXFORD CLAY WARLINGHAM       OCCBCMC
*************************************************************************************************************


               DEPTH      SIO2      TIO2      AL2O3     FE2O3     MGO       CAO       NA2O      K2O       S

DEPTH        1.00000   0.53450   0.51200   0.54224   0.04840  -0.51121  -0.67860   0.40223   0.19203   0.32475
SIO2         0.53450   1.00000   0.56154   0.35020  -0.12091  -0.50827  -0.84759   0.72805   0.24406   0.03352
TIO2         0.51200   0.56154   1.00000   0.88874   0.22873  -0.18495  -0.79777   0.71776   0.66743   0.06653
AL2O3        0.54224   0.35020   0.88874   1.00000   0.31549  -0.12465  -0.73528   0.58010   0.72350   0.13921
FE2O3        0.04840  -0.12091   0.22873   0.31549   1.00000   0.12187  -0.20891   0.09756   0.36476   0.72474
MGO         -0.51121  -0.50827  -0.18495  -0.12465   0.12187   1.00000   0.34962  -0.18771   0.02636  -0.24947
CAO         -0.67860  -0.84759  -0.79777  -0.73528  -0.20891   0.34962   1.00000  -0.79932  -0.53276  -0.26276
NA2O         0.40223   0.72805   0.71776   0.58010   0.09756  -0.18771  -0.79932   1.00000   0.46883   0.14056
K2O          0.19203   0.24406   0.66743   0.72350   0.36476   0.02636  -0.53276   0.46883   1.00000   0.07220
S            0.32475   0.03352   0.06653   0.13921   0.72474  -0.24947  -0.26276   0.14056   0.07220   1.00000
P2O5         0.46442   0.07606   0.06277   0.23501   0.26781  -0.38416  -0.25349   0.08586   0.04518   0.47771
V           -0.14743   0.02888   0.47563   0.46511   0.46378   0.53322  -0.30829   0.32201   0.52602   0.02649
CR           0.20643   0.13724   0.33086   0.40326   0.37638   0.06995  -0.39298   0.32171   0.28569   0.36182
MN          -0.65359  -0.53131  -0.33508  -0.29670  -0.02457   0.46467   0.56405  -0.42634  -0.02758  -0.36004
BA           0.59529   0.61484   0.55239   0.47556   0.05620  -0.38929  -0.64709   0.47936   0.31152   0.12932
LA           0.34670   0.14427   0.37228   0.41056   0.20216   0.00657  -0.37246   0.29553   0.30122   0.21268
CE           0.36067   0.20738   0.39781   0.52316   0.36118  -0.13227  -0.45512   0.32591   0.43517   0.32221
TH           0.43128   0.45085   0.70910   0.74453   0.28866  -0.11037  -0.70100   0.53863   0.51739   0.10092
PB           0.09615   0.07881   0.23538   0.18569   0.13818  -0.02970  -0.15092   0.09895   0.14235   0.05360
AS          -0.40982  -0.21963  -0.24444  -0.29380   0.30312   0.41597   0.21814  -0.13551  -0.10607   0.14485
GA           0.11073   0.08692   0.27895   0.25221   0.07681  -0.01853  -0.16938   0.11263   0.16887  -0.04262
ZN          -0.06841   0.04225   0.19428   0.16390   0.08248   0.02266  -0.09059   0.14683   0.18909   0.01273
CU           0.21340   0.02146   0.24283   0.29016   0.21607  -0.05589  -0.20593   0.06115   0.19867   0.18702
NI           0.03308   0.04255   0.25795   0.26761   0.20484   0.06825  -0.19180   0.11852   0.25351   0.11412
I            0.07170  -0.05392   0.05808   0.05366   0.04987   0.02819   0.02296   0.07882   0.06166   0.05068
RB           0.38092   0.25220   0.80983   0.95396   0.28426   0.01947  -0.64104   0.50479   0.76293   0.02106
SR          -0.05470  -0.60685  -0.00800   0.15559   0.01081   0.23967   0.37500  -0.24998   0.11929  -0.09651
Y            0.64818   0.40989   0.56410   0.66519   0.14619  -0.37234  -0.65255   0.39831   0.42145   0.21277
ZR           0.42470   0.88928   0.33514   0.07394  -0.24616  -0.61322  -0.62156   0.51636   0.01816   0.01350
NB           0.13967   0.41824   0.23384   0.21095   0.17512   0.02520  -0.45074   0.42480   0.23549   0.16732
MO           0.30643  -0.05598  -0.06079   0.08557   0.46806  -0.18378  -0.18664  -0.07413   0.04312   0.76811
CORG         0.58546   0.12739   0.24793   0.45245   0.14596  -0.20718  -0.46104   0.18153   0.21018   0.44543
CO2         -0.71502  -0.85957  -0.79402  -0.72538  -0.19352   0.47326   0.98799  -0.77876  -0.50952  -0.28249
H2O          0.57394   0.11238   0.51153   0.72748   0.39604  -0.12058  -0.55480   0.32040   0.48906   0.44008
FE2          0.32510   0.03407   0.06716   0.13980   0.72499  -0.24976  -0.26356   0.14107   0.07313   0.99997
FEO          0.33986   0.04319   0.08966   0.17988   0.72956  -0.25533  -0.28884   0.14938   0.10838   0.98801
RFE2O3      -0.42437  -0.22300   0.14215   0.11125   0.25213   0.51239   0.16110  -0.09235   0.27739  -0.43811
CDRAT        0.37883  -0.01847   0.17107   0.12804   0.08567  -0.37985  -0.00760  -0.08525  -0.01972   0.21374
LOI         -0.47335  -0.94111  -0.69995  -0.48334  -0.05698   0.45475   0.84357  -0.76300  -0.38160  -0.04775
ILL         -0.21501  -0.20507   0.18063   0.25197   0.15903   0.17641   0.03986  -0.04049   0.33817  -0.06323
KAOL         0.75563   0.69552   0.38323   0.24181  -0.12671  -0.61112  -0.59252   0.32465  -0.00460   0.14720
CHLR         0.20748   0.11136   0.52878   0.44193   0.15526  -0.13602  -0.22612   0.22072   0.32004  -0.05748
MIXLYR      -0.62560  -0.56064  -0.62490  -0.50104  -0.01798   0.51066   0.59130  -0.34464  -0.27885  -0.07786
QTZ          0.24624   0.77264   0.01765  -0.24513  -0.32562  -0.47732  -0.33561   0.32182  -0.20293  -0.08146
DOL         -0.63081  -0.42175  -0.61099  -0.53900   0.02055   0.70521   0.51152  -0.30363  -0.29401  -0.11666
CAL         -0.41979  -0.72103  -0.53567  -0.49954  -0.25358   0.09449   0.85351  -0.73399  -0.41187  -0.26180
PYT          0.32444   0.03342   0.06647   0.13395   0.72499  -0.25000  -0.26262   0.13994   0.07226   0.99999
TCLAY        0.43987   0.26655   0.82372   0.93334   0.39875  -0.04373  -0.67396   0.54570   0.70995   0.19449
TDOLCAL     -0.69007  -0.85484  -0.77405  -0.70494  -0.19636   0.46466   0.97963  -0.76762  -0.49864  -0.27841
TCARB       -0.63892  -0.85655  -0.76684  -0.69891  -0.18159   0.48022   0.97616  -0.75812  -0.49289  -0.27708
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APPENDIX (4.2C) contd.

	P2O5	V	CR	MN	BA	LA	CE	TH	PB	AS
DEPTH	0.45442	-0.14743	0.20643	-0.65359	0.59529	0.34670	0.36067	0.43123	0.09615	-0.40982
SIO2	0.07606	0.02888	0.13724	-0.53131	0.61484	0.14427	0.20738	0.45085	0.07881	-0.21963
TIO2	0.06277	0.47563	0.33086	-0.33508	0.55239	0.37228	0.39781	0.70910	0.23538	-0.24444
AL2O3	0.23501	0.46511	0.40826	-0.29570	0.47656	0.41056	0.52816	0.74453	0.18669	-0.29380
FE2O3	0.26781	0.46378	0.37638	-0.52457	0.05620	0.20216	0.36118	0.28866	0.13818	0.30312
MGO	-0.33416	0.53322	0.06995	0.46467	-0.38929	0.00657	-0.13227	-0.11037	-0.02970	0.41597
CAO	-0.26349	-0.30829	-0.39298	0.56405	-0.64709	-0.37246	-0.45512	-0.70100	-0.15092	0.21814
NA2O	0.03586	0.32201	0.32171	-0.42534	0.47936	0.29553	0.32591	0.53863	0.09895	-0.13551
K2O	0.04518	0.52602	0.28569	-0.02758	0.31152	0.30122	0.43517	0.51739	0.14235	-0.10607
S	0.47771	0.02649	0.36182	-0.36004	0.12932	0.21268	0.32221	0.10092	0.05360	0.14485
P2O5	1.00000	-0.18122	0.24192	-0.33797	0.15790	0.39722	0.45994	0.20310	0.02831	-0.15957
V	-0.13122	1.00000	0.42907	0.17829	0.03701	0.31598	0.28224	0.48442	0.11571	0.39054
CR	0.24192	0.42907	1.00000	-0.15932	0.08258	0.20609	0.25832	0.38124	0.05238	0.18121
MN	-0.33797	0.17829	-0.15932	1.00000	-0.33614	-0.18307	-0.04311	-0.45711	-0.07468	0.21643
BA	0.15790	0.03701	0.08253	-0.33514	1.00000	0.21029	0.23866	0.26721	0.09985	-0.29231
LA	0.39722	0.31598	0.20609	-0.18307	0.21029	1.00000	0.42502	0.36573	0.15651	0.04025
CE	0.45994	0.28224	0.25832	-0.04311	0.23866	0.42502	1.00000	0.36902	0.08577	-0.10822
TH	0.20310	0.48442	0.38124	-0.45711	0.26721	0.36573	0.36902	1.00000	0.19556	-0.06937
PB	0.02831	0.11571	0.05238	-0.07468	0.09985	0.15651	0.08577	0.19556	1.00000	0.59835
AS	-0.15957	0.39054	0.18121	0.21643	-0.29231	0.04025	-0.10822	-0.06937	0.59835	1.00000
GA	0.01509	0.14753	0.08092	-0.08593	0.10857	0.17922	0.09153	0.24413	0.97049	0.56159
ZN	-0.02269	0.14907	0.03305	-0.00374	0.08993	-0.02755	0.03536	0.08815	0.61238	0.35631
CU	0.20809	0.11225	0.16241	-0.14109	0.11790	0.27990	0.16439	0.26119	0.93519	0.52718
NI	0.03435	0.25376	0.22201	-0.04349	0.08513	0.19162	0.14841	0.25518	0.91804	0.62084
I	-0.02305	0.01806	-0.04319	-0.03285	-0.04149	0.02167	0.18961	0.02468	0.22489	0.11319
RB	0.13550	0.55041	0.38275	-0.16563	0.40078	0.39597	0.50364	0.71742	0.15038	-0.24632
SR	0.01685	0.03808	0.04337	0.28321	-0.15576	-0.07804	0.01716	-0.14444	-0.00603	-0.14465
Y	0.65704	0.04733	0.30801	-0.43146	0.49447	0.42918	0.59029	0.51469	0.10571	-0.37526
ZR	0.09187	-0.16414	0.01941	-0.46251	0.45961	0.10519	0.12954	0.26563	0.05679	-0.17910
NB	0.06717	0.43040	0.34826	-0.17540	0.24114	0.18620	0.33400	0.34669	0.04035	0.24245
MO	0.59967	-0.10444	0.31235	-0.25830	0.10844	0.25852	0.27237	0.00426	0.05394	0.03636
CORG	0.55236	-0.03012	0.35175	-0.42582	0.24518	0.37712	0.27658	0.30251	0.04253	-0.24776
CO2	-0.30052	-0.21518	-0.34970	0.59579	-0.66572	-0.34525	-0.45103	-0.68020	-0.15051	0.27774
H2O	0.51817	0.23306	0.40853	-0.37332	0.24011	0.39882	0.53358	0.54834	0.11660	-0.22322
FE2	0.47819	0.02723	0.36182	-0.36195	0.12961	0.21359	0.32140	0.10159	0.05364	0.14490
FEO	0.48207	0.04471	0.41030	-0.36948	0.13834	0.22026	0.33218	0.13561	0.05806	0.13308
RFE2O3	-0.33127	0.50745	-0.13421	0.49035	-0.12985	-0.05707	-0.01281	0.14408	0.09000	0.21103
CDRAT	0.26312	-0.18196	0.09684	-0.17919	0.17055	0.06534	0.17130	0.00475	0.06439	-0.16069
LOI	-0.00980	-0.19272	-0.16861	0.44730	-0.63216	-0.15763	-0.27649	-0.53474	-0.12790	0.17745
ILL	0.01051	0.20676	-0.02734	0.24075	-0.12055	0.04351	0.15812	0.04768	0.05155	-0.07919
KAOL	0.17967	-0.26215	0.00250	-0.48593	0.62281	0.10956	0.10282	0.24854	0.10078	-0.31805
CHLR	0.04656	0.14347	-0.08580	-0.05737	0.19376	0.13634	0.24760	0.28121	0.13358	-0.22746
MIXLYR	-0.18057	0.08361	0.04441	0.33542	-0.56692	-0.16646	-0.25805	-0.34827	-0.16309	0.43032
QTZ	-0.03211	-0.33236	-0.16127	-0.34298	0.31117	-0.13614	-0.10860	0.02091	0.01638	-0.07813
DOL	-0.26639	0.22423	0.00880	0.34970	-0.54744	-0.19132	-0.30297	-0.33038	-0.16335	0.51262
CAL	-0.17531	-0.41561	-0.43169	0.48599	-0.42871	-0.27921	-0.34119	-0.60722	-0.06118	-0.01437
PYT	0.47752	0.02633	0.36158	-0.36003	0.12902	0.21235	0.32229	0.10111	0.05331	0.14455
TCLAY	0.21512	0.54497	0.44243	-0.25577	0.41477	0.41849	0.52329	0.69917	0.13184	-0.22089
TDOLCAL	-0.20987	-0.21712	-0.34861	0.58824	-0.65163	-0.33363	-0.44573	-0.67856	-0.13980	0.26972
TCARB	-0.28045	-0.19997	-0.34093	0.59025	-0.65935	-0.33578	-0.44555	-0.66812	-0.13330	0.28205

APPENDIX (4.2C) contd.

	GA	ZN	CU	NI	I	RB	SR	Y	ZR	NB
DEPTH	0.11073	-0.06841	0.21340	0.03308	0.07170	0.38092	-0.05470	0.64818	0.42470	0.13967
SIO2	0.08692	0.04225	0.02146	0.04255	-0.05392	0.25220	-0.60685	0.40989	0.88928	0.41824
TIO2	0.27895	0.19428	0.24283	0.25795	0.05808	0.80983	-0.00800	0.56410	0.33514	0.23384
AL2O3	0.25221	0.16090	0.29016	0.26761	0.05366	0.95396	0.15559	0.66519	0.07394	0.21095
FE2O3	0.07681	0.08243	0.21607	0.20434	0.04987	0.28426	0.01081	0.14619	-0.24616	0.17512
MGO	-0.01853	0.02266	-0.05589	0.06825	0.02819	0.01947	0.23967	-0.37234	-0.61322	0.02520
CAO	-0.16938	-0.09059	-0.20593	-0.19180	0.02296	-0.64104	0.37500	-0.65255	-0.62156	-0.45074
NA2O	0.11263	0.14683	0.06115	0.11352	0.07882	0.50479	-0.24998	0.39831	0.51636	0.42480
K2O	0.16887	0.18909	0.19867	0.25351	0.06166	0.76293	0.11929	0.42145	0.01816	0.23549
S	-0.04262	0.01273	0.18702	0.11412	0.05068	0.02106	-0.09651	0.21277	0.01350	0.16732
P2O5	0.01509	-0.02269	0.20809	0.03435	-0.02305	0.13550	0.01685	0.65704	0.09187	0.06717
V	0.14753	0.14907	0.11225	0.25376	0.01806	0.55041	0.03808	0.04733	-0.16414	0.43040
CR	0.08092	0.03305	0.16241	0.22201	-0.04319	0.38275	0.04337	0.30801	0.01941	0.34826
MN	-0.08593	-0.00874	-0.14109	-0.04349	-0.03285	-0.16663	0.28821	-0.43146	-0.46951	-0.17640
BA	0.10357	0.08993	0.11790	0.08513	-0.04149	0.40078	-0.15576	0.49447	0.45961	0.24114
LA	0.17922	-0.02755	0.27990	0.19162	0.02167	0.39597	-0.07804	0.42918	0.10519	0.18620
CE	0.09153	0.03536	0.16439	0.14341	0.18961	0.50364	0.01716	0.59029	0.12954	0.33400
TH	0.24413	0.08815	0.26119	0.25518	0.02468	0.71742	-0.14444	0.51469	0.26563	0.34669
PB	0.97049	0.61238	0.93519	0.91304	0.22489	0.15038	-0.00603	0.10571	0.05679	0.04035
AS	0.56159	0.35631	0.52718	0.62084	0.11319	-0.24632	-0.14465	-0.37526	-0.17910	0.24245
GA	1.00000	0.60181	0.92859	0.91085	0.21968	0.22715	0.02084	0.15830	0.04014	0.02798
ZN	0.60181	1.00000	0.54388	0.58727	0.11841	0.17286	0.07579	0.04648	-0.01835	0.01662
CU	0.92859	0.54388	1.00000	0.90418	0.20292	0.25342	0.02579	0.25237	-0.01904	0.02313
NI	0.91085	0.58727	0.90418	1.00000	0.17494	0.26497	0.02906	0.15694	-0.02884	0.12016
I	0.21968	0.11841	0.20292	0.17494	1.00000	0.05305	0.13705	0.03978	-0.07122	0.10648
RB	0.22715	0.17286	0.25342	0.26497	0.05305	1.00000	0.18483	0.58216	-0.03357	0.22779
SR	0.02084	0.07579	0.02579	0.02906	0.13705	0.18483	1.00000	0.02045	-0.62097	-0.39296
Y	0.15830	0.04648	0.25237	0.15694	0.03978	0.58216	0.02045	1.00000	0.29352	0.16654
ZR	0.04014	-0.01835	-0.01904	-0.02884	-0.07122	-0.03357	-0.62097	0.29352	1.00000	0.32319
NB	0.02798	0.01662	0.02313	0.12016	0.10648	0.22779	-0.39296	0.16654	0.32319	1.00000
MO	-0.02953	0.02405	0.26818	0.14145	-0.07431	0.01841	-0.02986	0.35394	-0.06138	0.05666
CORG	0.03509	-0.03791	0.30761	0.14147	-0.09812	0.39614	0.06766	0.60034	0.01584	0.04270
CO2	-0.16793	-0.08654	-0.20464	-0.17058	0.02513	-0.61651	0.37059	-0.67125	-0.65187	-0.40892
H2O	0.12910	0.05429	0.32325	0.18912	0.02428	0.68827	0.18783	0.63818	-0.06775	0.15751
FE2	-0.04256	0.01253	0.18708	0.11407	0.05066	0.02192	-0.09770	0.21325	0.01381	0.16708
FEO	-0.03256	0.00989	0.20445	0.12044	0.04299	0.06752	-0.10917	0.24756	0.01308	0.18111
RFE2O3	0.13240	0.09234	-0.02625	0.08553	0.00904	0.22168	0.17671	-0.19093	-0.32979	-0.04165
CDRAT	0.08356	0.09587	0.07772	-0.00521	0.11640	0.00892	0.34010	0.27701	0.06063	-0.15843
LOI	-0.14737	-0.09844	-0.03823	-0.09529	0.00323	-0.38444	0.51905	-0.39597	-0.78892	-0.42225
ILL	0.07514	0.23597	0.07210	0.14040	-0.02592	0.32166	0.34552	0.14153	-0.27575	-0.18308
KAOL	0.07496	-0.03278	0.10641	-0.01866	-0.01281	0.06776	-0.38083	0.36620	0.68187	0.14490
CHLR	0.14936	0.13655	0.09168	0.04790	-0.02648	0.42213	0.23245	0.23345	0.04098	-0.11442
MIXLYR	-0.15776	-0.13592	-0.16486	-0.07068	0.03602	-0.37350	0.08534	-0.48318	-0.48919	0.00771
QTZ	-0.02783	-0.04348	-0.11784	-0.10734	-0.08653	-0.34276	-0.69208	0.04676	0.85327	0.20677
DOL	-0.17019	-0.14244	-0.18508	-0.07959	-0.07186	-0.40423	-0.00932	-0.54857	-0.44242	0.09784
CAL	-0.08176	0.00013	-0.11668	-0.14562	0.08406	-0.46293	0.47928	-0.44284	-0.50649	-0.57005
PYT	-0.04280	0.01239	0.18666	0.11376	0.05052	0.02089	-0.09688	0.21288	0.01383	0.16707
TCLAY	0.23646	0.13205	0.25999	0.24584	0.05167	0.93014	0.17524	0.60021	-0.01103	0.26003
TDOLCAL	-0.16040	-0.07809	-0.19715	-0.16393	0.02935	-0.60096	0.38724	-0.66380	-0.65759	-0.41300
TCARB	-0.15183	-0.06964	-0.19122	-0.16041	0.02395	-0.59579	0.39126	-0.66133	-0.66463	-0.40891

APPENDIX (4.2C) contd.

	MO	CORG	CO2	H2O	FE2	FEO	RFE2O3	CDRAT	LOI	ILL
DEPTH	0.30643	0.58546	-0.71502	0.57394	0.32510	0.33986	-0.42437	0.37883	-0.47335	-0.21501
SIO2	-0.05598	0.12739	-0.85957	0.11238	0.03407	0.04319	-0.22300	-0.01847	-0.94111	-0.20507
TIO2	-0.05079	0.24793	-0.29402	0.51153	0.06716	0.08966	0.14215	0.17107	-0.69995	0.18063
AL2O3	0.06567	0.45245	-0.72638	0.72748	0.13980	0.17988	0.11125	0.12804	-0.48384	0.25197
FE2O3	0.46806	0.14596	-0.19352	0.39504	0.72499	0.72956	0.25213	0.08567	-0.05698	0.15903
MGO	-0.18378	-0.20718	0.47326	-0.12058	-0.24976	-0.25533	0.51239	-0.37985	0.45475	0.17641
CAO	-0.18664	-0.46104	0.98799	-0.55430	-0.26356	-0.28864	0.16110	-0.00760	0.84357	0.03986
NA2O	-0.07413	0.18153	-0.77076	0.32040	0.14107	0.14938	-0.09235	-0.08525	-0.76300	-0.04049
K2O	0.04312	0.21015	-0.50952	0.48706	0.07313	0.10838	0.27739	-0.01972	-0.38160	0.33817
S	0.76811	0.44543	-0.28249	0.44008	0.99997	0.98801	-0.43811	0.21374	-0.04775	-0.06323
P2O5	0.59967	0.55236	-0.30052	0.51317	0.47819	0.48207	-0.33127	0.26312	-0.00980	0.01051
V	-0.10444	-0.03012	-0.21518	0.23306	0.02723	0.04471	0.50745	-0.18196	-0.19272	0.20676
CR	0.31235	0.35175	-0.34970	0.40553	0.36182	0.41030	-0.13421	0.09684	-0.16861	-0.02734
MN	-0.25830	-0.42662	0.59579	-0.37332	-0.36195	-0.36948	0.49035	-0.17919	0.44730	0.24075
BA	0.10844	0.24518	-0.66572	0.24011	0.12961	0.13834	-0.12985	0.17055	-0.63216	-0.12055
LA	0.25852	0.37712	-0.34525	0.39332	0.21359	0.22026	-0.05707	0.06534	-0.15763	0.04351
CE	0.27237	0.27658	-0.45103	0.53358	0.32140	0.33218	-0.01281	0.17130	-0.27649	0.15812
TH	0.00426	0.30251	-0.68020	0.54334	0.10159	0.13561	0.14408	0.00475	-0.53474	0.04768
PB	0.05394	0.04253	-0.15051	0.11550	0.05364	0.05806	0.09000	0.06439	-0.12790	0.05155
AS	0.03636	-0.24776	0.27774	-0.22322	0.14490	0.13308	0.21103	-0.16069	0.17745	-0.07919
GA	-0.02953	0.03509	-0.16793	0.12910	-0.04256	-0.03256	0.13240	0.08306	-0.14737	0.07514
ZN	0.02405	-0.03791	-0.08654	0.05429	0.01253	0.00989	0.09234	0.09587	-0.09844	0.23597
CU	0.26818	0.30761	-0.20464	0.32325	0.18708	0.20445	-0.02625	0.07772	-0.03823	0.07210
NI	0.14145	0.14147	-0.17058	0.18912	0.11407	0.12044	0.08663	-0.00621	-0.09529	0.14040
I	-0.07431	-0.09812	0.02513	0.02428	0.05066	0.04299	0.00904	0.11640	0.00323	-0.02592
RB	0.01841	0.39614	-0.61651	0.68327	0.02192	0.06752	0.22168	0.00892	-0.38444	0.32166
SR	-0.02986	0.06766	0.37059	0.18783	-0.09770	-0.10917	0.17671	0.34010	0.51905	0.34552
Y	0.35394	0.60034	-0.67125	0.63818	0.21325	0.24756	-0.19093	0.27701	-0.39597	0.14153
ZR	-0.06138	0.01584	-0.65187	-0.06775	0.01381	0.01308	-0.32979	0.06063	-0.78892	-0.27575
NB	0.05666	0.04270	-0.40892	0.15751	0.16708	0.18111	-0.04165	-0.15843	-0.42225	-0.18308
MO	1.00000	0.67845	-0.19514	0.49502	0.76841	0.76895	-0.47036	0.12804	0.15207	0.06479
CORG	0.67845	1.00000	-0.46053	0.76225	0.44623	0.47845	-0.50929	0.00679	0.02895	-0.03748
CO2	-0.19514	-0.46053	1.00000	-0.55379	-0.28329	-0.30927	0.20941	-0.07841	0.85848	0.07203
H2O	0.49502	0.76225	-0.55379	1.00000	0.44100	0.47068	-0.18025	0.10398	-0.08991	0.12595
FE2	0.76841	0.44623	-0.28329	0.44100	1.00000	0.98802	-0.43783	0.21287	-0.04816	-0.06280
FEO	0.76895	0.47845	-0.30927	0.47068	0.98802	1.00000	-0.47063	0.19778	-0.05892	-0.07864
RFE2O3	-0.47036	-0.50929	0.20941	-0.18025	-0.43783	-0.47063	1.00000	-0.15007	0.02059	0.32596
CDRAT	0.12804	0.00679	-0.07841	0.10398	0.21287	0.19778	-0.15007	1.00000	-0.06049	-0.00890
LOI	0.15207	0.02895	0.85848	-0.08991	-0.04816	-0.05892	0.02059	-0.06049	1.00000	0.11109
ILL	0.06479	-0.03748	0.07203	0.12595	-0.06280	-0.07864	0.32596	-0.00890	0.11109	1.00000
KAOL	0.12332	0.27339	-0.63850	0.14565	0.14711	0.15447	-0.38258	0.31322	-0.61970	-0.31326
CHLR	-0.12670	-0.00508	-0.29053	0.29251	-0.05739	-0.03963	0.23270	0.26660	-0.25681	0.07442
MIXLYR	-0.09919	-0.22591	0.63972	-0.29300	-0.07807	-0.08301	0.09837	-0.37349	0.59112	-0.25279
QTZ	-0.13350	-0.15493	-0.41385	-0.30751	-0.08138	-0.09378	-0.27159	-0.02338	-0.63812	-0.39732
DOL	-0.10263	-0.23021	0.60116	-0.30402	-0.11660	-0.12758	0.21297	-0.57162	0.54225	-0.08358
CAL	-0.16548	-0.41020	0.80807	-0.48069	-0.26279	-0.28740	0.10237	0.31211	0.66946	0.16038
PYT	0.76818	0.44557	-0.28255	0.44066	0.99997	0.98800	-0.43776	0.21403	-0.04758	-0.06363
TCLAY	0.13685	0.45894	-0.66026	0.74386	0.19519	0.23269	0.14554	0.05932	-0.39752	0.26945
TDOLCAL	-0.19183	-0.46219	0.99167	-0.56043	-0.27919	-0.30535	0.20070	-0.05851	0.84587	0.08545
TCARB	-0.19230	-0.46727	0.98943	-0.55336	-0.27783	-0.30355	0.21638	-0.05248	0.84357	0.08746

APPENDIX (4.2C) contd.

	KAOL	CHLR	MIXLYR	QTZ	DOL	CAL	PYT	TCLAY	TDOLCAL	TCARB
DEPTH	0.73563	0.20748	-0.62560	0.24524	-0.63081	-0.41979	0.32444	0.43987	-0.69007	-0.68892
SIO2	0.69552	0.11136	-0.56064	0.77264	-0.48175	-0.72103	0.03342	0.26655	-0.85484	-0.85655
TIO2	0.38383	0.52878	-0.62490	0.01765	-0.61099	-0.53567	0.06647	0.82372	-0.77405	-0.76684
AL2O3	0.24181	0.44193	-0.50104	-0.24513	-0.53900	-0.49954	0.13895	0.93834	-0.70494	-0.69891
FE2O3	-0.12671	0.15526	-0.01798	-0.32562	0.02055	-0.25358	0.72499	0.39875	-0.19636	-0.18159
MGO	-0.61118	-0.13602	0.51066	-0.47732	0.70521	0.09449	-0.25000	-0.04370	0.46466	0.48022
CAO	-0.59252	-0.22612	0.59130	-0.38561	0.51152	0.85351	-0.26262	-0.67396	0.97963	0.97616
NA2O	0.32465	0.22072	-0.34464	0.32182	-0.30363	-0.73399	0.13994	0.54575	-0.76762	-0.75812
K2O	-0.00460	0.32004	-0.27885	-0.20293	-0.29401	-0.41187	0.07226	0.70995	-0.49864	-0.49289
S	0.14720	-0.05748	-0.07786	-0.08146	-0.11666	-0.26180	0.99999	0.19449	-0.27841	-0.27708
P2O5	0.17967	0.04656	-0.18057	-0.03211	-0.26639	-0.17531	0.47752	0.21512	-0.28987	-0.28045
V	-0.26215	0.14347	0.08361	-0.33236	0.22423	-0.41561	0.02633	0.54497	-0.21712	-0.19997
CR	0.00250	-0.08580	0.04441	-0.16127	0.00880	-0.43169	0.36156	0.44243	-0.34861	-0.34093
MN	-0.48593	-0.05737	0.33542	-0.34298	0.34970	0.48399	-0.36003	-0.25677	0.58824	0.59025
BA	0.62281	0.19376	-0.56692	0.31117	-0.54744	-0.42871	0.12902	0.41477	-0.65160	-0.65935
LA	0.10956	0.13634	-0.16646	-0.13514	-0.19132	-0.27921	0.21235	0.41849	-0.33363	-0.33578
CE	0.10282	0.24760	-0.25805	-0.10360	-0.30297	-0.34119	0.32229	0.52329	-0.44573	-0.44555
TH	0.24854	0.28121	-0.34827	0.02091	-0.33038	-0.60722	0.10111	0.69917	-0.67856	-0.66812
PB	0.10078	0.13358	-0.16309	0.01538	-0.16335	-0.06118	0.05331	0.13184	-0.13980	-0.13330
AS	-0.31805	-0.28746	0.43032	-0.07813	0.51262	-0.01437	0.14455	-0.22089	0.26972	0.28205
GA	0.07496	0.14936	-0.15776	-0.02783	-0.17019	-0.08176	-0.04280	0.20846	-0.16040	-0.15183
ZN	-0.03278	0.13655	-0.13592	-0.04348	-0.14244	0.00013	0.01239	0.13205	-0.07809	-0.06964
CU	0.10641	0.09168	-0.16486	-0.11734	-0.18508	-0.11668	0.18686	0.25993	-0.19715	-0.19122
NI	-0.01866	0.04790	-0.07068	-0.10734	-0.07959	-0.14682	0.11376	0.24684	-0.16393	-0.16041
I	-0.01281	-0.02648	0.03602	-0.08553	-0.07186	0.08406	0.05052	0.05167	0.02935	0.02395
RB	0.06776	0.42213	-0.37350	-0.34276	-0.40423	-0.46293	0.02089	0.93014	-0.60096	-0.59579
SR	-0.38083	0.23245	0.08534	-0.69203	-0.00932	0.47928	-0.09688	0.17524	0.38724	0.39126
Y	0.36620	0.23345	-0.48316	0.04576	-0.54857	-0.44284	0.21288	0.60021	-0.66380	-0.66133
ZR	0.68187	0.04098	-0.48919	0.85327	-0.44242	-0.50649	0.01383	-0.01103	-0.65759	-0.66463
NB	0.14490	-0.11442	0.00771	0.20577	0.09784	-0.57005	0.16707	0.26003	-0.41300	-0.40891
MO	0.12332	-0.12670	-0.09919	-0.13350	-0.10263	-0.16548	0.75818	0.13685	-0.19183	-0.19230
CORG	0.27339	-0.00508	-0.22591	-0.15493	-0.23021	-0.41020	0.44557	0.45894	-0.46219	-0.46727
CO2	-0.63850	-0.29053	0.63972	-0.41335	0.60116	0.80807	-0.28253	-0.66026	0.99167	0.98943
H2O	0.14665	0.29251	-0.29800	-0.30751	-0.30400	-0.48069	0.44066	0.74386	-0.56043	-0.55336
FE2	0.14711	-0.05739	-0.07807	-0.08138	-0.11660	-0.26279	0.99997	0.19519	-0.27919	-0.27783
FEO	0.15447	-0.03963	-0.08301	-0.09378	-0.12758	-0.28740	0.98800	0.23289	-0.30535	-0.30355
RFE2O3	-0.33258	0.23270	0.09837	-0.27159	0.21297	0.10237	-0.43776	0.14554	0.20070	0.21638
CDRAT	0.31322	0.26660	-0.37349	-0.02338	-0.57162	0.31211	0.21403	0.05932	-0.05851	-0.05248
LOI	-0.61970	-0.25661	0.59112	-0.63812	0.54225	0.66946	-0.04758	-0.39752	0.84587	0.84357
ILL	-0.31326	0.07442	-0.25279	-0.39732	-0.08358	0.16038	-0.05363	0.26945	0.08545	0.08746
KAOL	1.00000	0.09081	-0.77503	0.62072	-0.66790	-0.31390	0.14704	0.10102	-0.62380	-0.63169
CHLR	0.09081	1.00000	-0.47775	-0.10363	-0.47944	-0.04080	-0.05620	0.44533	-0.29677	-0.27707
MIXLYR	-0.77503	-0.47775	1.00000	-0.31950	0.81651	0.21165	-0.07798	-0.38303	0.62169	0.62046
QTZ	0.62072	-0.10863	-0.31950	1.00000	-0.24019	-0.35297	-0.08125	-0.37471	-0.42087	-0.42561
DOL	-0.66790	-0.47944	0.81651	-0.24019	1.00000	0.03139	-0.11694	-0.39445	0.57489	0.58318
CAL	-0.31390	-0.04080	0.21165	-0.35297	0.03139	1.00000	-0.26228	-0.54699	0.83587	0.82719
PYT	0.14704	-0.05620	-0.07798	-0.08125	-0.11694	-0.26228	1.00000	0.19493	-0.27895	-0.27759
TCLAY	0.10102	0.44533	-0.38303	-0.37471	-0.39445	-0.54699	0.19493	1.00000	-0.66441	-0.65667
TDOLCAL	-0.62380	-0.29677	0.62169	-0.42087	0.57489	0.83587	-0.27895	-0.66441	1.00000	0.99743
TCARB	-0.63169	-0.27707	0.62046	-0.42561	0.58318	0.82719	-0.27759	-0.65667	0.99743	1.00000

APPENDIX (6.1A): Chemical analyses of the residue (leached sediments) as obtained from Beta-probe, of the representative samples of the Oxford Clay and Kellaways Formations from the Winterborne Kingston Borehole sediments. Comparison with the values of chemical analyses re-calculated on carbonate-free basis.

Sample No.	WBK-5		WBK-15		WBK-25		WBK-28		WBK-34		WBK-38	
Elements in %	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
SiO_2	73·02	59·14	67·46	59·80	68·30	55·83	61·55	56·33	64·48	53·10	62·09	53·82
TiO_2	0·76	0·52	0·81	0·67	0·70	0·60	0·83	0·77	0·85	0·72	0·80	0·78
Al_2O_3	11·74	10·68	16·16	14·38	12·86	12·59	18·73	18·21	17·92	16·20	18·17	17·22
Fe_2O_3(T)	5·18	7·36	5·46	7·41	6·66	8·70	5·36	7·14	6·83	7·77	6·41	7·40
MgO	1·07	1·54	1·34	1·63	0·93	1·48	1·53	1·92	1·64	1·85	1·60	1·82
CaO	0·49	-	0·31	-	0·29	-	0·29	-	0·39	-	0·41	-
Na_2O	0·09	0·78	0·20	0·60	0·20	0·73	0·20	0·88	0·18	0·72	0·22	0·71
K_2O	2·27	2·42	2·71	2·74	2·22	2·52	3·10	3·30	3·13	3·06	3·03	3·18
S	1·51	1·62	1·71	1·77	2·18	2·97	0·96	1·15	1·54	1·78	1·89	1·48
P_2O_5	0·05	0·40	0·04	0·20	0·05	0·24	0·05	0·16	0·05	0·195	0·05	0·17
		F=2·00		F=1·492		F=1·492		F=1·333		F=1·393		F=1·321

/contd.over

APPENDIX (6.1A): contd.

Sample No.	WBK-43		WBK-53		WBK-55		WBK-58		WBK-61		WBK-64	
Elements in %	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
SiO2	55·71	50·97	58·43	54·34	61·85	54·82	60·53	58·85	64·75	59·02	62·97	57·75
TiO_2	0·80	0·77	0·79	0·81	0·79	0·76	0·78	0·77	0·78	0·80	0·80	0·81
Al_2O_3	17·58	17·62	18·49	17·99	18·55	17·41	18·06	17·69	17·41	17·39	17·10	17·57
Fe_2O_3(T)	7·25	7·80	5·98	7·00	6·22	6·61	5·66	6·17	6·37	6·76	6·15	6·60
MgO	1·37	1·61	1·34	1·55	1·39	1·525	1·25	1·46	1·34	1·55	1·26	1·49
CaO	0·35	-	0·29	-	0·39	-	0·36	-	0·38	-	0·35	-
Na_2O	0·18	0·77	0·26	0·85	0·51	0·76	0·59	0·90	0·32	0·60	0·30	0·64
K_2O	2·97	3·04	2·86	3·03	3·10	3·175	3·10	3·29	2·89	3·16	2·82	3·12
S	3·22	2·62	1·88	2·15	1·88	2·09	1·71	2·04	1·94	1·75	1·75	1·78
P_2O_5	0·08	0·24	0·05	0·175	0·06	0·175	0·05	0·17	0·05	0·16	0·05	0·15
		F=1·351		F=1·250		F=1·250		F=1·224		F=1·250		F=1·234

EXPLANATIONS: APPENDIX (6.1A):

(a) = Chemical analysis of the leached material as obtained by Beta-probe.

(b) = Chemical analysis, re-calculated on carbonate-free basis from the original bulk rock chemical analyses obtained by Beta-probe.

F = Factors used for obtaining the carbonates corrected chemical analysis.

Fe_2O_3(T) = Total iron.

SAMPLES POSITION IN THE STUDIED SEQUENCE:

U.O.C. = WBK-5 to WBK-25; M.O.C. = WBK-28 to WBK-38; L.O.C. = WBK-43 to WBK-53;

K.F. = WBK-55 to WBK-64.

APPENDIX (6.1B) : Geochemical partition studies of the Winterborne Kingston Borehole sediments.

Explanation

T = Element content in total sediment.

K = Element content of the non-lattice (non-lithogenous) fraction.

A = Contribution made by the non-lattice held fraction to total sediment element content.

B = Contribution made by the lattice-held (lithogenous) fraction to total sediment element content.

C = Element content of the lattice-held (lithogenous) fraction.

D = Element content in the leached residue, determined by Beta-probe.

E = Element content re-calculated on carbonate-free basis.

F = % of the element associated with the lattice-held fraction.

* Original chemical analysis, not corrected for carbonates.

Sample No: WBK-5

Element in %	T	K	A	B	C	D	E	F
Al	2•825	0•21	0•10	2•72	5•38	6•21	5•77	96•35
Fe	2•57	1•315	0•65	1•92	3•80	4•29	5•25	75•75
Mg	0•46	0•58	0•29	0•18	0•35	0•93	0•95	38•05
Na	0•29	0•56	0•27	0•01	0•03	0•07	0•59	5•13
K	1•00	0•30	0•15	0•855	1•685	1•88	2•05	85•12
In p.p.m.								
Pb	27	180	89	0	0	n.d.	54	0
Cu	11	15	7	4	8	"	22	36•40
Zu	345	664	328	17	34	"	690	4•93
Ni	31	63	31	0	0	"	62	0
Cr	71	32	16	55	109	"	142	77•50
Sr	364	525	259	105	207	"	364*	28•80
Mn	595	860	425	170	336	"	595*	19•80

Sample No: WBK-15

Element in %	T	K	A	B	C	D	E	F
Al	5•10	0•34	0•13	4•97	7•82	8•78	9•78	97•5
Fe	3•48	2•85	1•03	2•44	3•85	3•82	5•18	70•2
Mg	0•66	0•77	0•28	0•37	0•58	0•81	0•98	57•0
Na	0•30	0•875	0•32	0	0	0•15	0•44	0
K	1•53	0•48	0•17	1•35	2•125	2•25	2•27	89
In p.p.m.								
Pb	38	279	101	0	0	n.d.	57	0
Cu	14	18	7	7	11	"	21	50
Zn	325	755	275	50	79	"	485	1•5
Ni	48	81	29	19	30	"	72	40
Cr	102	39	14	88	138	"	152	86
Sr	360	712	259	101	159	"	360*	28
Mn	502	1030	375	127	200	"	502*	25

/contd.over

Sample No: WBK-25

Element in %	T	K	A	B	C	D	E	F
Al	4·47	0·60	0·22	4·24	6·79	6·80	6·66	95
Fe	4·27	3·12	1·17	3·10	4·96	4·66	6·08	73
Mg	0·57	0·80	0·30	0·27	0·43	0·56	0·89	47
Na	0·36	0·88	0·33	0·03	0·05	0·15	0·54	3·5
K	1·40	0·58	0·216	1·19	1·90	1·84	2·09	85
In p.p.m.								
Pb	77	496	186	0	0	n.d.	115	0
Cu	17	18	7	10	16	"	25	59
Zn	625	1917	719	0	0	"	932	0
Ni	50	87	33	17	27	"	75	34
Cr	89	77	29	60	96	"	133	67
Sr	273	758	284	0	0	"	273*	0
Mn	486	1000	375	111	178	"	486*	23

Sample No. WBK-28

Element in %	T	K	A	B	C	D	E	F
Al	7·23	0·67	0·18	7·04	9·77	9·91	9·64	97
Fe	3·75	4·00	1·12	2·63	3·65	3·75	5·00	70
Mg	0·87	0·87	0·24	0·63	0·87	0·92	1·16	72
Na	0·49	1·34	0·37	0·12	0·16	0·15	0·65	24
K	2·06	0·755	0·21	1·85	2·565	2·57	2·72	90
In p.p.m.								
Pb	20	352	98	0	0	n.d.	27	0
Cu	18	28	8	10	14	"	24	56
Zn	138	268	75	63	87	"	184	46
Ni	62	105	29	33	46	"	83	53
Cr	171	144	40	131	182	"	228	77
Sr	390	961	269	121	170	"	390*	31
Mn	496	1073	300	196	272	"	496*	39

/contd.over

Sample No. WBK-34

Element in %	T	K	A	B	C	D	E	F
Al	6·15	0·71	0·23	5·92	8·76	9·48	8·54	96
Fe	3·90	3·03	0·98	2·92	4·32	4·78	5·41	75
Mg	0·80	0·87	0·28	0·52	0·765	0·99	1·11	65
Na	0·385	1·39	0·45	0	0	0·13	0·53	0
K	1·83	0·73	0·23	1·59	2·36	2·60	2·53	87
In p.p.m.								
Pb	53	478	158	0	0	n.d.	74	0
Cu	17	27	9	8	12	"	24	47
Zn	290	617	200	90	133	"	404	31
Ni	61	102	33	28	41	"	85	46
Cr	130	139	45	85	126	"	181	65
Sr	376	907	294	82	121	"	376*	22
Mn	526	964	312	214	316	"	526*	41

Sample No. WBK-38

Element in %	T	K	A	B	C	D	E	F
Al	6·90	0·44	0·12	6·78	9·41	9·61	9·08	98
Fe	3·92	2·71	0·72	3·16	4·385	4·48	5·17	81
Mg	0·83	0·89	0·25	0·58	0·81	0·96	1·10	70
Na	0·40	1·21	0·33	0·07	0·09	0·16	0·53	17
K	2·00	0·67	0·19	1·81	2·51	2·51	2·63	90
In p.p.m.								
Pb	26	202	56	0	0	n.d.	34	0
Cu	14	25	7	7	10	"	18	50
Zn	163	369	103	60	83	"	215	37
Ni	61	103	29	32	44	"	81	52
Cr	130	110	31	99	137	"	172	76
Sr	361	894	250	111	154	"	361*	31
Mn	515	939	262	253	351	"	515*	49

/contd.over

Sample No. WBK-43

Element in %	T	K	A	B	C	D	E	F
Al	6•90	0•57	0•16	6•74	9•49	9•30	9•32	98
Fe	4•14	2•63	0•76	3•38	4•75	5•07	5•24	82
Mg	0•72	0•82	0•235	0•48	0•68	0•83	0•91	67
Na	0•42	0•93	0•27	0•155	0•215	0•13	0•57	37
K	1•87	0•62	0•18	1•685	2•37	2•28	2•52	90
In p.p.m.								
Pb	135	1670	484	0	0	n.d.	182	0
Cu	27	22	6	21	30	"	36	78
Zn	1914	1724	500	1414	1991	"	2586	74
Ni	66	86	25	41	58	"	89	62
Cr	132	86	25	107	151	"	178	81
Sr	354	787	228	126	177	"	354*	36
Mn	451	733	213	238	335	"	451*	53

Sample No. WBK-53

Element in %	T	K	A	B	C	D	E	F
Al	7•615	0•51	0•12	7•49	9•82	9•78	9•52	98
Fe	3•92	3•17	0•75	3•17	4•15	4•18	4•89	81
Mg	0•75	0•82	0•19	0•55	0•72	0•81	0•93	74
Na	0•50	1•16	0•27	0•23	0•30	0•19	0•63	46
K	2•00	0•63	0•15	1•86	2•43	2•37	2•51	96
In p.p.m.								
Pb	44	357	84	0	0	n.d.	55	0
Cu	25	33	8	17	22	"	31	68
Zn	709	2590	612	97	127	"	886	14
Ni	65	106	25	40	52	"	81	62
Cr	146	103	24	122	160	"	182	84
Sr	339	846	200	139	182	"	339*	41
Mn	340	528	125	215	282	"	340*	63

/contd.over

Sample No. WBK-55

Element in %	T	K	A	B	C	D	E	F
Al	7·37	0·49	0·111	7·26	10·42	9·82	9·21	98·50
Fe	3·70	2·65	0·601	3·10	3·99	4·35	4·62	83·70
Mg	0·74	0·92	0·205	0·53	0·68	0·84	0·92	72·13
Na	0·45	0·88	0·20	0·25	0·33	0·38	0·56	55·74
K	2·11	0·78	0·17	1·93	2·49	2·57	2·64	91·73
In p.p.m.								
Pb	45	452	101	0	0	n.d.	56	0
Cu	21	33	7·5	13·5	17	"	26	64·3
Zn	499	1114	250	249	32	"	624	49·9
Ni	58	103	23	35	45	"	72	60·3
Cr	158	109	24	134	173	"	197	84·8
Sr	349	946	212	137	177	"	349*	39·2
Mn	363	612	137	226	291	"	362*	62·3

Sample No. WBK-58

Element in %	T	K	A	B	C	D	E	F
Al	7·65	0·90	0·17	7·47	9·27	9·56	9·36	97·72
Fe	3·52	0·22	0·43	3·09	3·83	3·96	4·31	87·70
Mg	0·72	0·99	0·19	0·52	0·65	0·75	0·88	73·11
Na	0·55	0·64	0·13	0·42	0·53	0·44	0·67	77·03
K	2·23	0·77	0·15	2·08	2·58	2·57	2·73	95·54
In p.p.m.								
Pb	46	564	109	0	0	n.d.	56	0
Cu	23	40	8	15	19	"	28	65·22
Zn	631	3222	625	6	7	"	772	0·95
Ni	58	103	20	38	47	"	71	65·52
Cr	154	271	53	101	125	"	188	65·58
Sr	325	1031	200	125	155	"	325*	38·46
Mn	316	628	122	194	241	"	316*	64·40

/contd.over

Sample No. WBK-61

Element in %	T	K	A	B	C	D	E	F
Al	7·36	0·89	0·185	7·175	9·04	9·21	9·20	97·5
Fe	3·78	1·87	0·38	3·40	4·28	4·45	4·72	89·8
Mg	0·75	0·90	0·19	0·55	0·70	0·81	0·94	75·0
Na	0·36	0·90	0·185	0·17	0·215	0·24	0·45	47·92
K	2·10	1·00	0·21	1·89	2·38	2·40	2·62	90·00
In p.p.m.								
Pb	37	424	87	0	0	n.d.	46	0
Cu	24	26	5	19	24	"	30	79·2
Zn	181	454	94	87	110	"	226	48·0
Ni	59	97	20	39	49	"	74	66·0
Cr	149	154	32	117	147	"	186	78·5
Sr	299	908	187	112	141	"	299*	37·5
Mn	356	666	137	219	276	"	356*	61·5

Sample No. WBK-64

Elements in %	T	K	A	B	C	D	E	F
Al	7·535	0·73	0·14	7·39	9·19	9·05	9·30	98·10
Fe	3·74	1·85	0·36	3·38	4·20	4·30	4·61	90·30
Mg	0·73	0·86	0·17	0·56	0·70	0·76	0·90	76·86
Na	0·385	0·89	0·17	0·215	0·27	0·22	0·47	55·77
K	2·10	0·86	0·17	1·93	2·41	2·34	2·59	92·09
In p.p.m.								
Pb	33	319	62	0	0	n.d.	41	0
Cu	26	22	4	22	27	"	32	84·6
Zn	291	446	87	204	254	"	359	70·0
Ni	58	73	14	44	55	"	72	94·3
Cr	149	143	28	121	150	"	184	81·2
Sr	295	909	178	117	145	"	295*	39·7
Mn	331	670	131	200	249	"	331*	60·4

APPENDIX (6.1C)

SUMMARY STATISTICS: Elements Partitioning Study of the Oxford Clay Sediments of the Winterborne Kingston Borehole Samples.

	Mean	Variance	S.Deviation	S.E.of Mean	Skewness	Kurtosis
LHAL	16·562	7·3277	2·7070	0·78144	-1·469 *	1·853
LHMG	1·1008	0·59717E-01	0·24437	0·70544E-01	-1·027	0·9541
LHFE	5·9783	0·31578	0·56194	0·16222	0·6883	-0·4131E-01
LHNA	0·24500	0·46482E-01	0·21560	0·62237E-01	0·7384	0·3070
LHK	2·7917	0·11049	0·33240	0·95955E-01	-1·473 *	1·467
LHPB	0·00000	0·90909E-11	0·30151E-05	0·87039E-06	0·3980E+06****	0·1907E+12 ****
LHZN	268·83	0·30293E+06	550·39	158·88	3·290 ****	11·10 ****
LHCR	141·17	621·61	24·932	7·1973	-0·1716	-0·2393
LHCU	17·583	48·447	6·9604	2·0093	0·4490	-0·8397
LHMN	277·25	2899·8	53·850	15·545	-0·4552	-0·4745
LHSR	149·00	2698·9	51·951	14·997	-2·369 ***	6·944 ****
LHNI	41·167	250·33	15·822	4·5674	-1·775 **	3·672 **
LGF	71·137	79·861	8·9365	2·5798	-1·097	1·136
LGFBM	71·137	68·551	8·2795	2·3901	-1·557 *	2·552 *
RTI	0·470	-	-	-	-	-
RAL	16·898	5·1687	2·2735	0·65630	-1·704 **	1·892
RMG	1·4233	0·76115E-01	0·27589	0·79643E-01	0·8134	2·476
RFE	6·2275	0·35784	0·59820	0·17268	0·5182	0·5564
RNA	0·27167	0·21433E-01	0·14640	0·42262E-01	1·401 *	1·513
RK	2·8250	0·94773E-01	0·30785	0·88869E-01	-1·134	0·4039

/contd.over

APPENDIX (6.1C) contd.

	Mean	Variance	S.Deviation	S.E.of Mean	Skewness		Kurtosis	
CCAL	16·625	5·6620	2·3795	0·68690	-1·902	**	2·670	*
CCMG	1·6225	0·24148E-01	0·15540	0·44859E-01	0·9933		-0·3230	
CCFE	7·2167	0·41606	0·64503	0·18620	0·7834		1·636	
CCNA	0·74167	0·11742E-01	0·10836	0·31282E-01	-0·1191E-02		-1·153	
CCK	2·9900	0·74000E-01	0·27203	0·78528E-01	-1·059		0·8687E-01	
QTZ	20·258	6·2645	2·5029	0·72252	0·1120		-1·199	
CORG	2·7017	1·5423	1·2419	0·35850	0·6945		-0·7731	
PYT	2·6417	0·51174	0·71536	0·20651	-0·1477		-0·8686	
CAL	26·167	73·788	8·5900	2·4797	1·622	*	3·001	*
TCLY	47·925	75·098	8·6659	2·5016	-1·235	*	1·056	
ILL	55·667	124·61	11·163	3·2224	-2·290	***	6·423	
KAOL	17·667	33·152	5·7577	1·6621	-1·501	*	3·152	*
CHLR	7·9167	12·083	3·4761	1·0035	-0·7266		-0·1630	
SMECT	19·417	361·17	19·005	5·4862	2·144	**	5·466	****
IL	27·561	71·367	8·4479	2·4387	-1·486	*	2·287	
KOL	8·9225	13·252	3·6403	1·0509	-0·9587		0·7260	
CH	4·1600	3·8963	1·9739	0·56982	-0·9102		-0·1958	
SMEC	8·0017	29·723	5·4518	1·5738	1·027		1·047	

Number of Cases = 12

Significance Levels = * = 5%; ** = 1%; *** = 0·1%; **** = 0·01%.

/contd.over

APPENDIX (6.1C) contd.

Note:
i) Major elements are tabulated as oxides.

ii) LGF = weight % of the residue.

iii) LGFBM = amount of lithogenous fraction obtained by adding the percentages of (Quartz + C_{org} + TClays).

iv) Elements having 'R' as prefix indicate the amount of element determined in the leached residue.

v) Elements having 'CC' as prefix indicate the amount of element re-calculated on a carbonate-free basis.

vi) Elements having 'LH' as prefix indicate the amount of element associated with the lattice-held fractions.

vii) IL, KOL, CH and SMEC represent the abundances of clay minerals, illite, kaolinite, chlorite and smectite, re-calculated in the bulk rock samples.

APPENDIX (6.2A): Chemical analyses of the residue (leached sediments), as obtained from Beta-probe, of the representative samples of the Oxford Clay and Kellaways Formations from the Warlingham Borehole sediments. Comparison with the values of chemical analyses re-calculated on the carbonate-free basis.

Sample No.	BR-134		BR-278		BR-627		BR-826		BR-988		BR-1301	
Elements in %	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
SiO_2	80.91	69.53	70.72	62.83	63.39	60.90	62.08	52.28	61.12	54.54	58.68	56.31
TiO_2	0.54	0.39	0.98	0.87	1.11	1.11	0.98	0.94	1.10	0.94	1.04	0.98
Al_2O_3	7.84	6.81	14.89	13.22	19.56	19.27	18.51	18.38	18.96	19.15	19.05	19.52
Fe_2O_3(T)	3.14	6.67	3.82	5.93	5.26	5.17	5.35	6.92	6.18	8.81	5.44	6.73
MgO	1.07	5.22	1.08	3.41	1.81	3.72	1.54	3.66	1.41	5.14	1.41	3.19
CaO	0.62	-	0.31	-	0.30	-	0.29	-	0.37	-	0.20	-
Na_2O	0.15	0.32	0.36	0.32	0.26	0.57	0.15	0.34	0.19	0.37	0.27	0.56
K_2O	1.83	2.29	3.01	3.18	3.95	4.04	3.49	3.89	3.16	5.12	3.27	3.84
S	n.d.	1.11	0.53	0.77	0.46	0.17	0.90	1.07	2.31	2.52	1.75	1.89
P_2O_5	0.00	0.09	0.03	0.11	0.04	0.10	0.03	0.12	0.09	0.26	0.05	0.20
		F=2.310		F=1.786		F=1.320		F=1.570		F=1.773		F=1.330

/contd.over

APPENDIX (6.2A) contd.

Sample No.	BR-1424		BR-1583		BR-1734		BR-1755		BR-1771	
Elements in %	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
SiO_2	60·12	57·90	55·67	55·64	57·26	53·39	68·00	67·65	56·47	54·29
TiO_2	1·04	1·04	0·96	0·97	1·03	0·93	0·75	0·76	0·96	0·91
Al_2O_3	20·35	19·76	19·59	19·75	22·33	21·65	14·80	14·66	22·37	21·45
Fe_2O_3(T)	5·10	4·54	4·75	5·60	5·22	5·00	4·43	5·26	4·77	4·73
MgO	1·56	4·01	1·47	1·84	1·94	1·99	0·82	1·04	1·67	1·71
CaO	0·30	-	0·17	-	0·11	-	0·14	-	0·08	-
Na_2O	0·23	0·78	0·18	0·39	0·18	0·43	0·33	0·43	0·24	0·48
K_2O	3·47	3·58	3·42	3·65	3·79	3·96	2·76	2·90	3·76	3·74
S	1·40	1·39	1·14	1·43	1·42	1·16	2·05	1·44	1·28	1·60
P_2O_5	0·06	0·28	0·03	0·17	0·05	0·17	0·04	0·40	0·04	0·13
		F=1·480		F=1·290		F=1·075		F=1·136		F=1·031

Explanations

(a) = Chemical analysis of leached material as obtained by Betaprobe.
(b) = Chemical analysis, re-calculated on carbonate free basis from the original chemical analysis.
F == Factors used for obtaining the carbonates corrected chemical analysis.
Fe_2O_3(T) = Total iron.

Samples: Position in the Studied Sequence

U.O.C. = BR-134 to BR-627; M.O.C. = BR-826 to BR-1301; L.O.C. = BR-1424 to BR-1734.
K.F. = BR-1755 to BR-1771.

APPENDIX (6.2B)

Geochemical partition studies results of the Warlingham Borehole Sediments

Explanation of Appendix (6.2B)

T = Element content in total sediment

K = Element content of the non-lattice held (non-lithogenous) fraction.

A = Contribution made by the non-lattice held fraction to total sediment element.

B = Contribution made by the lattice-held (lithogenous) fraction to total sediment element content.

C = Element content of the lattice-held (lithogenous) fraction.

D = Element content in the leached residue, determined by Beta-probe.

E = Element content re-calculated on carbonate-free basis.

F = % of element associated with the lattice-held fraction.

* Original chemical analysis, not corrected for carbonates.

+ Re-calculated on a calcite-free basis only.

Sample No. BR-134

Element in %	T	K	A	B	C	D	E	F
Al	1·56	0·07	0·04	1·52	3·63	4·15	3·60	97·44
Fe	2·02	1·36	0·79	1·23	2·94	2·20	4·66	60·89
Mg	1·36	1·17	0·69	0·67	1·60	0·645*	1·94^{+}	49·11
Na	0·104	0·24	0·14	0·00	0·00	0·14	0·24	0·00
K	0·82	0·22	0·12	0·70	1·66	1·52	1·90	84·85
In p.p.m.								
Pb	6	78	45	0	0	n.d.	14	0
Cu	9	13	8	1	2·4	"	21	11·11
Zn	14	177	103	0	0	"	32	0
Ni	28	43	25	3	7	"	65	10·71
Cr	71	21	12	59	141	"	164	83·10
Sr	239	269	156	83	198	"	n.d.	34·73
Mn	192	296	172	20	48	"	"	10·42

Sample No. BR-278

Element in %	T	K	A	B	C	D	E	F
Al	3·92	0·14	0·063	3·85	7·04	7·88	7·00	98·21
Fe	2·32	1·68	0·762	1·56	2·85	2·67	4·14	67·24
Mg	1·15	0·77	0·35	0·80	1·465	0·65*	1·88^{+}	69·60
Na	0·13	0·21	0·10	0·03	0·055	0·11	0·23	23·08
K	1·48	0·34	0·16	1·32	2·415	2·50	2·64	89·20
In p.p.m.								
Pb	9	76	34	0	0	n.d.	16	0·00
Cu	12	10	4·5	7·5	14	"	21	62·50
Zn	38	83	37	1	2	"	68	2·63
Ni	25	52	23	2	4	"	45	8·00
Cr	79	28	13	66	121	"	141	83·50
Sr	246	324	147	99	181	"	n.d.	40·24
Mn	208	462	209	0	0	"	"	0·00

/contd.over

Sample No. BR-627

Element in %	T	K	A	B	C	D	E	F
Al	7·73	0·31	0·074	7·66	10·15	10·35	10·20	99·09
Fe	2·74	1·71	0·42	2·32	3·08	3·68	3·62	84·67
Mg	1·70	1·42	0·35	1·35	1·79	1·09[*]	2·125[+]	79·41
Na	0·32	0·69	0·17	0·15	0·19	0·19	0·42	46·87
K	2·54	0·62	0·15	2·39	3·17	3·29	3·35	94·09
In p.p.m.								
Pb	22	197	48	0	0	n.d.	29	0
Cu	18	28	7	11	15	"	24	61·11
Zn	93	115	28	65	86	"	123	70·00
Ni	51	59	14	37	49	"	67	72·50
Cr	105	25	6	99	131	"	139	94·30
Sr	256	509	125	131	174	"	n.d.	51·17
Mn	313	636	156	157	208	"	"	50·16

Sample No. BR-826

Element in %	T	K	A	B	C	D	E	F
Al	6·20	0·19	0·069	6·13	9·62	9·79	9·73	98·87
Fe	3·08	1·41	0·51	2·57	4·04	3·74	4·83	83·44
Mg	1·40	0·96	0·35	1·05	1·66	0·93[*]	2·09[+]	75·00
Na	0·16	0·43	0·156	0·007	0·016	0·11	0·25	4·37
K	2·06	0·38	0·13	1·926	3·02	2·90	3·23	93·50
In p.p.m.								
Pb	16	95	34	0	0	n.d.	25	0·00
Cu	19	15	5	14	22	"	30	73·68
Zn	52	86	31	21	33	"	82	40·38
Ni	32	57	21	11	17	"	50	34·37
Cr	107	26	9	98	154	"	168	91·66
Sr	n.d.	n.d.	n.d.	n.d.	n.d.	"	n.d.	n.d.
Mn	166	267	97	69	108	"	"	41·6

/contd.over

Sample No. BR-988

Element in %	T	K	A	B	C	D	E	F
Al	5·715	0·87	0·40	5·31	9·80	10·03	10·13	92·91
Fe	3·48	2·57	1·17	2·30	4·24	4·32	6·17	66·09
Mg	1·75	2·09	0·95	0·80	1·465	0·85*	2·27+	45·71
Na	0·155	0·42	0·19	0·00	0·00	0·14	0·27	0·00
K	1·85	0·89	0·41	1·44	2·66	2·62	3·28	77·83
In p.p.m.								
Pb	19	78	36	0	0	n.d.	34	0·00
Cu	15	10	5	10	18	"	27	66·67
Zn	28	55	25	3	5	"	50	10·71
Ni	25	59	27	0	0	"	44	0
Cr	53	34	16	37	68	"	94	69·81
Sr	342	348	159	183	338	"	342	53·51
Mn	181	416	190	0	0	"	181	0·00

Sample No. BR-1301

Element in %	T	K	A	B	C	D	E	F
Al	7·77	1·26	0·31	7·46	9·92	10·08	10·33	96·00
Fe	3·54	1·81	0·45	3·09	4·11	3·80	4·71	87·28
Mg	1·45	1·46	0·36	1·08	1·44	0·85*	1·84+	74·48
Na	0·31	0·83	0·21	0·10	0·14	0·36	0·41	32·25
K	2·40	1·34	0·33	2·07	2·75	2·71	3·19	86·25
In p.p.m.								
Pb	18	101	25	0	0	n.d.	24	0·00
Cu	19	20	5	14	19	"	25	73·68
Zn	47	164	41	6	8	"	62·5	12·76
Ni	41	103	26	15	20	"	54·5	36·58
Cr	126	53	13	113	150	"	168	89·68
Sr	271	529	131	140	186	"	271	51·66
Mn	148	731	181	0	0	"	148	0·00

/contd.over

Sample No. BR-1424

Element in %	T	K	A	B	C	D	E	F
Al	7·06	0·45	0·15	6·91	10·48	10·77	10·45	97·87
Fe	2·15	1·39	0·475	1·67	2·54	3·57	3·18	77·67
Mg	1·67	2·05	0·70	0·97	1·47	0·94*	2·19$^+$	58·08
Na	0·39	0·40	0·13	0·26	0·385	0·17	0·58	66·67
K	2·00	0·59	0·20	1·81	2·75	2·88	2·96	90·50
In p.p.m.								
Pb	19	77	26	0·00	0·00	n.d.	28	0·00
Cu	21	14	5	16	24	"	31	76·19
Zn	33	73	25	8	12	"	49	24·24
Ni	36	55	19	17	26	"	53·3	47·20
Cr	102	42	14	88	133	"	151	86·27
Sr	271	449	153	118	179	"	271*	43·54
Mn	148	385	131	17	26	"	148	11·50

Sample No. BR-1583

Element in %	T	K	A	B	C	D	E	F
Al	8·10	0·35	0·08	8·02	10·43	10·37	10·45	99·01
Fe	3·03	1·46	0·335	2·70	3·51	3·32	3·91	89·11
Mg	0·86	1·08	0·25	0·615	0·80	0·89*	1·13$^+$	71·51
Na	0·22	0·67	0·155	0·07	0·09	0·13	0·28	31·82
K	2·35	0·60	0·14	2·21	2·87	2·84	3·03	94·14
In p.p.m.								
Pb	17	92	21	0·00	0·00	n.d.	22	0·00
Cu	18	20	5	13	16	"	23	72·22
Zn	43	95	22	21	26	"	55·5	48·83
Ni	48	81	19	29	36	"	62	60·42
Cr	132	43	10	122	153	"	170·3	92·42
Sr	321	812	188	133	166	"	321	41·43
Mn	105	257	59	46	58	"	105	43·81

/contd.over

Sample No. BR-1734

Element in %	T	K	A	B	C	D	E	F
Al	10·66	3·36	0·30	10·36	11·38	11·82	11·46	97·18
Fe	3·26	2·99	0·265	2·99	3·29	3·65	3·50	91·72
Mg	1·15	2·22	0·20	0·95	1·05	1·17*	1·20+	82·61
Na	0·30	1·67	0·15	0·15	0·16	0·13	0·32	50·00
K	3·05	3·47	0·315	2·74	3·01	3·15	3·28	89·84
In p.p.m.								
Pb	23	278	tr	0·00	0·00	n.d.	25	0·00
Cu	38	62	6	32·00	35·00	"	41	84·21
Zn	54	347	31	23·00	25·00	"	58	42·59
Ni	55	243	22	33·00	36·00	"	59	60·00
Cr	219	132	12	207·00	227·00	"	235	94·52
Sr	213	764	69	144	158	"	213	67·60
Mn	106	278	25	81	89	"	106	76·41

Sample No. BR-1755

Element in %	T	K	A	B	C	D	E	F
Al	6·83	0·65	0·10	6·73	7·80	7·67	7·77	98·54
Fe	3·24	3·74	0·50	2·73	3·16	3·10	3·68	84·26
Mg	0·55	1·02	0·14	0·42	0·48	0·49*	0·60+	76·36
Na	0·28	0·65	0·09	0·19	0·22	0·24	0·32	67·86
K	2·12	0·88	0·12	2·00	2·31	2·29	2·41	97·51
In p.p.m.								
Pb	15	139	19	0	0	n.d.	17	0
Cu	19	30	4	15	17	"	22	78·95
Zn	62	186	25	37	43	"	70	59·70
Ni	38	116	16	22	25	"	43	57·89
Cr	119	46	6	113	131	"	135	94·96
Sr	195	743	100	95	110	"	195	48·72
Mn	83	186	25	58	67	"	83	69·88

/contd.over

Sample No. BR-1771

Element in %	T	K	A	B	C	D	E	F
Al	11•01	4•31	0•21	10•81	11•36	11•84	11•35	98•18
Fe	3•21	5•02	0•24	2•955	3•12	3•34	3•31	92•38
Mg	0•52	2•64	0•13	0•40	0•42	1•00	0•54	76•92
Na	0•35	3•22	0•155	0•19	0•20	0•18	0•36	54•28
K	3•01	4•51	0•215	2•80	2•94	3•12	3•10	93•02
In p.p.m.								
Pb	24	309	15	9	9•5	n.d.	25	37•50
Cu	35	129	6	29	30	"	36	82•86
Zn	58	773	37	21	22	"	60	36•21
Ni	66	258	12	54	57	"	68	81•82
Cr	141	180	9	132	139	"	145	93•62
Sr	183	644	31	152	160	"	183	83•06

APPENDIX (6.2C)

SUMMARY STATISTICS: Elements Partitioning Study of Oxford Clay Sediments of Warlingham Borehole Samples

	Mean	Variance	S.Deviation	S.E. of Mean	Skewness		Kurtosis	
LHAL	17·054	18·684	4·3225	1·3669	-1·682	*	2·884	*
LHMG	2·1930	0·46949	0·68519	0·21668	-1·145		0·4908	
LHFE	4·8280	0·69733	0·83506	0·26407	0·3470		-1·198	
LHNA	0·17200	0·26618E-01	0·16315	0·51592E-01	0·9805		1·001	
LHK	3·2640	0·32923	0·57378	0·18145	-1·224		1·498	
LHPB	0·00000	0·11111E-10	0·33333E-05	0·10541E-05	0·3750E+06	****	0·1768E+12	****
LHZN	24·000	679·11	26·060	8·2408	1·638	*	3·089	*
LHCR	140·90	1531·4	39·134	12·375	0·5685		3·425	*
LHCU	18·200	69·733	8·3506	2·6407	0·1482		2·407	
LHMN	60·400	4133·4	64·291	20·331	1·382	*	2·326	
LHSR	169·00	6903·6	83·088	26·275	-0·4227E-01		3·191	*
LHNI	22·000	245·33	15·663	4·9531	0·1906		-0·7163	
LGF	68·845	243·22	15·595	4·9317	-0·2741		-0·7401	
LGFBM	69·027	227·46	15·082	4·7693	-0·1198		-0·2131	
RAL	17·557	17·197	4·1469	1·3114	-1·580	*	2·802	*
RMG	1·4110	0·11739	0·34262	0·10835	-0·2249		-0·3486	
RFE	4·8690	0·76692	0·87574	0·27693	-0·7741		0·6109	
RNA	0·20900	0·37656E-02	0·61364E-01	0·19405E-01	0·8828		-0·1362	
RK	3·2150	0·35854	0·59878	0·18935	-1·376	*	2·685	*
CCAL	17·025	19·171	4·3785	1·3846	-1·639	*	2·587	*

/contd.over

APPENDIX (6.2C) contd.

	Mean	Variance	S.Deviation	S.E.of Mean	Skewness		Kurtosis	
CCMG	2.8320	0.82164	0.90644	0.28664	-1.164		0.1176	
CCFE	5.9070	0.97893	0.98941	0.31288	0.1829		-1.378	
CCNA	0.44700	0.21846E-01	0.14780	0.46739E-01	1.453	*	1.807	
CCK	3.4000	0.45184	0.67219	0.21257	-1.043		-0.6181	
QTZ	21.200	59.289	7.6999	2.4349	1.904	**	3.809	**
CORG	2.1090	2.7391	1.6550	0.52336	1.309		1.201	
PYT	1.5850	0.58558	0.76523	0.24199	-0.4067		-0.7021	
CAL	21.720	106.87	10.338	3.2691	-0.9256E-01		-0.5258E-01	
DOL	7.6600	73.509	8.5738	2.7113	1.704	*	2.141	
TCLY	45.720	190.59	13.805	4.3657	0.2845		0.7790	
ILL	64.200	4.6222	2.1499	0.67987	0.1811		-0.4407	
KAOL	11.700	19.567	4.4234	1.3988	-2.388	***	6.592	****
CHLR	6.8000	7.5111	2.7406	0.86667	-0.8728		1.031	
MIXLYR[1]	17.300	41.344	6.4300	2.0333	2.272	**	5.840	****
IL	29.271	72.678	8.5251	2.6959	0.1168		0.4206	
KOL	5.7420	9.2251	3.0373	0.96047	-0.3349E-01		1.860	
CH	3.2030	2.5619	1.6006	0.50615	0.4321E-01		0.3590	
MLYR[2]	7.5080	4.5862	2.1415	0.67721	0.9944E-01		-0.6923	

Number of Cases = 10

Significance Levels: * = 5%; ** = 1%; *** = 0.1%; **** = 0.01%.

1. Mixed-layer mineral in the clay fraction ($< 2\mu$).
2. Mixed-layer mineral re-calculated in the Bulk rock.

APPENDIX (7.1A)

	ILLITE	KAOLINITE	CHLORITE	SMECTITE	V/h	V/P	% E.Layers	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
WBK-1	39	3	1	57	0·65	0·75	> 60% < 80%	3·07	0·45	0·35
WBK-2	35	2	2	61	0·61	0·71	" "	2·29	0·35	0·35
WBK-3	45	3	4	48	0·57	0·70	" "	2·25	0·40	0·32
WBK-4	37	3	3	57	0·67	0·76	" "	2·44	0·40	0·35
WBK-5	24	3	1	72	0·70	0·80	" "	3·00	0·40	0·30
WBK-6	38	3	3	56	0·63	0·73	" "	3·00	0·35	0·30
WBK-7	48	5	4	43	0·66	0·72	" "	2·62	0·33	0·30
WBK-8	38	5	4	53	0·70	0·80	" "	3·29	0·25	0·35
WBK-9	35	4	3	58	0·61	0·69	" "	2·89	0·30	0·25
WBK-10	30	4	2	64	0·58	0·68	" "	2·80	0·35	0·45
WBK-11	37	7	3	53	0·66	0·73	" "	3·25	0·35	0·40
WBK-12	39	7	4	50	0·57	0·66	" "	2·75	0·35	0·40
WBK-13	32	5	3	60	0·64	0·73	" "	3·11	0·35	0·30
WBK-14	38	4	3	55	0·53	0·60	" "	3·43	0·30	0·25
WBK-15	56	14	7	23	0·46	0·53	" "	5·66	0·25	0·25
WBK-16	41	6	2	51	0·55	0·61	" "	3·50	0·28	n.d.
WBK-17	43	8	4	45	0·63	0·70	" "	3·67	0·40	n.d.
WBK-18	56	18	8	18	0·57	0·72	" "	3·67	0·30	n.d.
WBK-19	50	14	4	32	0·52	0·62	" "	3·86	0·30	n.d.
WBK-21	50	12	4	34	0·55	0·64	" "	3·25	0·38	n.d.

/contd.over

APPENDIX (7.1A) contd.

	ILLITE	KAOLINITE	CHLORITE	SMECTITE	V/h	V/P	% E.Layers	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
WBK-22	50	14	4	32	0·56	0·65	>60% < 80%	4·20	0·35	n.d.
WBK-23	54	13	6	27	0·45	0·57	" "	4·50	0·30	n.d.
WBK-24	46	18	7	29	0·52	0·59	" "	3·46	0·35	0·30
WBK-25	50	14	3	33	0·44	0·49	" "	4·50	0·29	0·35
WBK-26	54	21	7	18	0·45	0·52	" "	3·65	0·35	0·30
WBK-27	55	16	11	18	0·59	0·69	" "	4·00	0·30	0·30
WBK-28	57	18	12	13	0·71	0·78	" "	2·91	0·40	0·32
WBK-29	61	19	10	10	0·47	0·60	"	4·50	0·25	0·30
WBK-30	63	14	5	18	0·45	0·55	"	4·40	0·25	0·25
WBK-32	60	19	10	11	0·52	0·65	"	4·00	0·32	0·30
WBK-33	56	17	8	19	0·35	0·44	<60%	4·22	0·30	0·30
WBK-34	53	16	6	25	0·44	0·52	>60% <80%	3·50	0·26	0·30
WBK-35	58	16	6	20	0·37	0·47	<60%	4·00	0·32	n.d.
WBK-36	64	21	5	10	0.27	0.37	"	4·60	0.25	0·30
WBK-37	62	16	8	14	0·18	0·25	"	4·25	0·32	0·30
WBK-38	55	17	8	20	0·57	0·68	>60% <80%	4·60	0·28	0·30
WBK-39	61	21	4	14	0·57	0·71	"	4·25	0·32	0·25
WBK-40	53	20	3	24	0·49	0·56	"	4·33	0·30	0·30
WBK-41	56	15	9	20	0·67	0·80	"	n.d.	n.d.	n.d.
WBK-42	56	19	12	13	0·59	0·66	"	n.d.	n.d.	n.d.
WBK-43	55	18	9	18	0·57	0·79	"	n.d.	n.d.	n.d.
WBK-44	60	24	7	9	0·47	0·54	"	3·86	0·36	0·28

/contd.over

APPENDIX (7.1A) contd.

	ILLITE	KAOLINITE	CHLORITE	SMECTITE	V/h	V/P	% E.Layers	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
WBK-45	60	20	11	9	0·37	0·50	< 60%	3·44	0·35	
WBK-46	56	25	9	10	0·43	0·50	> 60% < 80%	3·67	0·30	
WBK-47	58	25	6	11	0·27	0·31	< 60%	3·33	0·38	0·28
WBK-48	61	26	5	8	0·28	0·33	"	4·00	0·30	0·30
WBK-49	64	22	4	10	0·63	0·74	> 60% < 80%	3·11	0·45	0·29
WBK-50	67	22	5	6	0·39	0·54	"	3·25	0·35	0·30
WBK-51	64	26	5	5	0·36	0·44	< 60%	4·00	0·30	0·35
WBK-52	64	20	8	8	0·32	0·41	"	4·90	0·25	0·30
WBK-53	64	21	11	4	0·48	0·55	> 60% < 80%	4·90	0·25	0·25
WBK-54	66	19	11	4	0·43	0·56	"	4·80	0·28	0·30
WBK-55	63	21	10	6	0·42	0·50	"	5·00	0·25	0·29
WBK-56	64	19	11	6	0·50	0·60	"	n.d.	n.d.	n.d.
WBK-57	61	22	12	5	0·35	0·44	< 60%	4·33	0·30	0·25
WBK-58	61	23	10	6	0·55	0·65	> 60% < 80%	4·72	0·28	0·25
WBK-59	63	21	12	4	0·57	0·66	"	4·16	0·32	0·25
WBK-60	63	21	12	4	0·54	0·59	"	3·67	0·40	0·25
WBK-61	65	23	12	8	0·49	0·58	"	3·73	0·40	0·30
WBK-62	63	21	11	5	0·43	0·50	"	5·16	0·24	0·23
WBK-63	61	23	11	5	0·28	0·40	< 60%	4·42	0·30	0·22
WBK-64	65	24	6	5	0·28	0·35	"	5·35	0·22	0·28
WBK-65	64	22	8	6	0·28	0·35	"			

APPENDIX (7.1B)

Major Elements Oxides (%)	WBK-12	WBK-23	WBK-32	WBK-41	WBK-43	WBK-44	WBK-48	WBK-51	WBK-52	WBK-54	WBK-57	WBK-60
SiO_2	50·58	55·28	54·85	54·17	50·14	51·30	48·57	48·80	48·33	50·61	51·80	51·90
TiO_2	0·75	0·84	1·03	0·86	0·80	0·82	0·80	0·80	0·81	0·85	0·88	0·87
Al_2O_3	20·19	22·98	23·28	23·37	22·59	23·20	21·96	22·13	22·02	23·14	23·18	23·43
Fe_2O_3(T)	6·58	5·86	5·55	5·99	5·85	5·92	5·57	5·02	4·99	5·36	5·30	5·60
MgO	2·25	2·10	2·01	2·10	1·80	1·83	1·69	1·65	1·66	1·78	1·87	1·93
CaO	1·02	0·93	0·51	0·71	0·78	0·71	1·40	1·03	1·11	0·85	0·77	1·13
Na_2O	0·13	0·15	0·55	0·14	0·11	0·12	1·19	2·11	1·75	0·71	0·64	0·51
K_2O	3·17	3·65	3·77	3·68	3·36	3·41	3·19	3·28	3·28	3·49	3·52	3·59
S	0·43	0·18	0·20	0·22	0·40	0·45	0·56	0·37	0·35	0·37	0·40	0·30
P_2O_5	0·17	0·14	0·19	0·14	0·22	0·25	2·95	4·26	3·63	1·36	1·15	1·24
C_{org}	n.d.	1·64	2·65	1·92	4·39	4·67	5·03	4·39	3·75	4·12	3·66	2·84
H_2O^+	n.d.	6·58	5·65	6·66	8·81	6·88	6·81	5·64	7·90	7·11	7·14	6·26
Minor Elements (p.p.m.)												
V	203	220	214	222	211	210	179	169	177	175	176	196
Cr	170	189	175	192	194	192	196	182	192	199	225	199
Mn	185	214	210	212	193	179	196	185	187	201	204	190
Ni	61	77	73	76	71	73	71	66	67	68	68	68
Ba	263	423	456	452	315	327	403	440	431	530	563	453
Ce	95	95	79	93	92	102	123	109	109	93	94	86
Th	17	17	13	14	15	13	17	18	17	18	17	19

/contd.over

APPENDIX (7.1B) contd.

Minor Elements (p.p.m.)	WBK-12	WBK-23	WBK-32	WBK-41	WBK-43	WBK-44	WBK-48	WBK-51	WBK-52	WBK-54	WBK-57	WBK-60
Pb	71	50	64	39	185	284	67	56	52	39	46	57
As	13	13	8	13	n.d.	n.d.	7	6	6	7	n.d.	6
Zn	525	153	150	121	553	523	216	133	242	132	139	152
Cu	21	16	19	18	33	33	38	24	22	32	30	21
Rb	198	228	242	243	238	232	229	228	234	243	238	233
Sr	110	122	115	116	127	125	159	152	156	188	281	158
Y	23	28	21	29	31	34	45	38	36	34	29	35
Zr	144	150	162	155	148	142	152	162	162	157	159	152
Nb	23	18	26	20	17	23	20	17	18	16	20	19
Mo	n.d.	n.d.	n.d.	n.d.	10	17	11	4	n.d.	4	4	4
La	52	69	67	68	64	42	65	78	62	79	61	69
Clay Minerals %												
Illite	(36)39	(41)54	(42)60	(41)56	(38)55	(38)60	(36)61	(37)64	(37)64	(39)66	(41)61	(40)63
Kaolinite	7	13	19	15	18	24	26	26	20	19	22	21
Smectite	(53)50	(40)27	(29)11	(35)20	(35)18	(31) 9	(33) 8	(32) 5	(35) 8	(31) 4	(25) 5	(27) 4
Chlorite	4	6	10	9	9	7	5	5	8	11	12	12
V/h	0·57	0·45	0·52	0·67	0·57	0·47	0·28	0·36	0·32	0·43	0·35	0·54
V/P	0·66	0·57	0·65	0·80	0·79	0·54	0·33	0·44	0·41	0·56	0·44	0·59

/contd.over

APPENDIX (7.1B) contd.

	WBK-12	WBK-23	WBK-32	WBK-41	WBK-43	WBK-44	WBK-48	WBK-51	WBK-52	WBK-54	WBK-57	WBK-60
% of expandable layers	>60% <80%	>60% <80%	>60% <80%	>60% <80%	>60% <80%	>60% <80%	<60%	<60%	<60%	>60% <80%	>60% <80%	>60% <80%
C.I.W.	2·75	4·50	4·00	n.d.	n.d.	3·86	4·00	4·00	4·90	4·80	4·33	3·67
C.I.I. (2θ degrees)	0·35	0·30	0·32	n.d.	n.d.	0·36	0·30	0·30	0·25	0·28	0·30	0·40
C.I.K. (2θ degrees)	0·40	n.d.	0·30	n.d.	n.d.	0·28	0·30	0·35	0·30	0·30	0·25	0·25

Note: (i) Values of illite shown in parenthesis are calculated from the abundances of K_2O in the respective samples on the assumption that all K_2O belongs to illite.

(ii) Values of smectite shown in parenthesis are the modified values obtained by adding the difference of illite abundance in the X.R.D determined abundances of smectite. The difference of illite was obtained by subtracting the calculated abundances from the X.R.D. determined abundances of illite.

APPENDIX (7.1C)

Summary Statistics: Chemistry and Mineralogy of Clay Fraction of Oxford Clay, Winterborne Kingston

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness	Kurtosis
SiO_2	52.027	9.8439	3.1375	0.90572	0.7509	0.2424E-01
TiO_2	0.84250	0.48386E-02	0.69560E-01	0.20080E-01	1.816 **	4.871 ***
Al_2O_3	22.622	0.87623	0.93607	0.27022	-1.759 **	3.472 **
Fe_2O_{3T}	5.6325	0.19926	0.44638	0.12886	0.4775	0.5824
MgO	1.8850	0.34064E-01	0.18456	0.53279E-01	0.3375	-1.099
CaO	0.91250	0.57766E-01	0.24035	0.69382E-01	0.3885	0.2596
Na_2O	0.67583	0.45559	0.67497	0.19485	1.243 *	0.5812
K_2O	3.4492	0.39536E-01	0.19884	0.57399E-01	0.9751E-01	-1.234
S	0.35583	0.12936E-01	0.11373	0.32832E-01	-0.1082	-0.4584
P_2O_5	1.3083	2.2192	1.4897	0.43004	1.126	-0.1345
V	196.00	387.82	19.693	5.6849	-0.7173E-01	-1.849
Cr	192.08	189.90	13.780	3.9781	0.8164	2.574 *
Mn	196.33	138.24	11.758	3.3941	0.2175	-1.320
Ni	69.917	20.265	4.5017	1.2995	-0.2072	0.8757E-01
Ba	421.33	7370.8	85.853	24.784	-0.3071	-0.2695E-01
Ce	97.500	136.82	11.697	3.3766	0.7798	0.9736
Th	16.250	4.0227	2.0057	0.57899	-0.6541	-0.8323
Pb	84.167	5476.9	74.006	21.364	2.324 ***	4.962 ***
As	6.5833	23.356	4.8328	1.3951	-0.5894E-01	-0.9352
Zn	253.25	29877.	172.85	49.897	1.185	-0.4948

/c ntd.over

APPENDIX (7.1C) contd.

	Mean	Variance	S. Deviation	S.E. of Mean	Skewness	Kurtosis
Cu	25·583	52·265	7·2295	2·0870	0·3570	-1·347
Rb	223·83	783·24	27·986	8·0790	-2·608 ***	7·137 ****
Sr	150·75	2245·7	47·388	13·680	2·104 **	5·248 ***
Y	31·917	43·174	6·5707	1·8968	0·1768	0·3609
Zr	153·75	48·205	6·9429	2·0043	-0·3055	-1·037
Nb	19·750	8·7500	2·9580	0·85391	0·8740	0·2481
Mo	4·5000	30·091	5·4855	1·5835	1·281 *	1·042
La	64·667	102·97	10·147	2·9293	-0·8581	1·385
C_{org}	3·2550	2·2191	1·4897	0·43003	-0·9632	0·4560
H_2O^+	6·2867	4·6885	2·1653	0·62507	-2·441 ***	7·514 ****
Fe^{2+}	0·83500	0·44590	0·66776	0·19276	-0·3572	-1·774
Fe_2O_3	2·7075	4·2010	2·0496	0·59168	-0·6350	-1·625
Ill.	57·583	93·356	9·6621	2·7892	-1·876 **	4·078 **
Kaol.	18·917	36·083	6·0069	1·7341	-1·001	1·472
Chlr.	7·6667	8·7879	2·9644	0·85576	0·1303E-01	-1·826
Smect.	15·833	274·70	16·574	4·7845	1·890 **	3·594 **

Number of Cases = 12

Significance Levels = * = 5%; ** = 1%; *** = 0·1%; **** = 0·01%.

Ill = Illite; Kaol = Kaolinite; Chlr = Chlorite; Smect = Smectite; Fe_2O_{3T} = Total iron.

APPENDIX (7.1D)

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********************************************************************************************************
CORRELATION COEFFICIENTS   MINERALOGY AND CHEMISTRY OF CLAY FRACTION OF WINTERBORNE KINGSTON        OCCFWM
********************************************************************************************************


             DEPTH      SIO2       TIO2       AL2O3      FE2O3      MGO        CAO        NA2O       K2O        S

DEPTH       1.00000   -0.80784    0.08199    0.51163   -0.71288   -0.72397    0.17877    0.42807    0.00539    0.25569
SIO2       -0.80784    1.00000    0.17940   -0.20323    0.77221    0.97152   -0.37528   -0.67461    0.34922   -0.45786
TIO2        0.08199    0.17940    1.00000    0.64859   -0.23122    0.19721   -0.60235   -0.13162    0.81979   -0.60413
AL2O3       0.51163   -0.20323    0.64859    1.00000   -0.32118   -0.06499   -0.49299   -0.21168    0.80294   -0.46598
FE2O3      -0.71288    0.77221   -0.23122   -0.32118    1.00000    0.78616   -0.16301   -0.81272   -0.00428    0.00989
MGO        -0.72397    0.97152    0.19721   -0.06499    0.78616    1.00000   -0.37391   -0.74927    0.45594   -0.52814
CAO         0.17877   -0.37528   -0.60235   -0.49299   -0.16301   -0.37391    1.00000    0.49147   -0.65491    0.48430
NA2O        0.42807   -0.67461   -0.13162   -0.21168   -0.81272   -0.74927    0.49147    1.00000   -0.42481    0.20320
K2O         0.00539    0.34922    0.81979    0.80294   -0.00428    0.45594   -0.65491   -0.42481    1.00000   -0.83230
S           0.25569   -0.45786   -0.60413   -0.46598    0.00989   -0.52814    0.48430    0.20320   -0.83230    1.00000
P2O5        0.48457   -0.73736   -0.28947   -0.25284   -0.76178   -0.79101    0.63796    0.97612   -0.53499    0.33466
V          -0.58820    0.65096    0.24886    0.21783    0.71739    0.74035   -0.52262   -0.79868    0.52632   -0.50248
CR          0.71828   -0.43219    0.04813    0.50163   -0.39788   -0.32938    0.03616    0.00200    0.13838    0.20615
MN         -0.17447    0.34237    0.59134    0.47497    0.02408    0.43904   -0.37735   -0.31173    0.74324   -0.64809
NI         -0.03823    0.03307    0.42168    0.68672    0.07385    0.18109   -0.33713   -0.38009    0.65805   -0.47127
BA          0.58305   -0.27745    0.53264    0.60896   -0.67851   -0.22539   -0.12728    0.31135    0.50487   -0.34395
CE          0.20294   -0.59061   -0.62625   -0.42004   -0.28180   -0.51550    0.71772    0.59720   -0.74325    0.64474
U          -0.09350    0.11568    0.44738    0.17918    0.11927    0.19096   -0.12324   -0.07073    0.31931   -0.18901
TH          0.28147   -0.23017   -0.39585   -0.26559   -0.33280   -0.24581    0.71333    0.44337   -0.33909    0.16041
PB         -0.01144   -0.13368   -0.20476    0.08306    0.30140   -0.14536   -0.27730   -0.35613   -0.18916    0.40058
AS         -0.62340    0.60829   -0.01014   -0.29745    0.38738    0.52121    0.15203   -0.11178    0.17368   -0.51120
ZN         -0.35543    0.14870   -0.50120   -0.46865    0.58463    0.08544   -0.06831   -0.40383   -0.50878    0.51844
CU          0.46542   -0.59923   -0.29964   -0.01802   -0.15543   -0.52580    0.21830    0.09686   -0.49798    0.86230
RB          0.02508   -0.05671    0.22345    0.19670   -0.03737    0.03362   -0.09981    0.00752    0.19520   -0.17417
SR          0.62345   -0.37154    0.08019    0.23374   -0.53953   -0.37570    0.08618    0.27088   -0.02154    0.26056
Y           0.64384   -0.84077   -0.44305    0.00032   -0.49429   -0.79574    0.72028    0.58882   -0.50592    0.57245
ZR          0.40378   -0.36465    0.49271    0.24472   -0.81465   -0.38274   -0.05170    0.68628    0.25007   -0.34797
NB         -0.45790    0.55287    0.46280   -0.07929    0.43702    0.48040   -0.39032   -0.35208    0.21291   -0.09795
MO          0.33579   -0.47156   -0.27518    0.13827    0.05105   -0.46423    0.07688   -0.10766   -0.33964    0.69286
I           0.20074   -0.17448   -0.32771    0.03907    0.21005   -0.13220   -0.27468   -0.32778   -0.21188    0.41087
LA          0.28323   -0.26210    0.23054    0.25809   -0.52142   -0.22329    0.13233    0.42292    0.26658   -0.36523
CORG        0.74498   -0.91839   -0.03619    0.32899   -0.64341   -0.90906    0.15061    0.46514   -0.24699    0.52361
H2O         0.68451   -0.71559    0.20377    0.69051   -0.57984   -0.53526   -0.10928    0.15403    0.26157   -0.02287
FE2         0.77328   -0.80991   -0.26157    0.10236   -0.62243   -0.32778    0.36459    0.54960   -0.43981    0.60036
FE3         0.78898   -0.82117   -0.28893    0.16855   -0.47685   -0.30703    0.31964    0.32025   -0.40068    0.65121
ILL         0.88556   -0.75715    0.36599    0.65887   -0.86249   -0.70321    0.05090    0.52019    0.23829   -0.02282
KAOL        0.67683   -0.85237    0.07988    0.31544   -0.68952   -0.35755    0.19265    0.61149   -0.18573    0.39576
CHLR        0.59491   -0.12153    0.60178    0.72965   -0.31928   -0.02324   -0.42085   -0.19844    0.62120   -0.30408
SMECT      -0.89411    0.79404   -0.36314   -0.64924    0.82896    0.74538   -0.02429   -0.49737   -0.18853   -0.08366
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APPENDIX (7.1D) contd.

	P205	V	CR	MN	NI	BA	CE	U	TH	PB
DEPTH	0.48457	-0.58820	0.71828	-0.17447	-0.03823	0.58305	0.20294	-0.09350	0.28147	-0.01144
SIO2	-0.73736	0.65096	-0.43219	0.34237	0.03307	-0.27745	-0.59061	0.11568	-0.23017	-0.13368
TIO2	-0.28947	0.24886	0.04813	0.59134	0.42168	0.53264	-0.62625	0.44738	-0.39585	-0.20476
AL2O3	-0.25284	0.21783	0.50163	0.47497	0.68672	0.60396	-0.42004	0.17918	-0.26559	0.08306
FE2O3	-0.76178	0.71739	-0.39788	0.02403	0.07385	-0.67351	-0.23180	0.11927	-0.33280	0.30140
MGO	-0.79101	0.74035	-0.32938	0.43904	0.18109	-0.22539	-0.61650	0.19096	-0.24681	-0.14636
CAO	0.63796	-0.52262	0.03616	-0.37735	-0.38713	-0.12728	0.71772	-0.12324	0.71333	-0.27730
NA2O	0.97612	-0.79868	0.00200	-0.31173	-0.38009	0.31135	0.59720	-0.07073	0.44337	-0.35613
K2O	-0.53499	0.52632	0.13838	0.74324	0.65805	0.50487	-0.74325	0.31931	-0.33909	-0.18916
S	0.33466	-0.50248	0.20615	-0.64809	-0.47127	-0.34395	0.64474	-0.18901	0.16041	0.40058
P205	1.00000	-0.82829	0.07569	-0.39219	-0.39776	0.24716	0.71241	-0.11058	0.52501	-0.30629
V	-0.82829	1.00000	-0.37083	0.37024	0.61733	-0.43306	-0.53082	0.30653	-0.65366	0.32661
CR	0.07569	-0.37083	1.00000	0.17431	0.11443	0.62038	0.07078	-0.18048	0.24915	-0.05493
MN	-0.39219	0.37024	0.17431	1.00000	0.62920	0.52817	-0.40983	0.51235	-0.17348	-0.51650
NI	-0.39776	0.61733	0.11443	0.62920	1.00000	0.15274	-0.14761	0.47752	-0.55126	0.18042
BA	0.24716	-0.43306	0.62038	0.52817	0.15274	1.00000	-0.15553	0.11602	0.29037	-0.59131
CE	0.71241	-0.53082	0.07078	-0.40983	-0.14761	-0.15553	1.00000	0.02564	0.24994	0.05850
U	-0.11058	0.30653	-0.18048	0.51235	0.47752	0.11602	0.02564	1.00000	-0.48604	-0.23187
TH	0.52501	-0.65366	0.24915	-0.17348	-0.55126	0.29037	0.24994	-0.48604	1.00000	-0.55887
PB	-0.30629	0.32661	-0.05493	-0.51650	0.18042	-0.59131	0.05850	-0.23187	-0.55887	1.00000
AS	-0.13938	0.32763	-0.55773	0.42183	0.09019	-0.08370	-0.03925	0.36981	0.12427	-0.59101
ZN	-0.33802	0.30438	-0.28996	-0.59624	-0.23259	-0.87228	0.05798	-0.32451	-0.34424	0.77470
CU	0.20303	-0.43804	0.43838	-0.36292	-0.12407	-0.05175	0.48324	-0.08471	0.00157	0.45976
RB	-0.01067	0.34507	0.05190	0.07063	0.39170	-0.12741	0.02666	0.31037	-0.40408	0.19112
SR	0.28831	-0.67216	0.85938	0.08272	-0.26134	0.70347	0.09586	-0.27376	0.43113	-0.28326
Y	0.72822	-0.60631	0.32437	-0.39969	-0.06172	0.10574	0.83137	-0.03804	0.41562	0.06229
ZR	0.55880	-0.49933	0.15987	0.32964	-0.05890	0.74564	-0.01511	0.21601	0.19422	-0.64782
NB	-0.44015	0.43853	-0.38526	0.02875	0.07339	-0.27778	-0.29296	0.43096	-0.63207	0.23318
MO	0.00323	-0.05975	0.24954	-0.49755	0.13437	-0.32159	0.38254	-0.11620	-0.26028	0.82005
I	-0.25835	0.06938	0.30369	-0.18420	0.03665	-0.13243	0.03463	-0.06517	-0.37190	0.49629
LA	0.37469	-0.33027	0.06653	0.44524	0.05506	0.60496	-0.08119	0.12317	0.48688	-0.68957
CORG	0.51281	-0.51689	0.44849	-0.29813	0.10282	0.23333	0.43505	-0.05437	-0.01019	0.36788
H2O	0.17813	-0.10449	0.59591	0.20544	0.54314	0.42272	0.11468	0.02898	-0.12286	0.18723
FE2	0.62949	-0.70943	0.55516	-0.60095	-0.28352	0.21135	0.54436	-0.38799	0.28339	0.28935
FE3	0.42714	-0.58403	0.54489	-0.52673	-0.24014	0.11489	0.35176	-0.41379	0.31596	0.36163
ILL	0.50871	-0.53542	0.56790	0.02420	0.15513	0.73208	0.12386	-0.02149	0.21430	-0.11164
KAOL	0.62937	-0.51642	0.28265	-0.28736	0.12592	0.27110	0.53693	0.11342	-0.03358	0.25474
CHLR	-0.24222	-0.03970	0.61659	0.33617	0.13870	0.65383	-0.61549	-0.02239	0.00812	-0.14277
SMECT	-0.48899	0.51720	-0.56137	0.03204	-0.16675	-0.65792	-0.15766	-0.02884	-0.10882	-0.00989

APPENDIX (7.1D) contd.

	AS	ZN	CU	RB	SR	Y	ZR	NB	MO	I
DEPTH	-0.62340	-0.35543	0.46542	0.02508	0.62345	0.54384	0.40378	-0.45790	0.33579	0.20074
SIO2	0.60829	0.14870	-0.59923	-0.05671	-0.37154	-0.34077	-0.35465	0.55287	-0.47156	-0.17448
TIO2	-0.01014	-0.50120	-0.29964	0.22345	0.08019	-0.44305	0.49271	0.46280	-0.27518	-0.32771
AL2O3	-0.29745	-0.46865	-0.01802	0.19670	0.23374	0.00032	0.24472	-0.07929	0.13827	0.03907
FE2O3	0.38738	0.58463	-0.15543	-0.03737	-0.53953	-0.49429	-0.81465	0.43702	0.05105	0.21005
MGO	0.62121	0.08644	-0.62580	0.03362	-0.37570	-0.79574	-0.33274	0.48040	-0.46423	-0.13220
CAO	0.15203	-0.06831	0.21830	-0.09981	0.08618	0.72028	-0.05170	-0.39032	0.07685	-0.27468
NA2O	-0.11178	-0.40383	0.09686	0.00752	0.27088	0.58382	0.63628	-0.35208	-0.10766	-0.32778
K2O	0.17368	-0.50878	-0.49798	0.19520	-0.02154	-0.50592	0.25007	0.21291	-0.33964	-0.21188
S	-0.51120	0.51844	0.86230	-0.17417	0.26056	0.57245	-0.34797	-0.09795	0.69286	0.41087
P2O5	-0.13938	-0.33802	0.20303	-0.01057	0.28831	0.72822	0.55880	-0.44015	0.00323	-0.25835
V	0.32763	0.30438	-0.43804	0.34507	-0.67216	-0.50531	-0.49933	0.43853	-0.05975	0.06938
CR	-0.55773	-0.28996	0.43838	0.05190	0.85938	0.32437	0.15987	-0.38526	0.24954	0.30369
MN	0.42183	-0.59624	-0.36292	0.07063	0.08272	-0.39969	0.32964	0.02875	-0.49756	-0.18420
NI	0.09019	-0.23259	-0.12407	0.39170	-0.26134	-0.06172	-0.05890	0.07339	0.13437	0.03665
BA	-0.08070	-0.87228	-0.05175	-0.12741	0.70847	0.10674	0.74564	-0.27778	-0.32159	-0.18243
CE	-0.08925	0.05798	0.48324	0.02665	0.09586	0.30137	-0.01511	-0.29296	0.38254	0.08463
U	0.36981	-0.32451	-0.08471	0.31037	-0.27376	-0.03304	0.21601	0.43096	-0.11620	-0.06517
TH	0.12427	-0.34424	0.00157	-0.40408	0.43113	0.41552	0.19422	-0.63207	-0.26028	-0.37190
PB	-0.59101	0.77470	0.45976	0.19112	-0.28326	0.06229	-0.64782	0.23318	0.82005	0.49629
AS	1.00000	-0.30709	-0.68193	-0.18540	-0.49232	-0.30465	0.01558	0.10652	-0.69441	-0.38322
ZN	-0.30709	1.00000	0.33256	0.01969	-0.38421	-0.13822	-0.75906	0.22683	0.51252	0.50482
CU	-0.68193	0.33256	1.00000	-0.22369	0.38656	0.58482	-0.22685	-0.18386	0.81494	0.51524
RB	-0.18540	0.01969	-0.22369	1.00000	-0.13212	-0.04111	0.05433	0.31462	0.07343	-0.21837
SR	-0.49232	-0.38421	0.38656	-0.13212	1.00000	0.23145	0.39712	-0.29557	0.04179	0.09459
Y	-0.30465	-0.13822	0.58482	-0.04111	0.23145	1.00000	0.07124	-0.52970	0.51327	0.05482
ZR	0.01558	-0.75906	-0.22685	0.06433	0.39712	0.07124	1.00000	-0.18923	-0.51678	-0.34239
NB	0.10652	0.22683	-0.18386	0.31462	-0.29557	-0.52970	-0.18923	1.00000	0.01401	-0.13433
MO	-0.69441	0.51252	0.81494	0.07343	0.04179	0.51327	-0.51678	0.01401	1.00000	0.43462
I	-0.38322	0.50482	0.51524	-0.21837	0.09459	0.05482	-0.34239	-0.13433	0.43462	1.00000
LA	0.27127	-0.73682	-0.18423	-0.28237	0.16731	0.19452	0.65550	-0.59059	-0.44913	-0.39662
CORG	-0.75430	-0.02790	0.76922	0.04222	0.36615	0.73500	0.21082	-0.34587	0.69965	0.26047
H2O	-0.54806	-0.23307	0.35654	0.24230	0.29762	0.43565	0.29141	-0.47704	0.34511	0.28417
FE2	-0.75482	0.01968	0.61645	0.06553	0.57453	0.72425	0.13971	-0.30077	0.57851	0.18102
FE3	-0.79977	0.16212	0.77572	-0.14355	0.46383	0.70859	-0.01749	-0.50602	0.67406	0.32961
ILL	-0.49154	-0.58638	0.27842	0.02542	0.53488	0.54908	0.59786	-0.36072	0.19835	-0.08820
KAOL	-0.58763	-0.20398	0.58070	0.18129	0.27003	0.73971	0.33224	-0.16507	0.59547	-0.01205
CHLR	-0.37860	-0.36722	0.01277	-0.02406	0.51523	-0.17270	0.34955	-0.09361	-0.10096	0.15155
SMECT	0.59153	0.48835	-0.39278	-0.08213	-0.51665	-0.57051	-0.54269	0.28884	-0.33002	0.02301

APPENDIX (7.1D) contd.

	LA	CORG	H2O	FE2	FE3	ILL	KAOL	CHLR	SMECT
DEPTH	0.28323	0.74498	0.68451	0.77328	0.78898	0.88556	0.67683	0.59491	-0.89411
SIO2	-0.26210	-0.91839	-0.71559	-0.80991	-0.82117	-0.75715	-0.85237	-0.12153	0.79404
TIO2	0.23054	-0.03619	0.20377	-0.26157	-0.28893	0.35599	0.07988	0.60178	-0.36314
AL2O3	0.25809	0.32899	0.69051	0.10236	0.16855	0.65887	0.31544	0.72965	-0.64924
FE2O3	-0.52142	-0.64341	-0.57984	-0.62243	-0.47685	-0.36249	-0.68952	-0.31928	0.82896
MGO	-0.22329	-0.90906	-0.58626	-0.82778	-0.80703	-0.70321	-0.85755	-0.02824	0.74638
CAO	0.13233	0.15061	-0.10928	0.36459	0.31964	0.06090	0.19265	-0.42085	-0.02429
NA2O	0.42292	0.46514	0.15403	0.54960	0.32025	0.52019	0.61149	-0.19844	-0.49737
K2O	0.26658	-0.24699	0.26157	-0.43981	-0.40068	0.23829	-0.13573	0.62120	-0.18853
S	-0.36523	0.52361	-0.02287	0.60036	0.65121	-0.02282	0.39576	-0.30408	-0.08306
P2O5	0.37469	0.51281	0.17813	0.62949	0.42714	0.50871	0.62937	-0.24222	-0.48899
V	-0.33027	-0.51689	-0.10449	-0.70943	-0.58403	-0.53542	-0.51642	-0.03970	0.51720
CR	0.06653	0.44849	0.59591	0.55516	0.54489	0.56790	0.28265	0.61659	-0.56137
MN	0.44524	-0.29813	0.20544	-0.60095	-0.52673	0.02420	-0.28736	0.33617	0.03204
NI	0.05506	0.10282	0.54314	-0.28352	-0.24014	0.15513	0.12592	0.13870	-0.16675
BA	0.60496	0.23333	0.42272	0.21135	0.11489	0.73208	0.27110	0.65883	-0.65792
CE	-0.08119	0.48505	0.11468	0.54436	0.35176	0.12386	0.53693	-0.61549	-0.15766
U	0.12317	-0.05437	0.02898	-0.38799	-0.41379	-0.02149	0.11342	-0.02239	-0.02884
TH	0.48688	-0.01019	-0.12288	0.28339	0.31596	0.21430	-0.03358	0.00812	-0.10882
PB	-0.68957	0.36788	0.18723	0.28935	0.36163	-0.11164	0.25474	-0.14277	-0.00989
AS	0.27127	-0.75430	-0.54806	-0.75482	-0.79977	-0.49154	-0.58763	-0.37860	0.59153
ZN	-0.73682	-0.02790	-0.23307	0.01963	0.16212	-0.58638	-0.20398	-0.36722	0.48835
CU	-0.18423	0.76922	0.35654	0.61645	0.77572	0.27342	0.53070	0.01277	-0.39278
RB	-0.28287	0.04222	0.24230	0.06553	-0.14355	0.02542	0.18129	-0.02406	-0.08218
SR	0.16731	0.36615	0.29762	0.57453	0.46383	0.53483	0.27003	0.51523	-0.51665
Y	0.19452	0.73600	0.43665	0.72425	0.70869	0.54908	0.73971	-0.17270	-0.57051
ZR	0.65550	0.21082	0.29141	0.13971	-0.01749	0.59786	0.33224	0.34955	-0.54269
NB	-0.59059	-0.34587	-0.47704	-0.30077	-0.50602	-0.55072	-0.15507	-0.09361	0.28884
MO	-0.44913	0.69965	0.34511	0.57851	0.67406	0.19835	0.59547	-0.10096	-0.33002
I	-0.39662	0.26047	0.28417	0.18102	0.32961	-0.08820	-0.01205	0.15155	0.02301
LA	1.00000	0.11463	0.25378	-0.13926	0.04686	0.43878	0.14712	0.24612	-0.35725
CORG	0.11463	1.00000	0.72269	0.78332	0.83435	0.72900	0.91903	0.15854	-0.81267
H2O	0.25378	0.72269	1.00000	0.43591	0.55487	0.71479	0.57081	0.47746	-0.73097
FE2	-0.13926	0.78332	0.43591	1.00000	0.83276	0.65709	0.74888	0.13123	-0.69813
FE3	0.04686	0.83435	0.55487	0.83276	1.00000	0.60308	0.64783	0.27917	-0.65785
ILL	0.43878	0.72900	0.71479	0.65709	0.60308	1.00000	0.75339	0.56797	-0.98370
KAOL	0.14712	0.91903	0.57081	0.74888	0.64783	0.75339	1.00000	0.02816	-0.83186
CHLR	0.24612	0.15854	0.47746	0.13123	0.27917	0.56797	0.02816	1.00000	-0.53877
SMECT	-0.35725	-0.81267	-0.73097	-0.69813	-0.65785	-0.93370	-0.83186	-0.53877	1.00000

APPENDIX (7.2A)

Sample No.	ILLITE	KAOLINITE	MIXED-LAYER	CHLORITE	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
BR-115	58	0	42	0	1·95	1·00	0
BR-123	65	0	33	1	2·11	0·70	0
BR-129	65	0	39	2	2·28	0·68	0
BR-131	60	0	34	1	1·45	0·90	0
BR-134	65	0	34	1	1·58	0·80	0
BR-145	65	0	33	2	2.08	0·70	0
BR-154	66	0	33	1	1·40	0·90	0
BR-167	66	0	33	1	1·51	0·80	0
BR-180	61	0	37	2	1·94	0·70	0
BR-199	70	2	24	4	2·81	0·55	0·20
BR-211	66	10	19	5	2·45	0·55	0·20
BR-236	68	12	18	2	1·62	0·60	0·40
BR-246	65	12	17	6	2·48	0·60	0·20
BR-278	64	10	17	9	2·81	0·40	0·30
BR-303	69	11	14	6	2·03	0·70	0·40
BR-320	73	10	11	6	1·61	0·80	0·40
BR-356	66	13	10	10	2·55	0·60	0·40
BR-405	69	11	17	3	1·80	0·80	0·40
BR-444	77	8	11	4	1·79	0·80	0·45
BR-468	73	10	16	1	2·32	0·60	0·45
BR-502	73	9	11	5	1·53	1·15	0·45

/contd.over

APPENDIX (7.2A) contd.

Sample No.	ILLITE	KAOLINITE	MIXED-LAYER	CHLORITE	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
BR-543	65	10	17	8	2·30	0·60	0·40
BR-560	64	8	20	8	1·65	0·90	0·40
BR-606	67	10	13	10	2·45	0·55	0·40
BR-627	66	11	13	10	2·43	0·55	0·40
BR-656	68	10	16	6	1·90	0·80	0·40
BR-688	69	8	17	6	1·90	0·80	0·40
BR-706	68	11	15	6	1·76	0·80	0·45
BR-736	66	14	14	6	1·72	0·80	0·40
BR-765	67	14	14	5	1·80	0·70	0·40
BR-801	65	11	15	9	2·60	0·55	0·40
BR-812	60	19	18	3	2·40	0·60	0·40
BR-820	67	13	16	4	2·36	0·55	0·40
BR-826	68	10	16	6	2·18	0·70	0·40
BR-855	62	12	16	10	2·85	0·50	0·40
BR-891	70	12	12	6	1·85	0·75	0·40
BR-920	70	12	11	7	2·64	0·55	0·40
BR-958	63	13	16	8	2·15	0·70	0·40
BR-981	69	11	10	10	2·97	0·45	0·40
BR-988	68	12	15	5	1·89	0·75	0·40
BR-1008	68	10	15	7	1·96	0·65	0·30
BR-1052	71	13	12	4	2·34	0·55	0·30

/contd.over

APPENDIX (7.2A) contd.

Sample No.	ILLITE	KAOLINITE	MIXED-LAYER	CHLORITE	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
BR-1093	64	13	16	7	2·40	0·55	0·30
BR-1123	65	13	13	9	2·70	0·50	0·40
BR-1157	63	11	17	9	2·94	0·50	0·40
BR-1194	66	11	16	7	2·43	0·55	0·40
BR-1220	66	11	17	6	2·00	0·70	0·40
BR-1257	69	12	14	5	2·37	0·55	0·40
BR-1301	62	12	18	7	2·25	0·70	0·40
BR-1339	69	11	14	6	2·34	0·58	0·30
BR-1377	64	16	16	4	2·81	0·50	0·40
BR-1386	61	12	16	11	2·73	0·55	0·30
BR-1392	65	16	14	5	2·68	0·55	0·40
BR-1424	61	12	17	10	2·66	0·50	0·40
BR-1436	68	15	13	4	2·37	0·60	0·20
BR-1467	64	14	11	11	2·67	0·55	0·40
BR-1513	65	16	15	4	2·18	0·60	0·40
BR-1544	67	14	10	9	2·15	0·60	0·40
BR-1583	66	14	15	5	2·33	0·60	0·40
BR-1636	70	13	12	5	1·90	0·80	0·40
BR-1676	65	18	10	7	2·28	0·70	0·40
BR-1683	66	14	14	6	2·56	0·55	0·40

/contd.over

APPENDIX (7.2A) contd.

Sample No.	ILLITE	KAOLINITE	MIXED-LAYER	CHLORITE	C.I.W.	C.I.I. (2θ degrees)	C.I.K. (2θ degrees)
BR-1691	72	12	13	3	2·28	0·70	0·40
BR-1698	68	13	15	3	2·37	0·60	0·20
BR-1713	65	14	16	5	2·24	0·70	0·40
BR-1721	65	17	17	1	2·22	0·70	0·40
BR-1734	62	16	14	8	2·37	0·60	0·40
BR-1750	62	16	17	5	2·42	0·50	0·20
BR-1755	64	16	13	7	2·28	0·70	0·40
BR-1757	67	18	9	6	1·71	0·80	0·40
BR-1762	68	15	13	4	2·36	0·70	0·20
BR-1771	65	15	15	5	1·89	0·80	0·40
BR-1781	63	21	13	3	1·92	0·70	0·20
BR-1811	59	33	6	2	1·91	0·70	0·20
BR-1831	59	26	11	4	2·66	0·50	0·40
BR-1852	58	34	6	2	2·40	0·55	0·20
BR-1877	59	31	7	3	2·22	0·75	0·20
BR-1890	58	30	9	3	1·92	0·70	0·20

APPENDIX (7.2B)

Major Elements Oxides (%)	BR-167	BR-278	BR-468	BR-627	BR-826	BR-988	BR-1194	BR-1301	BR-1339	BR-1583	BR-1676	BR-1755
SiO_2	50·57	40·89	49·73	49·23	47·78	47·01	45·85	46·48	47·59	45·33	45·30	46·49
TiO_2	0·79	0·88	0·85	0·92	0·89	0·92	0·82	0·91	0·97	0·91	0·89	0·85
Al_2O_3	19·45	23·66	23·50	24·92	23·64	22·85	24·13	24·29	23·69	24·01	25·13	24·05
Fe_2O_3(T)	6·40	5·62	5·70	6·20	5·10	5·56	5·16	5·44	5·11	4·35	4·04	4·05
MgO	2·73	2·06	2·42	2·24	2·02	1·81	1·83	1·90	2·16	2·12	1·97	2·20
CaO	1·11	0·77	1·01	0·63	0·47	0·82	0·56	0·51	0·19	0·23	0·12	0·11
Na_2O	0·76	1·54	0·46	0·50	1·60	1·60	2·23	1·03	0·39	0·58	0·70	0·76
K_2O	4·18	4·32	4·44	4·72	4·24	3·72	4·06	4·06	4·06	3·96	3·53	3·93
P_2O_5	1·83	2·54	1·29	0·65	2·82	3·22	3·53	1·21	0·49	0·29	0·44	0·24
L.O.I	10·30	10·62	10·27	10·27	10·25	11·00	14·25	13·50	13·50	17·07	16·00	17·00
Minor Elements (p.p.m.)												
V	186	213	229	263	219	187	182	204	198	181	181	178
Cr	176	206	173	188	193	165	197	189	177	224	198	211
Mn	138	186	220	199	158	162	174	191	178	173	155	159
Ni	64	84	76	78	80	65	74	71	66	75	68	72
Ba	385	556	462	403	392	412	548	497	462	483	453	446
Ce	45	76	65	85	62	74	66	92	75	75	72	90
Th	13	11	13	14	12	13	16	17	13	14	13	11
Pb	22	26	21	32	24	26	24	24	28	24	24	22

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APPENDIX (7.2B) contd.

Minor Elements (p.p.m.)	BR-167	BR-278	BR-468	BR-627	BR-826	BR-988	BR-1194	BR-1301	BR-1339	BR-1583	BR-1676	BR-1755
As	9	8	9	6	11	10	n.d.	10	n.d.	n.d.	7	n.d.
Zn	68	94	103	98	94	75	92	88	93	84	72	97
Cu	15	27	23	26	25	24	33	33	31	22	30	35
Rb	229	255	279	274	265	254	268	259	267	279	244	253
Sr	72	104	97	106	86	104	125	126	105	110	105	119
Y	22	29	23	24	23	29	29	31	22	22	29	36
Zr	131	164	149	158	164	162	157	151	162	161	170	164
Nb	25	20	14	17	18	14	20	15	20	17	22	19
Mo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5	n.d.	n.d.	4	4
La	31	65	27	27	37	40	32	37	44	34	45	56
Clay Minerals(%)												
Illite	(47)66	(49)64	(50)73	(53)66	(48)68	(42)68	(46)66	(46)62	(46)69	(45)66	(40)65	(44)64
Kaolinite	0	10	10	11	10	12	11	12	11	14	18	16
Mixed-Layer	(52)33	(32)17	(39)16	(26)13	(36)16	(41)15	(36)16	(34)18	(37)14	(36)15	(35)10	(33)13
Chlorite	1	9	1	10	6	5	7	7	6	5	7	7

/contd.over

APPENDIX (7.2B) contd.

	BR-167	BR-278	BR-468	BR-627	BR-826	BR-988	BR-1194	BR-1301	BR-1339	BR-1583	BR-1676	BR-1755
C.I.W.	1·51	2·81	2·32	2·43	2·18	1·89	2·43	2·25	2·34	2·33	2·28	2·28
C.I.I. (2θ degrees)	0·80	0·40	0·60	0·55	0·70	0·75	0·55	0·70	0·58	0·60	0·70	0·70
C.I.K. (2θ degrees)	0	0·30	0·45	0·40	0·40	0·40	0·40	0·40	0·30	0·40	0·40	0·40

Note: (i) Values of illite shown in parenthesis are calculated from the abundances of K_2O in the respective samples on the assumption that the entire amount of K_2O belongs to illite.

(ii) Values of mixed-layer mineral shown in parenthesis are the modified values obtained by adding the difference of illite values in the X.R.D. determined abundances of mixed-layer minerals. The difference of illite value was obtained by subtracting the calculated abundances of illite from the X.R.D. determined values of illite.

APPENDIX (7.2C)

Summary Statistics: Chemistry and Mineralogy of Clay Fraction of Oxford Clay, Warlingham Samples

	Mean	Variance	S.Deviation	S.E. of Mean	Skewness	Kurtosis
SiO_2	46·854	6·4306	2·5359	0·73204	-0·8755	1·948
TiO_2	0·88333	0·24242E-02	0·49237E-01	0·14213E-01	-0·3227	0·1357
Al_2O_3	23·610	2·0925	1·4466	0·41759	-2·381 ***	7·067 ****
Fe_2O_{3T}	5·2308	0·59037	0·76836	0·22181	-0·3075	-0·6822
MgO	2·1217	0·68106E-01	0·26097	0·75336E-01	1·124	1·567
CaO	0·54417	0·11555	0·33993	0·98130E-01	0·2259	-1·066
Na_2O	1·0125	0·34717	0·58921	0·17009	0·8901	-0·2707
K_2O	4·1017	0·99724E-01	0·31579	0·91161E-01	0·1321	0·5816
P_2O_5	1·5458	1·4576	1·2073	0·34852	0·5002	-1·380
V	201·75	656·20	25·616	7·3948	1·366 *	1·705
Cr	191·42	294·08	17·149	4·9504	0·3087	-0·3453
Mn	174·50 *	495·18	22·253	6·4238	0·4868	0·3409
Ni	72·917 *	40·447	6·3598	1·8359	0·1205	-0·9722
Ba	458·25 *	3170·6	56·308	16·255	0·4748	-0·5725
Ce	73·083 *	166·45	12·901	3·7243	-0·5615	0·9383
Th	13·333	3·1515	1·7753	0·51247	0·7973	0·6346
Pb	24·750	8·9318	2·9886	0·86274	1·320 *	2·273
As	5·8333	20·333	4·5092	1·3017	-0·5189	-1·681
Zn	88·167	123·61	11·118	3·2094	-0·7392	-0·6196
Cu	27·000	32·727	5·7208	1·6514	-0·5349	0·1949
Rb	260·50	216·45	14·712	4·2471	-0·7092	0·4646

/contd.over

APPENDIX (7.2C) contd.

	Mean	Variance	S.Deviation	S.E. of Mean	Skewness	Kurtosis
Sr	104·92	234·45	15·312	4·4201	-0·6848	0·8582
Y	26·583	20·629	4·5419	1·3111	0·6747	-0·3015
Zr	157·75	104·75	10·235	2·9545	-1·767 **	3·834 **
Nb	18·417	10·811	3·2879	0·94915	0·3851	-0·3206E-01
Mo	1·0833	3·9015	1·9752	0·57020	1·391 *	0·2936E-01
La	39·583	132·45	11·509	3·3222	1·133	0·9174
Ill.	66·000	12·000	3·4641	1·0000	1·701 **	3·675 **
Kaol.	11·667	18·061	4·2498	1·2268	-1·846 **	5·742 ****
Chlr.	6·0000	5·8182	2·4121	0·69631	-0·4664	0·8451
Mix.Lyr.	16·333	46·606	6·8269	1·9707	2·477 ***	7·025 ****

Number of Cases = 12

Significance Levels = * = 5%; ** = 1%; *** = 0·1%; **** = 0·01%.

Fe_2O_{3T} = Total iron

Mix.Lyr = Mixed-layer clay mineral.

APPENDIX (7.2D)

CORRELATION COEFFICIENTS   CHEMISTRY AND MINERALOGY OF OXFORD CLAY CLAY FRACTION ,WARLINGHAM SAMPLES

	DEPTH	SI02	TI02	AL203	FE203	MGO	CAO	NA20	K20	P205
DEPTH	1.00000	-0.20835	0.40520	0.56986	-0.83099	-0.59818	-0.87044	-0.02329	-0.67290	-0.34065
SI02	-0.20835	1.00000	-0.17858	-0.41884	0.43147	0.58223	0.34865	-0.40800	0.30574	-0.14349
TI02	0.40520	-0.17858	1.00000	0.52383	-0.17574	-0.43912	-0.46531	-0.27858	-0.07991	-0.31770
AL203	0.56986	-0.41884	0.52383	1.00000	-0.52927	-0.64388	-0.64669	-0.01350	-0.06018	-0.28894
FE203	-0.83099	0.43147	-0.17574	-0.52927	1.00000	0.41881	0.86992	0.05873	0.67885	0.39072
MGO	-0.59818	0.58223	-0.43912	-0.64388	0.41881	1.00000	0.43165	-0.59651	0.44837	-0.34605
CAO	-0.87044	0.34865	-0.46531	-0.64669	0.86992	0.43165	1.00000	0.18635	0.47917	0.53250
NA20	-0.02329	-0.40800	-0.27858	-0.01350	0.05873	-0.59651	0.13635	1.00000	-0.14347	0.90364
K20	-0.67290	0.30574	-0.07991	-0.06018	0.67885	0.44837	0.47917	-0.14347	1.00000	0.03474
P205	-0.34065	-0.14349	-0.31770	-0.28894	0.39072	-0.34605	0.53250	0.90364	0.03474	1.00000
LOI	0.84036	-0.34550	0.08878	0.41828	-0.87765	-0.29560	-0.81732	-0.16571	-0.63319	-0.51372
V	-0.51539	0.28086	0.24723	0.23483	0.57939	0.19562	0.34245	-0.21251	0.85515	-0.04060
CR	0.37936	-0.60693	-0.05240	0.41887	-0.64001	-0.13327	-0.59199	0.03201	-0.12319	-0.31167
MN	-0.21019	0.00470	0.27713	0.45731	0.28177	-0.04399	0.20377	-0.21290	0.58875	-0.13314
NI	-0.26337	-0.43221	0.00677	0.42155	0.01025	-0.12753	0.01489	0.21573	0.57132	0.12451
BA	0.12706	-0.74565	-0.03509	0.37928	-0.22185	-0.43111	-0.15043	0.36129	-0.06501	0.15363
CE	0.51504	-0.36889	0.55480	0.72259	-0.35455	-0.43579	-0.53531	-0.15825	-0.04333	-0.42027
U	-0.86276	-0.07626	-0.50581	-0.58690	0.53041	0.59569	0.70670	-0.02369	0.37917	0.20734
TH	0.25787	0.16303	0.04854	0.17629	0.16173	-0.30938	0.02611	0.14254	-0.00757	0.07663
PB	-0.02591	-0.05995	0.65487	0.36063	0.28514	-0.22321	-0.12416	-0.08738	0.34918	-0.08170
AS	-0.53593	0.18276	-0.07916	-0.27874	0.51537	0.06569	0.60721	0.14456	0.15918	0.37559
ZN	-0.06347	-0.03975	0.15666	0.48347	0.02425	-0.03990	-0.08944	-0.04295	0.63663	-0.08813
CU	0.65139	-0.41403	0.27111	0.71262	-0.53835	-0.52232	-0.65008	0.18717	-0.25614	-0.14321
RB	0.17549	0.00530	0.41540	0.57200	-0.06928	-0.23346	-0.16551	-0.09601	0.42304	-0.11805
SR	0.64497	-0.45819	0.26328	0.70780	-0.44724	-0.56974	-0.51447	0.19128	-0.22483	-0.13295
Y	0.39765	-0.46158	-0.13957	0.33388	-0.42034	-0.47411	-0.30437	0.33198	-0.41209	0.04558
ZR	0.58769	-0.61178	0.57188	0.78517	-0.68411	-0.70437	-0.71302	0.15735	-0.35708	-0.10148
NB	-0.15579	-0.05333	-0.43614	-0.41228	-0.05161	0.39218	-0.08385	-0.01279	-0.15920	-0.05517
MO	0.53156	-0.17322	0.02493	0.35762	-0.50561	-0.24720	-0.48798	-0.16970	-0.46371	-0.43177
I	0.21712	-0.11813	-0.15097	0.09361	0.07144	-0.37740	-0.03766	0.48605	-0.04802	0.35161
LA	0.12003	-0.76614	0.12942	0.16033	-0.40841	-0.25543	-0.34901	0.16426	-0.31422	-0.02965
ILL	-0.13443	0.32195	0.13858	0.08944	0.12193	0.15687	0.24010	-0.28461	0.19031	-0.05326
KAOL	0.71216	-0.39110	0.52715	0.87884	-0.73295	-0.59519	-0.71005	0.01634	-0.39244	-0.24109
CHLR	0.17728	-0.51885	0.45162	0.66803	-0.12655	-0.57045	-0.33262	0.28273	0.15635	0.08398
MIXLYR	-0.43775	0.26342	-0.55804	-0.82850	0.43911	0.55534	0.43770	0.03435	0.09249	0.14743

APPENDIX (7.2D) contd.

	LOI	V	CR	MN	NI	BA	CE	U	TH	PB
DEPTH	0.84036	-0.51539	0.37986	-0.21019	-0.26337	0.12706	0.51504	-0.86276	0.25787	-0.02591
SIO2	-0.34550	0.28086	-0.60693	0.00470	-0.43221	-0.74565	-0.36889	-0.07626	0.16303	-0.05995
TIO2	0.08878	0.24723	-0.05240	0.27713	0.00677	-0.03509	0.55480	-0.50581	0.04854	0.65487
AL2O3	0.41828	0.23483	0.41887	0.45731	0.42155	0.37928	0.72259	-0.58690	0.17629	0.36063
FE2O3	-0.87765	0.57939	-0.64001	0.28177	0.01025	-0.22185	-0.35455	0.53041	0.16173	0.28514
MGO	-0.29660	0.19562	-0.18827	-0.04399	-0.12753	-0.43111	-0.43579	0.59569	-0.30938	-0.22321
CAO	-0.81732	0.34245	-0.59199	0.20377	0.01489	-0.15043	-0.53531	0.70670	0.02611	-0.12416
NA2O	-0.16571	-0.21251	0.03201	-0.21290	0.21573	0.36129	-0.15825	-0.02369	0.14254	-0.08738
K2O	-0.63319	0.85515	-0.12319	0.58875	0.57132	-0.06501	-0.04333	0.37917	-0.00757	0.34918
P2O5	-0.51372	-0.04060	-0.31167	-0.13314	0.12451	0.15363	-0.42027	0.20734	0.07663	-0.08170
LOI	1.00000	-0.66119	0.66548	-0.25142	-0.17255	0.32370	0.41328	-0.52248	0.13551	-0.23884
V	-0.66119	1.00000	-0.25387	0.66463	0.52384	-0.20813	0.14751	0.14400	-0.00400	0.55246
CR	0.66548	-0.25387	1.00000	-0.11614	0.53215	0.44030	0.33512	-0.15083	-0.10053	-0.10953
MN	-0.25142	0.66463	-0.11614	1.00000	0.47503	0.37020	0.39059	0.10724	0.25774	0.24263
NI	-0.17255	0.52384	0.53215	0.47503	1.00000	0.38060	0.19177	0.19907	-0.18251	0.14229
BA	0.32370	-0.20813	0.44030	0.37020	0.38060	1.00000	0.28729	0.15277	0.26283	-0.08873
CE	0.41328	0.14751	0.33512	0.39059	0.19177	0.28729	1.00000	-0.48622	0.15745	0.37076
U	-0.52248	0.14400	-0.15083	0.10724	0.19907	0.15277	-0.43622	1.00000	-0.37488	-0.28444
TH	0.13551	-0.00400	-0.10053	0.25774	-0.18251	0.26283	0.15745	-0.37488	1.00000	0.08567
PB	-0.23884	0.55246	-0.10953	0.24263	0.14229	-0.08873	0.37076	-0.28444	0.08567	1.00000
AS	-0.71345	0.37816	-0.50924	0.04711	0.03751	-0.36359	-0.25289	0.36435	-0.04921	-0.09107
ZN	-0.11772	0.57536	0.15695	0.72426	0.65721	0.29210	0.40679	-0.03694	-0.08598	0.16826
CU	0.52557	-0.14888	0.29004	0.16710	0.05997	0.49078	0.71194	-0.53440	0.19693	0.11698
RB	0.04298	0.45819	0.17890	0.73973	0.54263	0.26024	0.32640	-0.32547	0.24365	0.27395
SR	0.59868	-0.17273	0.39206	0.34432	0.11755	0.54323	0.78790	-0.53056	0.47937	0.13261
Y	0.42098	-0.35415	0.26971	-0.11738	-0.04537	0.33992	0.59174	-0.20319	-0.02631	-0.18920
ZR	0.41348	-0.05990	0.42537	0.02694	0.31110	0.24289	0.52480	-0.52045	-0.28520	0.31876
NB	0.12846	-0.36563	0.17238	-0.65667	-0.24600	-0.03891	-0.49381	0.30914	-0.24401	-0.10871
MO	0.54769	-0.29960	0.24848	-0.11893	-0.23821	0.10115	0.55335	-0.32508	0.19876	-0.27335
I	0.16075	-0.22552	-0.02850	0.09964	-0.12034	0.57753	0.05470	-0.19593	0.73195	-0.02492
LA	0.25431	-0.30906	0.38605	-0.21743	0.16840	0.39017	0.34925	0.19494	-0.58884	-0.02445
ILL	-0.20775	0.26021	-0.43461	0.59084	-0.01651	-0.00746	-0.14849	0.09456	-0.08870	-0.04391
KAOL	0.50019	-0.02589	0.37879	0.16438	0.23769	0.15234	0.58751	-0.67288	-0.02008	0.14315
CHLR	0.03175	0.34722	0.28791	0.23034	0.46816	0.26439	0.61639	-0.32332	-0.12738	0.71882
MIXLYR	-0.21717	-0.23860	-0.11700	-0.48352	-0.30500	-0.13446	-0.50817	0.48513	0.10252	-0.32081

APPENDIX (7.2D) contd.

	AS	ZN	CU	RB	SR	Y	ZR	NB	MO	I
DEPTH	-0.53593	-0.06347	0.65139	0.17549	0.64497	0.39765	0.58769	-0.15579	0.53156	0.21712
SIO2	0.18276	-0.03975	-0.41403	0.00530	-0.45819	-0.46158	-0.61178	-0.05333	-0.17322	-0.11813
TIO2	-0.07916	0.15666	0.27111	0.41540	0.26328	-0.13957	0.57188	-0.43614	0.02493	-0.15097
AL2O3	-0.27874	0.48347	0.71262	0.57200	0.70780	0.33388	0.73517	-0.41228	0.35762	0.09361
FE2O3	0.51537	0.02425	-0.53835	-0.06928	-0.44724	-0.42034	-0.63411	-0.05161	-0.50561	0.07144
MGO	0.06669	-0.03990	-0.62232	-0.23346	-0.66974	-0.47411	-0.70437	0.39218	-0.24720	-0.37740
CAO	0.60721	-0.08944	-0.66008	-0.16551	-0.51447	-0.30437	-0.71302	-0.08385	-0.48798	-0.03766
NA2O	0.14456	-0.04295	0.18717	-0.09601	0.19128	0.33198	0.15735	-0.01279	-0.16970	0.48605
K2O	0.15918	0.53663	-0.25614	0.42304	-0.22483	-0.41209	-0.35708	-0.15920	-0.46371	-0.04802
P2O5	0.37559	-0.08813	-0.14321	-0.11805	-0.13295	0.04558	-0.10148	-0.05517	-0.43177	0.35161
LOI	-0.71345	-0.11772	0.52557	0.04298	0.59868	0.42098	0.41348	0.12846	0.54769	0.16075
V	0.37816	0.57536	-0.14888	0.45819	-0.17273	-0.35415	-0.05990	-0.36563	-0.29960	-0.22552
CR	-0.50924	0.15695	0.29004	0.17890	0.39206	0.26971	0.42537	0.17238	0.24848	-0.02850
MN	0.04711	0.72426	0.16710	0.73973	0.34432	-0.11738	0.02694	-0.65667	-0.11893	0.09964
NI	0.03751	0.65721	0.05997	0.54263	0.11755	-0.04537	0.31110	-0.24600	-0.23821	-0.12034
BA	-0.36359	0.29210	0.49078	0.26024	0.64323	0.33992	0.24289	-0.03891	0.10115	0.57753
CE	-0.25289	0.40679	0.71194	0.32640	0.78790	0.59174	0.52480	-0.49381	0.56335	0.05470
U	0.36435	-0.03694	-0.53440	-0.32547	-0.53056	-0.20319	-0.52045	0.30914	-0.32508	-0.19593
TH	-0.04921	-0.08598	0.19693	0.24365	0.47937	-0.02531	-0.23520	-0.24401	0.19876	0.73195
PB	-0.09107	0.16826	0.11698	0.27395	0.13261	-0.13920	0.31876	-0.10871	-0.27335	-0.02492
AS	1.00000	-0.22607	-0.42642	-0.30969	-0.49266	-0.10579	-0.27282	-0.20950	0.02211	-0.29414
ZN	-0.22607	1.00000	0.40736	0.72585	0.33599	0.04471	0.23289	-0.44723	-0.12488	0.09021
CU	-0.42642	0.40736	1.00000	0.17390	0.83131	0.59975	0.57914	-0.13533	0.59534	0.48204
RB	-0.30969	0.72585	0.17390	1.00000	0.37833	-0.29318	0.29794	-0.66246	-0.32378	0.08764
SR	-0.49266	0.33599	0.83131	0.37833	1.00000	0.54130	0.44712	-0.38207	0.48720	0.54035
Y	-0.10579	0.04471	0.69975	-0.29318	0.64130	1.00000	0.34957	-0.08472	0.70342	0.19942
ZR	-0.27282	0.23289	0.57914	0.29794	0.44712	0.34957	1.00000	-0.21004	0.18100	-0.16944
NB	-0.20950	-0.44723	-0.13533	-0.66246	-0.38207	-0.08472	-0.21004	1.00000	-0.00583	0.07917
MO	0.02211	-0.12488	0.59534	-0.32378	0.48720	0.70342	0.18100	-0.00583	1.00000	0.11168
I	-0.29414	0.09021	0.48204	0.08764	0.54035	0.19942	-0.16944	0.07917	0.11168	1.00000
LA	-0.13109	0.04535	0.41700	-0.33633	0.20150	0.57727	0.52001	0.23324	0.29760	-0.15500
ILL	-0.06402	0.37295	-0.15138	0.54761	-0.08055	-0.36979	0.00000	-0.45495	-0.42516	-0.16216
KAOL	-0.16920	0.22640	0.57959	0.41002	0.53741	0.35481	0.88411	-0.43157	0.39349	-0.14954
CHLR	-0.20060	0.39662	0.51387	0.29716	0.48491	0.37341	0.71071	-0.20633	-0.01908	0.00353
MIXLYR	0.20869	-0.47032	-0.46554	-0.63810	-0.46499	-0.16516	-0.80147	0.57241	-0.02247	0.17413

APPENDIX (7.2D) contd.

	LA	ILL	KAOL	CHLR	MIXLYR
DEPTH	0.12003	-0.13443	0.71216	0.17728	-0.43775
SIO2	-0.76614	0.32195	-0.39110	-0.51885	0.26342
TIO2	0.12942	0.13858	0.52715	0.45162	-0.55804
AL2O3	0.16033	0.08944	0.87884	0.66803	-0.82850
FE2O3	-0.40841	0.12193	-0.73295	-0.12655	0.43911
MGO	-0.25643	0.15687	-0.69619	-0.57045	0.55534
CAO	-0.34901	0.24010	-0.71005	-0.33262	0.43770
NA2O	0.16426	-0.28461	0.01634	0.28273	0.03435
K2O	-0.31422	0.19031	-0.39244	0.15635	0.09249
P2O5	-0.02965	-0.05326	-0.24109	0.08393	0.14743
LOI	0.25431	-0.20775	0.50019	0.03175	-0.21717
V	-0.30906	0.26021	-0.02589	0.34722	-0.23860
CR	0.38605	-0.43461	0.37879	0.28791	-0.11700
MN	-0.21743	0.59084	0.16438	0.23034	-0.48352
NI	0.16840	-0.01651	0.23769	0.46816	-0.30500
BA	0.39017	-0.00746	0.15234	0.26439	-0.18446
CE	0.34925	-0.14849	0.58751	0.61639	-0.50817
U	0.19494	0.09456	-0.67288	-0.32332	0.48513
TH	-0.58884	-0.08870	-0.02008	-0.12738	0.10252
PB	-0.02445	-0.04391	0.14315	0.71882	-0.32081
AS	-0.13109	-0.06402	-0.16920	-0.20060	0.20869
ZN	0.04535	0.37295	0.22640	0.39662	-0.47032
CU	0.41700	-0.15138	0.57959	0.51387	-0.46554
RB	-0.33638	0.54761	0.41002	0.29716	-0.63810
SR	0.20150	-0.08055	0.53741	0.48491	-0.46499
Y	0.57727	-0.36979	0.35481	0.37341	-0.16516
ZR	0.52001	0.00000	0.88411	0.71071	-0.80147
NB	0.23324	-0.45495	-0.43157	-0.20633	0.57241
MO	0.29760	-0.42516	0.39349	-0.01908	-0.02247
I	-0.15500	-0.16216	-0.14954	0.00353	0.17413
LA	1.00000	-0.33521	0.21809	0.40608	-0.10915
ILL	-0.33521	1.00000	0.09880	-0.15232	-0.51511
KAOL	0.21809	0.09880	1.00000	0.50550	-0.85125
CHLR	0.40608	-0.15232	0.50550	1.00000	-0.59071
MIXLYR	-0.10915	-0.51511	-0.85125	-0.59071	1.00000

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