UNIVERSITY OF SOUTHAMPTON

FACULTY OF SCIENCE

GEOLOGY

Doctor of Philosophy

MINERALOGICAL AND GEOCHEMICAL STUDIES OF UPPER EOCENE SEDIMENTS IN THE HAMPSHIRE BASIN OF SOUTHERN ENGLAND

by

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To My Parents TIJANI ADELODUN & AJOKE OTOLORIN

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

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MINERALOGICAL AND GEOCHEMICAL STUDIES OF UPPER EOCENE SEDIMENTS IN THE HAMPSHIRE BASIN OF SOUTHERN ENGLAND

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Sediments of the marine Barton Clay Formation, Barton Sand Formation, and the non-marine 'Lower Headon Beds' exposed along the coastal cliffs on mainland Hampshire and the Isle of Wight have been investigated mineralogically and geochemically.

Sandy-clays and quartz-sand predominate and are dominated by quartz, clays and microcline feldspar with small amounts of anatase, goethite, pyrite, albite, oligoclase, biogenic calcite, aragonite and organic-carbon. The clay assemblage comprises degraded illite, smectite, kaolinite, illite-smectite and traces of chlorite.

Geochemically the sediments are silica-rich but poor in alkali and alkaline-earths. Their trace element contents show strong association with clays and feldspars; whilst substantial concentrations of As, Ce, Cr, Cu, I, Mn, Pb, Sr, Zn occur with plant remains and/or carbonates. In general, the sediments show no significant facies-related compositional variation nor evidence for substantial diagenetic alteration.

Support is provided for sediment derivation from Cretaceous sediments and intrabasinally-exposed Tertiary sediments on adjoining land areas in England and horst structures in the English Channel. Continuous low-scale tectonic movements and episodic eustatic sea-level fluctuations caused alternating periods of slow, clayey deposition and relatively shorter periods of rapid, sandy sedimentation.

Palaeosols related to red-yellow podzols and hydromorphic swamps have been identified. These contain abundant authigenic kaolinite and goethite. Lepidocrocite, jarosite and gypsum occur in association with the hydromorphic palaeosols, although these are difficult to distinguish from Recent weathering products.

Authigenesis of Fe- and Ca-rich phases was widespread. Freshwater limestones were formed, dominantly composed of micritic low-Mg calcites. Glauconitic-mica formed in the Barton Clay, predominantly within microfossil tests. Its time of formation appears to be substantially less than previously considered likely. Calcian-siderite ironstones and ferroan-calcite septarian concretions formed in early diagenesis at very shallow depths. The siderite shows between 1 and 10 mol% Ca^{2+} substitution. The substitution is facies-related, and greatest in marine and 'brackish' sediments. Ferroan calcite occurs in association with glauconie within marine sediments only. It is believed to form rather than siderite as a result of the early depletion of iron-oxide during glauconitisation. The formation of these low-Mg carbonate phases is highly unusual at shallow depths, and is believed to result from the high influx of iron-oxide and dissolved $CaCO_3$.

The clay assemblage, the red-yellow podzol palaeosols and the authigenic phases, together, suggest the prevalence of a warm, humid, probably subtropical palaeoclimate with moderate-intense weathering and active erosion.

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CHAPTER 1

INTRODUCTION

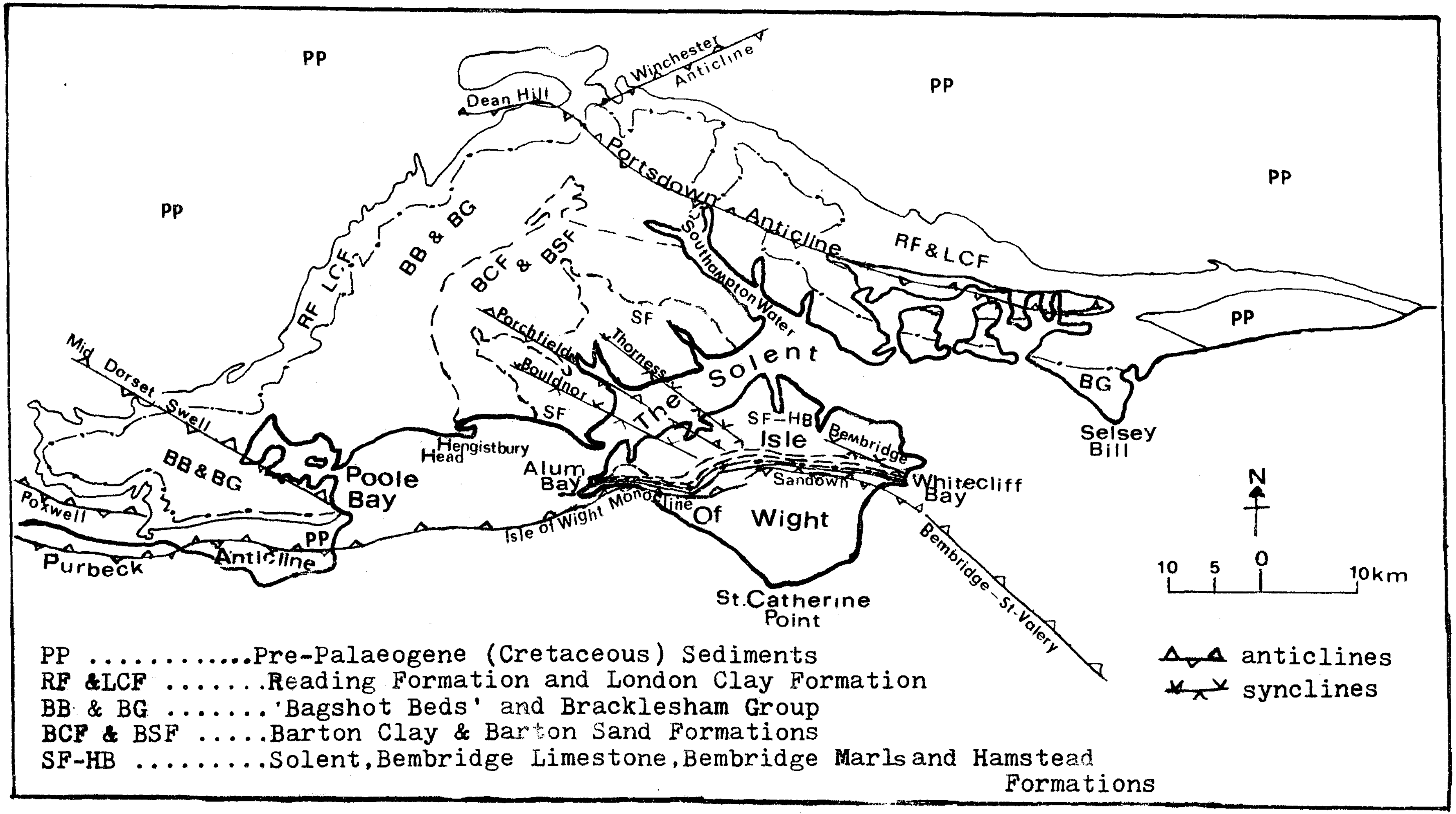
1.1 Aims of the Study

The present study principally aims at investigating the mineralogical and geochemical compositions of the Upper Eocene deposits in the Hampshire Basin of southern England (Fig.1). The deposits successively consist of the Barton Clay Formation, Barton Sand Formation and the 'Lower Headon Beds' (Table 1) exposed on the cliffs between Highcliffe and Mudeford on mainland Hampshire, and at Alum Bay and Whitecliff Bay on the Isle of Wight. The Barton Clay comprises a pebble bed at the base, fossiliferous marine clays and glauconitic sandy clays. The Barton Sand predominantly consists of very sparsely fossiliferous sands, whilst the 'Lower Headon Beds' comprise non-marine clays, sands, lignites and freshwater limestones. Banded and nodular diagenetic calcareous concretions and sideritic ironstones are also common in the succession.

The study of these sediments and the other Palaeogene Beds of the Hampshire Basin started, in earnest, in the early nineteenth century. Notable among the pioneering workers were Webster (1814), Prestwich (1846-1852), the Marchioness of Hastings (1852), Forbes (1856), Fisher (1862), Gardner et al. (1888) and Reid & Strahan (1889). Their studies were mainly on the litho- and bio-stratigraphy. These were also the main areas of interest of almost all later workers, including White (1915, 1921), Burton (1929, 1933), Curry (1942-1978), Edwards (1967, 1970), Murray & Wright (1974), Stinton (1975), Keen (1978), Bujak et al. (1980) and Hooker et al. (1980). Floral studies, useful in palaeo-environmental interpretation, have also been undertaken by authors including Chandler (1961, 1964) and Hubbard & Boulter (1982). However, there have only been a few broad-scale mineralogical studies. These are on the clay mineralogy (Blondeau & Pomerol, 1964; Gilkes, 1966 & 1978), and heavy mineral assemblages (Walder, 1964; Blondeau & Pomerol, 1968). Geochemical and sedimentological studies are virtually non-existent, although geotechnical studies of some cliff sections have been made by Barton (1973) and a few others.

The previous studies contributed usefully to the reconstruction of the palaeo-environments, sedimentations and tectonics of the Hampshire Basin. They failed, however, to account for the occurrence of some lithologies such as the goethitic red-yellow podzols and 'red earth'

Fig.1 :Extent of The Palaeogene Hampshire Basin of Southern England



PP ....Pre-Palaeogene (Cretaceous) Sediments
RF &LCF ....Reading Formation and London Clay Formation
BB & BG ....'Bagshot Beds' and Bracklesham Group
BCF & BSF .....Barton Clay & Barton Sand Formations
SF-HB ....Solent,Bembridge Limestone,Bembridge Marls and Hamstead Formations

Table 1: The Palaeogene Succession, Hampshire Basin*.

NANNO-PLANCKTON ZONES	SERIES	STAGE & (SUB-STAGE)	SUCCESSION		THICKNESS (m)	Probable Time Equivalent
22	OLIGOCENE	RUPELIAN	Bouldnor Member (Upper Hamstead Beds)	HAMSTEAD FORMATION	78	
			Porchfield Member (Lower Hamstead Beds)			
21		LATTORFIAN	BEMBRIDGE MARL FORMATION		23–34	
			BEMBRIDGE LIMESTONE FORMATION			
			Osborne Member	SOLENT FORMATION	23–33	Osborne Beds
20			'Upper Headon' Member		43–55	Upper Headon Beds
			'Middle Headon' Member			Middle
19	UPPER EOCENE	BARTONIAN (LUDIAN)	'Lower Headon' Member		8–29	Lower
18			BARTON SAND FORMATION (Upper Barton Beds)		29–64	Barton Sands Barton Beds
17		(MARINESIAN)	Naish Member (Middle Barton Beds)	BARTON CLAY FORMATION	35–90	Barton Clay
			Highcliffe Member (Lower Barton Beds)			
16		(AUVERSIAN)	Huntingbridge Member (Huntingbridge Clay)			Hengistbury Beds
15	MIDDLE EOCENE	LUTETIAN	SELSEY FORMATION	BRACKLESHAM GROUP	~150	Boscombe Beds Creechbarrow Limestone
14			MARSH FARM FORMATION			Bournemouth Formation
13			EARNLEY FORMATION			
12	LOWER EOCENE	CUISIAN	Upper Member) WITTERING FORMATION			Poole Formation
			(Lower Member)			
		YPRESIAN	(Bagshot Beds)		10–42	
11 10			LONDON CLAY FORMATION		30–140	
9	PALAEOCENE	SPARNACIAN	READING FORMATION		25–47	

*(after Stinton, 1975; West, 1980)

palaeosols in the succession at Alum Bay. Other lithological units requiring attention are the diagenetic carbonates; in particular their compositions and mode(s) of formation.

The present studies have thus been devoted to detailed mineralogical and geochemical investigations of the Upper Eocene sediments. The sediments show vertical variations from basal transgressive marine sediments to upper, non-marine sediments and freshwater limestones; the marine sediments significantly being the youngest thick marine sequence in the Hampshire Basin, whilst the non-marine sediments constitute the lowermost unit of a fluvio-marine sedimentation that spans the late Upper Eocene into the Oligocene times.

The study provides new information on Eocene palaeogeography, sedimentation and tectonics in southern England. Opinions on the sediment provenance are reassessed, whilst more light is shed on the mode of formation of authigenic and diagenetic phases in the sediments.

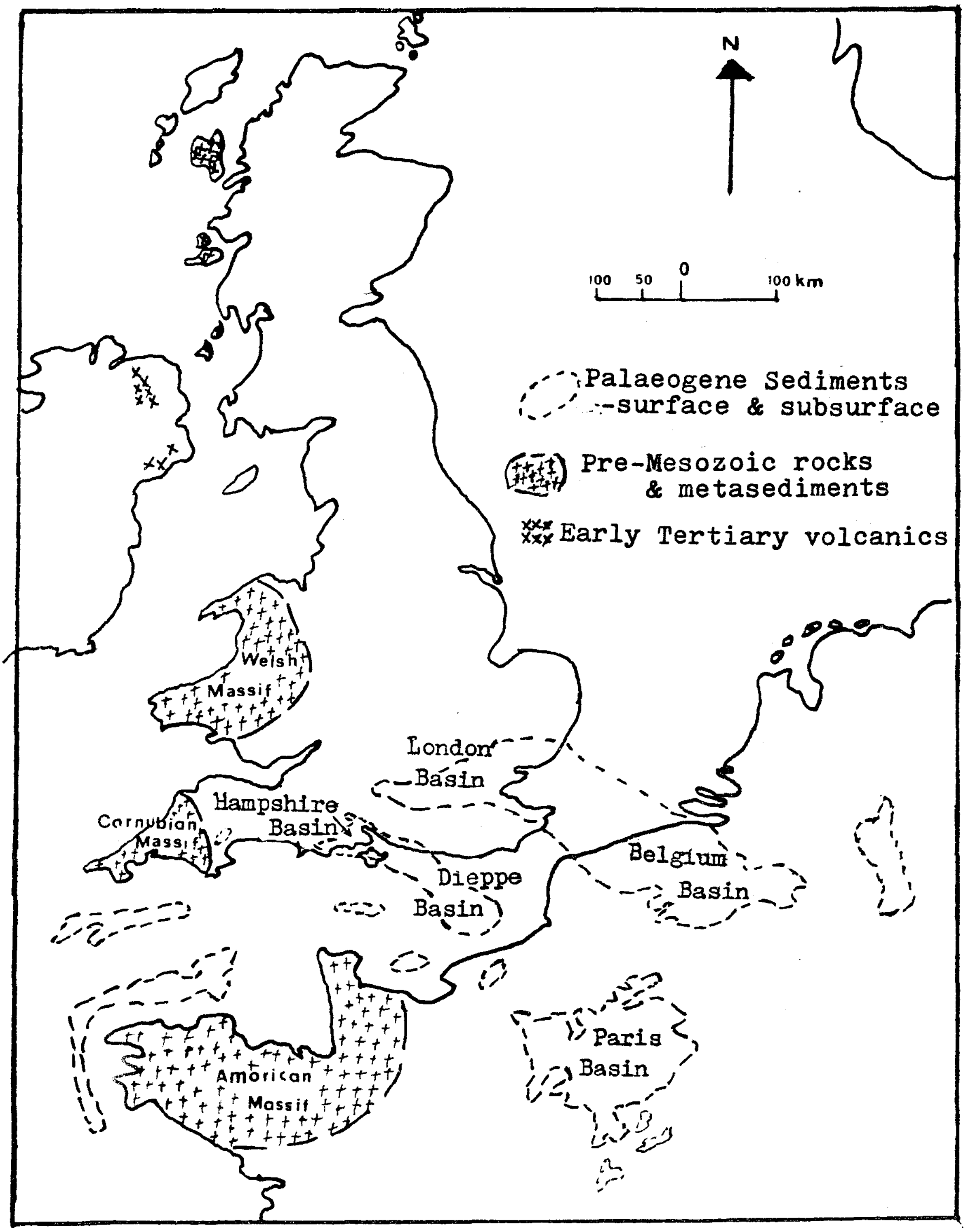
1.2 The Hampshire Basin and its Development

1.2.1 Occurrence

The Hampshire Basin is the north-western part of a large flat-floored, NW-SE trending Tertiary syncline - the Hampshire-Dieppe Basin (Fig.2) that extends from southern England into the English Channel (Groupe Norois, 1972; Smith & Curry, 1975). This is bounded by the Weald-Artois anticline to the north-east, and a strong flexure, the Bembridge-St.Valéry line, to the south-west. Although strictly continuous, it is convenient to treat the Hampshire Basin as a separate entity for the purpose of the present study. In fact, along with the London Basin located to the north, the Hampshire Basin constitutes the British part of an extensive Palaeogene Anglo-Paris-Belgian depositional basin (Fig.2).

The Hampshire Basin extends from Dorset into Wiltshire, Hampshire and the Isle of Wight (Melville & Freshney, 1982). Its Palaeogene succession, many parts of which are still poorly defined litho- and chronostratigraphically, comprises the Reading Formation, London Clay Formation, Bagshot Sand, Bracklesham Group, Barton Clay Formation, Barton Sand Formation, Solent Formation and the Hamstead Formation (Table 1). The problems of definition as regards the Upper Eocene portion of the succession are discussed later. The Palaeogene deposits are 500-700m thick and are

Fig.2: Palaeogene Occurrences In Northwestern-Europe



composed of cyclic and often diachronous transgressive marine sands and clays, and regressive brackish to freshwater clays, sands, lignites and limestones (Melville & Freshney, op.cit.). They are underlain by the Belemnitella mucronata Zone of the Upper Cretaceous Chalk (Curry, 1965); whilst near the surface, Pleistocene superficial deposits often overlie them.

1.2.2 Development

A full discussion of the development of the Hampshire Basin is beyond the scope of the present study, but a brief review of its geology, in the context of the post-Hercynian tectonism and stratigraphy of north-west Europe is given below.

1.2.2A Pre-Tertiary (Permian-Cretaceous)

The European craton was consolidated in late Carboniferous and early Permian times (Ziegler, 1982). Differential movements in this post-Hercynian craton led to the development of fault-controlled basins (or troughs) separated from each other by structural highs. One of the basins created was the South-Western Basin of Permian time that occupied much of Devon and western parts of the English Channel (Owen, 1976, Fig.59). With desert-type climatic conditions prevailing, deposition of continental facies was widespread. By Middle Triassic times, the basin extended eastwards and northwards with marine transgressions and 'complex quasi-marine lagoon' deposition (Anderton et al., 1979).

At the end of the Triassic, the European craton suffered differential, but largely extensional, crustal movements. These movements are believed (i.e. Owen, 1976; Kent, 1978) to be along, and controlled by, lines of weakness in the Hercynian Basement. These also relate to the contemporaneous rifting phase of the Arctic North-Atlantic Ocean and the establishment of the Viking-Central (North Sea) Graben (Anderton et al., op.cit.). Most of the fault-controlled structures trend east-west. A few trend NW-SE, whilst ENE lineaments predominate in the Western Approaches of the English Channel. Opinions, however, differ on which of the structural trends primarily developed from movements on the deep-seated Hercynian structures. Stoneley (1982) considered the E-W structures as primary, whereas Drummond (in Stoneley, 1982) disagreed in favour of the NW-SE structures. Drummond (op.cit.) further argued that the NW-SE structures dictated the Mesozoic basinal development and sedimentation whilst the E-W trending structures were post-Cretaceous mini-inversions with little or no Mesozoic history.

These owed their prominence to mid-Tertiary 'over-printing' of deeper underlying structures.

By the early Jurassic, much of Britain and Ireland became land, and the Wessex-Weald Basin was formed in southern England. The Basin extended south-eastwards into northern France. It was bounded by the London-Brabant Massif to the north, landmasses in Cornwall and Devon to the west, and the Amorican Massif to the south. Transgressive phases were deposited in the Early Jurassic. These coincided with the opening of the central Atlantic and western Tethys Oceans, and the start of the disintegration of the proto-continent Pangea. Towards the Middle Jurassic, volcanism accompanied more rifting in the central North Sea, while part of the existing basins became uplifted. Deposition of regressive fluvio-deltaic phases became common (Anderton et al., 1979). Basinal subsidence was renewed in Upper Jurassic times and marine sediments accumulated in seas extending over much of Europe, including southern and eastern England and the Celtic Sea.

During late Jurassic and earliest Cretaceous times, block-faulting movements took place in the region of the North Sea, and over the Rockall Trough further to the west. The Wessex-Weald Basin became partially separated from the North Sea to the north (Anderton et al., op.cit.). During this period, the sandy, regressive Wealden facies was deposited over wide areas, although the North Sea Graben continued to receive fan deposits, whilst some of its flanks received marine sands and muddy sediments. By late Lower Cretaceous (Aptian-Cenomanian?) times, the North Sea and the Weald Basin were reconnected. Materials erupted during the volcanism accompanying the movements could have been the primary source of the Cretaceous fuller's earths (Young & Morgan, 1981). By now, some structural highs such as the 'Mid Dorset Swell' (Drummond, 1970) became well established, influencing sedimentation even well into the Tertiary (Donovan, 1972). Later in the Cretaceous, there was a relative crustal stability with gentle regional downwarping and gradual eustatic rise of the sea level. With progressive transgression from the east, clastic shelf sedimentation, of early Upper Cretaceous, changed to dominantly pelagic Upper Cretaceous Chalk deposits.

1.2.2B Tertiary

During late Cretaceous and early Tertiary times, crustal separation of Greenland from northern Europe was initiated (Sutton, 1968, Ziegler, 1975). Contemporaneous volcanism (the Thulean igneous activity) occurred in Greenland, W. Scotland, N. Ireland and the Faroes (Ziegler, op.cit.). All these were synchronous with the commencement of the spreading phase of the North and Central Atlantic. To the south, the Tethys Sea, that was in existence during the Mesozoic, also began to close. The accompanying compressional stresses continued into the Miocene, culminating as the Alpine Orogeny.

In the 'North Sea area', the Central-Viking Graben developed further into an axial basin flanked by faulted-blocks. Prograding fan deposits continued to be accumulated in the North Sea graben while coastal plain environmental deposition was established over the flanking blocks. These North Sea deposits contain bedded tuffs and volcanic material that was probably derived from the Thulean igneous province to the north and northwest. In fact, the Thulean volcanism ceased during the Lower Eocene, by which time volcanic activity had shifted westwards into the ridges of the spreading Atlantic Ocean. The Thulean igneous province, itself, began to subside, whilst the fault-bounded continental margin of the spreading Atlantic Ocean started to be established.

In the early Tertiary times, much of Britain started to assume its present tectonic style, with uplift in areas to the north and west, and subsidence in the south-east. Also, some of the earlier Mesozoic basins began to 'invert' along their fault margins (Ziegler, 1975). Secondary basins were created adjacent to the structural highs. These include the London Basin and Hampshire Basin in southern England. Others are the Dieppe Basin in the English Channel, the Paris Basin in France, and the Belgian Basin in Belgium (Fig. 2).

In response to tectonic movements and eustatic sea-level changes (Hallam, 1963; Vail, 1977) the Basins were periodically inundated from the 'North Sea' and/or the 'Atlantic Ocean'. Tertiary sedimentation started during the latest Palaeocene times in the Hampshire Basin, although the London Basin and the other Tertiary basins received sediments earlier in the Palaeocene period. The London Basin and the Hampshire Basin are separated by a series of structural highs constituting part of the Weald-Artois structure. The age of these structures is arguably pre-Tertiary (Prestwich, 1854; Stamp, 1921; Wooldridge & Linton, 1955) or Eocene

(Wrigley, 1940; Curry, 1965). Jones (1981), considering various opinions on the Weald structures and reviewing current information on the structure, stratigraphy and geomorphology of the region, believed that . . . 'the central Weald was the site of a landmass or island for much of the Palaeogene'.

Tectonic movements, on a small scale, continued throughout the Palaeogene in the Hampshire Basin (White, 1921). These contributed to the interplay of transgression and regression of the sea, and the consequent cyclical deposits. Continuous movements on monoclinal folds could also have caused intrabasinal exposure of upthrown Upper Cretaceous Chalk, and probably also earlier-deposited Eocene sediments (Small, 1980; Plint, 1982, 1983).

In the late Eocene and throughout Oligocene times, tectonic movements increased in intensity and became widespread (White, 1921). Many structural highs, including the Wealden-Artois barrier in the southern North Sea became enhanced. Consequently, sediment deposition in south-eastern England became limited to the Hampshire-Isle of Wight region, with the dominant marine Eocene sediments gradually giving way to fluvio-marine Oligocene sediments.

Tectonic movements also took place during the Tertiary in the west of England, western Scotland, northern Ireland and the Hebrides. These resulted in the establishment of NW-SE trending faults with attendant periodic eruption of lavas, as well as the emplacement of dyke swarms and granites. A typical major structure is the Sticklepath - Lustleigh dextral wrench fault which trends north-westerly across the Bristol Channel into Ireland (Anderton et al., 1979). Transtensile movements (Reading, 1982) along this and nearby related faults led to the development of fault-controlled basins during Late Eocene and Oligocene times. These basins include the Bovey Tracey Basin (Edwards, 1976); Stanley Banks Basin (Fletcher, 1975; Boulter & Craig, 1979); Petrockstow Basin (Bristow, 1968; Freshney, 1970), and the Dulston Basin (Freshney et al., 1982). Others to the north include the Cardigan Bay Basin (Woodland, 1971), Celtic Sea and the Sea of Hebrides (Smythe & Kenolty, 1975; Evans et al., 1979). Fluvio-lacustrine conditions prevailed in most of the basins, and with terrigenous clastics being derived from adjoining positive structures, the gross lithology of the sediments is alternating sands and clays (i.e. Brooks

& James, 1975). The sediments are often highly kaolinitic. This is attributed to the prevalence of humid, warm tropical to sub-tropical climatic conditions and weathering in the region (Freshney et al., 1982). Similar climatic deductions were made by Isaac (1981, 1983) from occurrences of deeply and moderately-developed residual weathering profiles on Upper Cretaceous sedimentary rocks and Upper Palaeozoic meta-sediments respectively, in eastern Devon.

The Tertiary tectonics culminated in the Miocene as intense compressional stresses that led to the development of the highly deformed Alpine mountain belt in southern Europe. These also led to the progressive dwindling of the Tethys Sea into what is now the present-day Mediterranean Sea (Ziegler, 1982). The movements also caused significant but less pronounced structural changes in other parts of Europe. In the Hampshire Basin, some NW-SE trending monoclinal flextures were developed (White, 1921; Daley & Edwards, 1971) possibly as expressions of posthumous movements on deep-seated 'Hercynian' structures in the region (White, 1921; Jones, 1981). Continuous regional warping and emergence led to the cessation of sedimentation in southern England during late Oligocene, Miocene and much of the Pliocene times. However, sedimentation during that period continued in shelf seas adjoining Britain, and also in northern Europe (Anderton et al., 1979). During the late Pliocene and early Pleistocene, sedimentation resumed with the deposition of unconsolidated superficial gravel, sand and clay deposits. These unconformably overlie the Palaeogene sediments and erosional surfaces on the chalk (White, 1921; West, 1980; Jones, 1981). During the Quaternary, eustatic sea level rises led to flooding and the drowning of pre-existing drainage systems and the establishment of present-day coast-lines. Recent deposits in the region include alluvium loam, peat, tufa, rain-washed and blown sand (White, 1921; West, 1980).

During the Tertiary, Britain and much of Europe underwent considerable climatic changes. Axelrod & Bailey (1969) have employed world-wide floral and isotopic data to suggest that in Early Tertiary times, tropical-like conditions existed in palaeo-latitudes ranging between 45°N and 50°S, with moist warm temperature climates extending into the present-day polar region. The palaeo-climatic data also showed that from lower Middle Eocene times onwards, the climate in much of Europe deteriorated; so much so that by late Miocene and Neogene times, cool temperate climatic conditions prevailed.

Britain, in the Eocene, lay at about 40°N, but by late Miocene times had drifted along, with the rest of cratonic Europe, to about 50°N (Smith et al, 1981) . Several extensive studies of floral assemblages in southern England (e.g. Reid & Chandler, 1933) indicate that there was a prevalence of seasonally very humid and warm (frost-free) tropical-like conditions in early Eocene times (Daley, 1972). Hubbard & Boulter (1983) further deduced from palynological data that, from the time of deposition of the Bracklesham Group to the 'Lower Headon Beds' (Middle Eocene - Upper Eocene), the climate was characterised by mild equable winters but very variable summers and mean annual temperatures (~ 10°-18°C). Hubbard & Boulter (1983) also deduced two warm episodes with ~15-20°C temperatures occurring during the latest Lower Eocene and latest Upper Eocene times. Foraminifera and isotope studies (Murray & Wright, 1974; Buchardt, 1978) also indicate that the Eocene water bodies possessed annual average temperatures of 10°C - 18°C. The progressive deterioration of the climate documented from floral assemblages (Collinson et al., 1981; Hubbard & Boulter, 1983) apparently commenced during the deposition of the lower parts of the Bracklesham Group (late Lower Eocene) but only became very significant at the onset of deposition of the Middle Headon Beds, the earliest Oligocene sediments. By that time, the climate had become cooler. Daley (1972), from the review of the floral works of Chandler (1925-1964), argued that the Oligocene climate was comparable to present-day Eastern Margin Warm Temperature Climate as in sub-tropical south-east Asia and south-eastern United States. Hubbard & Boulter (1983) further showed that the Oligocene climate was characterised by fairly constant maximum summer temperatures and mean annual temperatures (~ 8 - 10°C), but varying and often very severe winters. Those two authors also deduced a brief high temperature (~ 20°C) episode in the Oligocene around the time of deposition of the 'Bembridge Beds'.

In the adjoining Palaeogene Paris Basin, floral studies (i.e. Chatteauneuff,1980) indicate the prevalence of alternating warm, humid and hot, dry climatic conditions; lateritization and podzolisation were believed to be widespread in the regions surrounding the basin. Dry conditions prevailed during the Auversian and this was attended by deposition of the marly limestone and calcareous sands comprising the Sables d'Auvers, and the predominantly sandy Beauchamp Formation with its latosol top (Pomerol, 1973). Changes to wetter conditions then allowed more clastic sedimentation: the sandy, marine Sable de Marnes and the lagoonal-continental Calcaire de Saint-Oune and Sables de Mancean. These sediments are the equivalent of the wholly marine Barton Clay Formation (Curry et al., 1968). Upon their deposition, environmental changes to drier climate with little detrital derivation led to the deposition of white marly limestones comprising the Marnes à *Pholadomya ludensis*, the time equivalent of the Barton Sand Formation and the 'Lower Headon Beds'. During this period and well into the Oligocene times, the existence of extensive hypersaline water bodies allowed gypsum to develop within the marl deposits, and also the authigenic formation of illites and fibrous clays such as sepiolite (Fontes & Lucas, 1968; Millot, 1970).

1.3 The Upper Eocene Stratigraphy

1.3.1 Definition

The litho-stratigraphical units of which the Palaeogene succession in the Hampshire Basin is comprised (Table 1), are often poorly defined and do not strictly conform to the recommendations of the International Sub-Commission on Stratigraphical Classification (ISSC, Hedberg, 1976). Corrective attempts on the stratigraphical sub-divisions have been made by some authors including Stinton (1975), Cooper (1976) and Curry et al. (1978). Yet many of the solutions proposed are still unsatisfactory, attracting strong objections (i.e. Keen, 1978; Daley et al., 1979).

The Upper Eocene sediments in the Hampshire Basin were first defined by Gardner et al. (1888) to comprise the marine 'Barton Beds' only. But advances in the palaeontology of the Palaeogene deposits have led to the dating and consideration of the 'Lower Headon Beds' and the 'Huntingbridge Clay' respectively above and below the 'Barton Beds' as Upper Eocene (Curry, 1966; Costa et al., 1976). Some authors, including Cray (1973), Stinton (1975), Keen (1978) and Liengjarern et al. (1980), would even place the Eocene/Oligocene boundary somewhere between the base of the 'Middle Headon Beds' and the top of the 'Bembridge Beds'.

Solution of the problems of defining and dating the Upper Eocene succession is beyond the scope of the present study which is principally mineralogical and geochemical. On the basis of current suggestions in the literature, the Upper Eocene is taken to range from the 'Huntingbridge Clay' through the 'Barton Beds' to include the 'Lower Headon Beds'. A brief review of the literature and current definitions of the deposits concerned are given below.

1.3.2 The 'Barton Beds'

The 'Barton Beds' first named by Gardner et al. (1888) are the 'Upper Bagshot Beds' of the early nineteenth century workers, notable amongst whom was Prestwich (1846-1857). The deposit is mainly exposed on the cliffs at Highcliffe and Barton-on-Sea on mainland Hampshire and at Alum Bay and Whitecliff Bay on the Isle of Wight (Fig. 1). The deposit has also been proved to exist below Southampton Water (Curry, Hudson & West, 1968) and below the Solent (Dyer, Hamilton & Pingree, 1969). Equivalents of the deposit have also been described from Afton and Gunville on the Isle of Wight (Curry, 1942) and the New Forest on mainland Hampshire. Gardner et al. (op.cit.) provided a cyclothemic arrangement of the 'Barton Beds' into 'Lower, Middle and Upper divisions', with the 'Lower and Middle Barton Beds' constituting the authors' 'Barton Clay'. Later, White (1921) defined the sands that dominate the Upper Barton, on the Isle of Wight, as the 'Barton Sands'. Burton (1929, 1933) further sub-divided the section on mainland Hampshire into fourteen units using letters for each; but with the lowermost three units being successively labelled A1, A2 and A3.

Stinton (1975) re-defined the 'Barton Beds' as a formation - the 'Barton Formation' - including the overlying 'Lower Headon Beds' (of Forbes, 1856, and Tawney & Keeping, 1883) as the uppermost unit of the formation. The 'Lower, Middle and Upper Barton divisions' and the 'Lower Headon Beds' successively became the 'Highcliffe', 'Naish', 'Becton' and 'Hordle' Members of the 'Barton Formation'. This definition was adopted by Curry et al. (1978) and Melville & Freshney (1982). Still, this does not strictly meet the ISSC guidelines and has particularly been opposed by Daley&Insole (1979). Objections arise from the fact that the 'Lower and Middle Barton Beds' are similarly clayey lithologically, whereas the 'Upper Barton Beds' predominantly comprise sands. Furthermore, sediments of the 'Lower Headon Beds' are mostly clayey and are actually lithologically indistinct from the succeeding 'Middle Headon Beds' and the faunalistically similar 'Upper Headon Beds'. In fact, the 'Headon Beds' constitute fresh-brackish water cyclothems of sands, clays, lignites and limestones (Forbes, 1856) that are distinct from the dominantly marine 'Barton Beds'. The distinction was realised and effected by West (1980), who grouped the 'Headon Beds' together as the 'Headon Formation'.

In separate and independent works, Hooker *et al.* (1980) and West (1980) advanced the sub-divisions of the 'Barton Beds' into two litho-units - the Barton Clay Formation and the Barton Sand Formation - corresponding to the earlier definitions by Gardner *et al.* (1888) and White (1921). West (*op.cit.*) further intimated that the Institute of Geological Sciences (IGS), London may formalise these new definitions, although some modifications with regard to the base of the 'Barton Clay' and the underlying 'Huntingbridge Clay' may be made. The problem of defining the base of the 'Barton Beds' is discussed later.

Another important aspect of the new units is their facies-controlled interface. The basal part of the Barton Sand at Barton-on-Sea is defined by a silty-sand, the 'Bed H' or 'Chama Bed' of Burton (1933). This, however, grades eastwards into sandy-clay facies and so constitutes the uppermost part of the 'Barton Clay' on the Isle of Wight. A possible consideration of the 'Chama Bed' as a mappable unit (Freshney, per.comm., 1983) may not be very satisfactory because the gross sandy lithology of the deposit is similar to that of the succeeding white sand (Bed I of Burton, 1933) universally considered as part of the Barton Sand Formation.

The age of the 'Barton Beds' is established to be Upper Eocene (Bartonian)(Curry *et al.*, 1978). The deposit constitutes the ostracod zone of *Cytheretta lattiscosta* (Zone 11) of Keen (1978), whilst the greater part of it also constitutes five dinoflagellate (coded BAR 1-5) assemblage zones of Bujak *et al.* (1980). On a world-wide Tertiary correlation, the deposit corresponds to the Planktonic Foraminifera Zones 13, 14 and 15; and Nannoplankton Zones 16, 17 and 18 of Martini (1971) (see Table 1, Curry *et al.*, 1978).

1.3.3 The Huntingbridge Clay and Problem of Base to the 'Barton Beds'

Two horizons have been suggested as the base for the 'Barton Beds'. These are: i) a biostratigraphical base - the *Nummulites prestwichianus* Bed of Fisher (1862), and ii) a lithostratigraphical base - a pebble bed that occurs 3-15m below the *Nummulites* bed (Prestwich, 1847; Curry, 1958).

The *N.prestwichianus* Bed, a fossiliferous glauconitic sandy-clay or silty-clay, is more or less a synchronous transgressive facies (Murray & Wright, 1974) that was first defined at Alum Bay and Highcliffe (Fisher, *op.cit.*). It was later recognised at Whitecliff Bay (Keeping, 1887), Afton (Curry, 1942), Hengistbury Head (Curry, 1942) and Fawley (Curry *et al.*, 1968). There are, however, two main problems limiting the use of the horizon.

Firstly, the N.prestwichianus Bed does not correspond to a lithological break between the clayey sediments of the 'Barton Beds' and the immediately underlying sediment. The latter, at Whitecliff Bay comprises the Fisher Beds XVIII - XIX (in part) (Fisher, 1862) and was regarded as the uppermost 'Huntingbridge Clay Division' of the Bracklesham Group (i.e. Curry et al., 1977; Kemp et al., 1979). Equivalents of the 'Huntingbridge Division' also occur in localities where the N.prestwichianus Bed has been proved, and also at Lee-on-Solent (Kemp et al., 1979). But the 'Huntingbridge Clay' is arguably late Middle Eocene (Upper Latetian) or early Upper Eocene (Auversian). The Lutetian age suggestion was based on a mollusc assemblage (i.e. Fisher, 1862; Gardner et al., 1888; Curry, 1942; Kemp et al., 1979); fish otoliths (Stinton, 1975-78) and ostracods (Keen, 1978); large percentages of which typify or range throughout the Bracklesham Group from late Lower Eocene times. The younger (Auversian) age has been based on dinoflagellate cysts (Eaton, 1976; Bujak et al., 1980); foraminifera (Murray & Wright, 1974), vertebrates (Hooker, 1977) and even ostracods (Keen, 1978). In fact the Auversian dating may also apply to some underlying sediments of the Selsey Formation. That formation (at least in part) arguably straddles the Middle Eocene and Upper Eocene interval. At Fawley, for instance, the sediments (especially Bed M of Curry et al., 1968) were found by Hodson & West (1970) to contain coccoliths that suggest post 'Upper Lutetian' age; whereas, there are also foraminiferal (i.e. Nummulites variolarius) and mollusc assemblages that have been considered (i.e. Pomerol, 1964) typical of the Upper Lutetian. However, as the controversy is palaeontological and yet to be resolved, the limit of the Auversian is, for the present study, taken as the base of the Huntingbridge Clay. The deposit has been correlated to the Nannoplankton Zones 15 (in part) and 16 (in part), and also constitutes the ostracod zone of Cytheretta cellulosa (Zone 10) of Keen (1975) and the dinoflagellate - Cyclonephelium intricatum (Zone B-5) of Bujak et al. (1980).

The second problem of using the N.prestwichianus Bed as a datum concerns the reported occurrences of foraminifera identified as Nummulites cf prestwichianus in sediments of the Huntingbridge Clay. The notable case is that described by Stinton (1970) from the base of the Huntingbridge Clay exposure at Studley Wood in the New Forest (SU-227156). Curry (1958, and in private communication to Costa et al., (1976), however, believed the foraminifera from the 'Huntingbridge Clay' to be of a different variety from, and presumably older than, that occurring in the N.prestwichianus Bed of Fisher (1862).

The pebble bed, the alternative suggested datum, occurs at the base of the 'Huntingbridge Clay' and constitutes a lithological break that satisfies the ISSC criteria. Its occurrence is, however, very limited, being notably absent in the sections at Whitecliff Bay, Lee-on-Solent, Fawley and the New Forest. Also, its correlation amongst several pebbly horizons in the predominantly sandy western parts of the Hampshire Basin, in Dorset, is difficult (cf. Fisher, 1862; Gardner, 1879; Curry, 1958b).

In the present study, the pebble bed is employed as a stratigraphical datum. The 'Huntingbridge Clay' has thus been grouped with the 'Barton Clay' to constitute the Barton Clay Formation, whilst the predominantly sandy 'Upper Barton Bed' or 'Barton Sands' is regarded as the Barton Sand Formation (see Table 2).

1.3.4 The 'Lower Headon Beds' and top of the 'Barton Beds'

The top of the 'Barton Beds' is marked by changes from marine to non-marine sediments. The transition is well defined on the Isle of Wight where the 'Barton Sands' with impressions and/or burrows of marine fauna give way to green clays with freshwater fossils (White, 1921; Daley & Edwards, 1972). On the mainland, transition is from a predominantly sand deposit (the 'Long Mead End Sand' of Gardner et al., 1888; or 'Bed K' of Burton, 1929) through a lignitic clay (Beds 1-4 in the Hordle Section of Tawney & Keeping, 1853, or the 'Lignite Bed' of Gardner et al., 1888; or 'Bed L' of Burton, 1929) into a green clay at the base of the 'Mammal Bed' of Gardner et al. (1888). 'Beds K and L' are brackish in character, especially in the sections exposed on the foreshore at Long Mead End, where brackish water molluscan assemblages occur. These were employed by Prestwich (1857), the Marchioness of Hastings (1852), Gardner et al. (1888), Burton (1929) and Curry (1958b) in grouping the deposits into the marine 'Upper Barton Beds'. The succeeding green clays, by their freshwater molluscan fossil contents, now thus mark the base of the 'Lower Headon Beds'.

As previously stated, the 'Lower Headon Beds' are grossly clayey and lithologically/faunalistically closely related to the Middle and Upper Headon Beds; these, together, constitute the 'Headon Beds'. But the

'Headon Beds' and the succeeding Osborne Beds, Bembridge Limestone, Bembridge Marls and Hamstead Beds have been differently defined in the literature.

Firstly, Hooker et al. (1980) and West (1980) considered each deposit to be individually mappable; hence meriting 'formation' status. This is appropriate for the Bembridge Limestone, Bembridge Marls and the Hamstead Beds, but not for the others whose lithologies are essentially similarly clayey. Secondly, Stinton (1975) proposed the Solent Formation and Hamstead Formation. The former comprises sediments from the Middle Headon Beds to the Bembridge Limestone. This is unsatisfactory because the 'Lower Headon Beds' were excluded, whilst the separately mappable Bembridge Limestone was included. Similar objections also apply to the grouping of the Bembridge Marls and the Hamstead Beds as the Hamstead Formation. Melville & Freshney (1982) also gave a scheme consisting of the 'Solent Formation', 'Bembridge Formation' and 'Hamstead Formation'. The authors' 'Solent Formation', as per Stinton (1975) also does not include the 'Lower Headon Beds'; but neither was the Bembridge Limestone included, rather this was grouped with the Bembridge Marls as the Bembridge Formation. The shortcomings of these definitions are similar to those of Stinton's.

It is the view of the present author that the 'Lower, Middle and Upper Headon Beds' should be grouped with the Osborne Beds to constitute a Solent Formation, with each bed assigned a Member status. Each of the Bembridge Limestone, Bembridge Marls and the Hamstead Beds can, as already proposed by West (1980), constitute separate formations.

The age of the Hamstead Formation is widely regarded as being Rupelian (Lower Oligocene) (i.e. Curry, 1966), but the age of the Headon Beds - Bembridge Marls is arguably uppermost Upper Eocene or Lower Oligocene. The 'Lower Headon Beds', which are of interest in the present study, have been regarded as constituting the uppermost part of the Bartonian Stage in Britain (Curry, 1966); whilst some authors (i.e. Cray, 1973) correlated them with the Lower Ludian of France. The deposit was also correlated to the Planktonic Foraminifera Zone 16, and Nannoplankton Zones 19 (in part) and 20 (in part).

1.3.5 The Eocene/Oligocene Boundary

The problems of dating or correlation of the sediments succeeding the 'Barton Beds', and hence defining the Upper Eocene/Lower Oligocene boundary, has preoccupied many workers since the last century. Cray (1973) attributed some of the problems to the widespread use of confused and poorly-clarified stage and sub-stage terminology. Except for the Bartonian (sensu-anglico) stage, virtually all the Eocene and Oligocene stages were defined from sections on continental Europe (i.e. Cavalier, 1969). Unfortunately, only very few representatives of the index fossils occur in the British Tertiary; hence correlation has not been facilitated.

There are three main suggestions regarding the position of the Upper Eocene/Lower Oligocene boundary in the Hampshire Basin. The literature on these has been concisely reviewed by Cray (1973). They are:

i) the base of the 'Lower Headon Beds' proposed by Reid & Strahan (1889). It was essentially based on changes from marine sedimentation of the 'Barton Beds' to the fresh-brackish water 'Headon Beds' and succeeding sediments. That criteria is very tenuous and has found no support in recent times.

ii) the base of the Middle Headon Beds, first adopted by Wrigley & Davies (1937), and later by Curry (1958, 1966). This horizon was based on the correlation by mollusca and foraminifera of the Brockenhurst Bed at the base of the 'Middle Headon Bed' with the type Lattorfian (Lower Oligocene) of Germany. The fauna data is, however, not overwhelming in support and many other authors believe that the 'Headon Beds', and even the 'Osborne Beds' and 'Bembridge Beds' are probably Upper Eocene (Ludian) in age. They would suggest an Eocene/Oligocene boundary occurring somewhere between -

iii) the top of the 'Upper Headon Beds' and the base of the 'Hamstead Beds'. Support for this includes calcareous nannoplanktons (Martini, 1970), ostracods (Keen, 1978) and vertebrates (Stehli, 1910; Cray, 1973; Hooker et al., 1980).

The controversy on the position of the Eocene/Oligocene boundary is complex, and its ultimate solution would, essentially, be palaeontological; this is, however, outside the scope of the present study. Only the base of the 'Middle Headon Beds' is the most definitive boundary so far suggested in the literature; it has thus been adopted for the purpose of the present work.

1.3.6 Summary

The stratigraphical definitions and dating adopted for the Upper Eocene succession in the Hampshire Basin are:

a) that the Upper Eocene ranges from the base of the 'Huntingbridge Clay' to the top of the 'Lower Headon Beds';

b) that the succession comprises -

  i) the Barton Clay Formation, made up of the Huntingbridge Clay Member, Highcliffe Member and the Naish Member;

  ii) the Barton Sand Formation; and

  iii) the 'Lower Headon Beds' or 'Lower Headon' Member of the Solent Formation (Table 1).

These definitions are considered (Freshney, per comm. 1983; West, per. comm. 1983) adequate for the mineralogical and geochemical aims of the present study.

1.4 Aspects of Previous Studies

Records of studies on the Upper Eocene sediments in the Hampshire Basin date back to the eighteenth century; the earliest possibly being illustrations of fossils from the 'Barton Beds' by Dr. Solonder (1776 - quoted in Gardner *et al.*, 1888). The foundation of present-day knowledge of the sediments was, however, laid by Prestwich (1846). His and other later works in the nineteenth century mainly covered the litho- and/or biostratigraphy of the sediments. Similar studies continued into the twentieth century, but with increasing knowledge of the vertebrate, micro-faunal and floral assemblages, which facilitated correlation and deduction of the palaeo-environments and sedimentation.

Studies of the sediments from the point of view of other disciplines of geology are very limited and few. The known works include the clay mineralogy by Gilkes (1966), heavy minerals by Walder (1964) and Blondeau & Pomerol (1968); and engineering geology by Barton (1973).

With the exception of the general stratigraphy that has been elucidated in earlier sections, a brief review of the previous works is given below.

1.4.1 Sedimentation

Prior to the Bartonian transgression, two major palaeo-environments existed in the Hampshire Basin. These are believed (Murray & Wright, 1974; Hooker, 1977) to be a silting-up marine embayment and a fringing flood-plain (cf. Fig. 25f of Murray & Wright, 1974). The former prevailed in the eastern part of the Isle of Wight, whilst the latter prevailed westwards from Alum Bay. In the flood-plains, there were extensive depositions of non-marine sands, freshwater clays and lignites. Much of these constitute the Boscombe Sands, one of the uppermost members of the Bracklesham Group (Melville & Freshney, 1982). At Alum Bay and Highcliffe, the establishment of coastline conditions led to the deposition of sand-supported flinty-pebble beds. The pebbles were possibly derived from contemporaneously exposed nearby Chalk deposits (Plint, 1982), although Hooker (1977) has also suggested probable erosion of equivalents of some early Eocene gravel beds proved to be below the Creechbarrow Limestone Formation in Dorset. Then the Huntingbridge Clay, with its carbonaceous and often pyritic, sandy-clay gross-lithology, became deposited in what was first thought to be a deep water with poor circulation and low Eh (Curry et al., 1968), but later proved to be a hyposaline marsh regime (Murray & Wright, 1974).

As the transgression continued westwards, the Barton Sea became effectively established, and shelf conditions that had only prevailed at Whitecliff Bay during the deposition of the Huntingbridge Clay spread to Alum Bay and Highcliffe. It was then that deposition of the Highcliffe Member started, with the Nummulites prestwichianus Bed. The Barton Sea continued to deepen steadily; with a near-shore shelf regime being established around Barton-on-Sea, and contemporaneous off-shore shelf and intertidal conditions prevailing at Alum Bay and Whitecliff Bay. The marine clays, mottled sands and glauconitic sandy clays deposited constitute the bulk of the Barton Clay Formation. The thickness of the formation increases from about 35m at Highcliffe/Barton to about 90m at Alum Bay and Whitecliff Bay.

After the deposition of the Barton Clay, the Barton Sea started to silt up. Curry (1965) and Murray & Wright (1974) presumed that the shallowing of the Barton Sea could be consequent on the existence of a sand-bar or shoal barrier in areas to the south of the Isle of Wight. The barrier may be synonymous with the 'tectonic barrier' inferred by Plint (1982) to exist in the same area during Middle Eocene sedimentation in the Hampshire Basin. A predominantly sand-facies deposition attended the sea shallowing. This, the Barton Sand, is sparsely fossiliferous, but increases in thickness from about 30m at Barton to about 44m at Alum Bay and about 63m at Whitecliff Bay.

The consequence of the silting up of the Barton Sea was the development of shallow brackish water and freshwater coastal-plain environments with the deposition of river-channel sands, freshwater green and mottled clays, and the accumulation of lignitic clays and limestones (Edwards, 1967). They are the sediments constituting the non-marine 'Lower Headon Beds', the first of the fluvio-marine cyclothems of Webster (1814). In contrast to the 'Barton Beds', the thickness of the 'Lower Headon Beds' decreases from about 28m on the mainland to about 19m on Headon Hill and 8·5m at Whitecliff Bay.

The deposition of the Lower Headon sediments was brought to an end by a widespread sea incursion, which was also from an easterly direction, and in which the Brockenhurst Bed, a fossiliferous brown clay, at the base of the 'Middle Headon Beds' was deposited. The probable sources of detritals for the Upper Eocene deposits are discussed later.

1.4.2 Structure

As already described, the Upper Eocene deposits are part of the transgressive and regressive Palaeogene deposits in the gently subsiding Hampshire Basin. The Palaeogene sediments were affected by a series of upheavals initiated at the end of the Cretaceous, and which culminated as the Miocene Alpine Orogeny (White, 1921; Daley & Edwards, 1971). The sediments now occupy shallow synclinal and monoclinal folds with sub-parallel WNW-ESE trends (Fig.1) and which young northwards.

The sediments exposed at the type locality (mainland Hampshire) exhibit a near-horizontal attitude with an apparent easterly dip of 1° or a true dip of 1° to the north-east (Curry, 1976). The very low easterly dip and the arcuate form of the coast-line account for the rather lengthy (over 8 km) exposure of the sediments from Mudeford to Milford-on-Sea (Fig.3). Those on the Isle of Wight are steeply dipping (55°-85°) and, hence, are exposed over much shorter lateral distances (Figs. 3 & 4). However, at Alum Bay, from the top of the Barton Clay, there is a gradual decrease in the beds' inclination to about 21° at the base of the 'Lower Headon Beds' on Headon Hill, and to nearly horizontal towards Totland Bay. This has led to a considerable (northwards) persistence of the upper part of the Barton Sand and the 'Lower Headon Beds'.

1.4.3 Palaeontology

The Upper Eocene sediments are generally rich in animal and plant remains. The fossils have provided valuable information on the palaeoenvironmental and depositional conditions prevailing during Upper Eocene times in the Hampshire Basin. A short account of the fossil assemblages found is as follows.

1.4.3A Invertebrates

The dominant invertebrate remains are the molluscan shells, particularly gastropods and pelecypods (bivalves).

The Huntingbridge Clay at Highcliffe and Alum Bay is only sparsely fossiliferous and, like the section described from Fawley (Curry et al., 1968), mainly contains poorly preserved and pyritised molluscan shells, moulds and casts. In contrast, more fossiliferous sections of the deposit occur at Afton and Gunville (Curry, 1942), Gosport (Kemp et al., 1979) and in the New Forest (Stinton, 1970). Characterising fossiliferous horizons in the sediment comprise the 'Huntingbridge shell bed' (Stinton, 1970) in the New Forest; the 'Coral bed' (Fisher, 1862) at Gosport and the New Forest; and the 'Rimella Canalis bed' (Curry, 1942) at Afton and Gosport. The fossils, comprehensive lists of which are contained in Curry (1942) and Kemp et al. (1979), include Ectinochilus planum, Cardita sp and Crasatella sp. Most of the fossils range from late Lower Eocene, and throughout the Middle Eocene into the Upper Eocene.

A description of several hundred fossil species in the other members of the Barton Clay and Barton Sands is given by Gardner et al. (1888) and Burton (1929, 1931). Fossils characterising the Highcliffe Member include Athleta and Pholadomya. Those in the Naish Member include Clavilithes, Athleta, Turritella, Volutocorbis and Crassatella. The lower parts of the Barton Sands at Barton are characterised by Turritella and Chama squamosa, whilst towards the top, estuarine and tidal-flats genera such as Olivella branderi, Polymesoda (Cyrena), Batillaria concava and Bayania fasciata occur. The Barton Sand is largely unfossiliferous at Alum Bay, and only contains a few impressions of molluscs at Whitecliff Bay.

In the 'Lower Headon Beds' the predominating molluscan assemblage is considerably rich in Viviparus lentus (Solander), Galba (Lymnae) longiscata and Planorbina discus. The Viviparus and Galba are common in clays, whilst the Planorbis and Galba occur in the limestones. They are pulmonates, indicating conditions of well-vegetated ponds, sheltered bays, large lakes and mud-flats or margins of sluggish rivers (Edwards, 1967). Also, there are bivalves in parts of the deposit. Species, such as Polymesoda convexa, present in some horizons do indicate occasions of strong tidal influx, whilst Unio solandri at other horizons emphasizes the prevalence of shallow freshwaters.

1.4.3B Vertebrates

One of the pioneering works on vertebrates in the Hampshire Basin was that of the Marchioness of Hastings on the 'Headon Beds'. Recent works include those of Cray (1973), Hooker et al. (1980) and Stinton (1975-1978).

Vertebrate remains are very few in the Barton Clay and Barton Sand. Those found include a cetacean (water-mammal) - Zygorhiza wanklyni (Seeley); turtles - Eochelone branticata; fish - 'Scyliorhinus' sp. and Myliobatis spp; fish otoliths - Hoplobrotula undata. They were inhabitants of shallow shelf to brackish water bodies, and suggest a shallow sea environment with nearby land areas during deposition of the sediments.

Vertebrate remains in the 'Lower Headon Beds' are more numerous and varied. Those enumerated by Hooker et al. (1980) include Artiodactyla (pig-like archaic woodland mammal), Oxyaenidae (carnivore); Theridomys sp. (rodent); Crocodilus hastingsiae (warmth-loving crocodile); Emys and Trionyx (river turtle); Myliobatis (fish) and some birds. They strongly underline the prevalence of a warm, continental condition during deposition of the 'Lower Headon Beds'.

1.4.3C Microfaunal

Foraminifera, ostracods and dinoflagellates are the most extensively studied microfossils in the Palaeogene sediments in the Hampshire Basin.

The work of Murray & Wright (1974) is the most comprehensive, and up-to-date, on foraminifera. The authors found the Huntingbridge Clay to be largely barren, except in its upper part at Alum Bay, where some of the species that typify the Highcliffe Member do occur. Here the assemblage predominantly consists of Rotaliina sp. such as Cibicides pygmens and C.ungerinus. There are also a few agglutinated (Textulariina) species such as the Trochammina and Amobaculites. The other common forms include

Glandulina laevigata, *G.gibba* and *Quinqueloculina ludwigi*. These assemblages indicate conditions of tidal marsh to near-shore shelf, with 0-100m depth and hyposaline to normal salinity. Occasions of apparent improvements in water and/or communication with the open sea are marked by sudden bursts of some planktonic species such as the *Nummulites prestwichianus* and *N.rectus*.

The foraminifera assemblage in the Naish Member is also dominated by the Rotaliids. These indicate the existence of normal marine, but more muddy bottom conditions. Two horizons in the Highcliffe and Naish Members at Alum Bay were found by Murray & Wright (1974) to be devoid of foraminifera. The authors believed the horizons, which comprised laminated sands, clays and mottled sands with scattered flint pebbles, to 'result from inter-tidal conditions developed when the rate of subsidence of the basin was slower than the rate of sediment accumulation'.

The onset of shoaling of the Barton Sea was marked, at the top of the Naish Member and lower part of the Barton Sand, by the presence of *Glandulina aequalis* and *Quinqueloculina bicarinata*, along with the assemblages occurring in the Highcliffe Member. With the sea becoming clear and with a sandy bottom, there was an increase in the abundance of Miliolina species. Towards the top of the Barton Sand, foraminifera become sparse, but a few pyritised species of *Amobaculites* and *Trochammina* occur as indicators of prevailing hyposaline estuarine or marsh conditions. The 'Lower Headon Beds', being non-marine, are devoid of foraminifera.

The predominance of Cibicides species is thought (Murray & Wright, 1974) to be an indication of the cool water aspect of the Barton Sea. The authors also employed the presence of *Quinqueloculina seminulum* to suggest summer bottom temperatures of at least 10°C; and that the water temperature was probably similar to the 16-18°C of the present-day English Channel.

There are a few works on ostracods, and notable amongst these is that of Keen (1977, 1978). Ostracods are very sparse in the Barton Sand, but those that abound in the Barton Clay include *Cyamocytheridea angusta*, *Cytheretta costellata antecalva*, *Leguminocythereis haskinsi* and *Pterygocythereis fimbriata bartonensis*. They are generally of shallow marine and hyposaline to normal-sea salinity environments.

Ostracods in the ‘Lower Headon Beds’ may be grouped into three assemblages (Keen, 1977). The first comprises *Canadona* sp. and *Cypridopsis* sp. This is a freshwater (0-5‰) assemblage occurring in association with the remains of Charaphyte algae in freshwater limestones and carbonaceous clays. The second assemblage also comprises freshwater species typified by the *Moenocypris* sp. They are common in clays, occurring in association with the seeds of water plants and shells of *Viviparus*, *Melanopsis* and *Unio*. They indicate shallow (2-15m depth?) river mouths and lakes, possibly with poorly aerated waters and a bare muddy bottom (Keen, *op.cit*.). The third assemblage includes *Cytheromorpha* sp. and *Neocyprides* sp. They are brackish water (3-16·5‰) fauna suggesting the environment of a polyhaline bay with some freshwater outlets. In general, the ostracod assemblages indicate the existence of a complex system of bays, with lagoons not unlike those in present-day Texan coast and southern Florida.

Dinoflagellates occur mainly in the marine sediments, and there have only been a very few works on these calcareous microplanktons. The works include those of Eaton (1976), Costa *et al*. (1976), Bujak *et al*. (1980) and Liengjarern et al. (1980). The assemblages in the Barton Clay and basal parts of the Barton Sand mainly comprise *Spiniferites* spp. *Impletosphaeridium* sp. and *Homotryblium tenuispinosum* Davey & Williams. Others include *Areoligera*, *Wetzeliella*, *Cyclonephelium* and *Areosphaeridium* species. Most of these range from the Middle Eocene period, although some, such as *Cyclonephelium divaricatum* and *Adnatosphaeridium vittatum* do not range beyond the Huntingbridge Clay (Eaton, 1976); whilst a few, such as *Wetzeliella* (*Rhombodinium*) *draco* (Gocht) and *Heteraulacacvsta*? sp., first appear at the base of the Highcliffe Member. The dinoflagellates indicate the prevalence of full marine conditions, although the occurrence in the basal part of the Highcliffe Member of species such as *Pediastrum* would suggest a somewhat strong freshwater influence.

1.4.3D Plant Remains

The Upper Eocene sediments, especially the non-marine ‘Lower Headon Beds’ are abundant in fossil fruits, seeds, leaves and, in places, stumps and roots. Detailed descriptions of many of these are contained in Chandler (1960, 1961). Other recent works also include those of Fowler *et al*. (1973), Feist-Castel (1977), Collinson *et al*. (1981) and Hubbard & Boulter (1983).

The plant assemblage is dominated by coniferous and angiosperms (ferns) species. The cones include impressions of Pinus dixioni; twigs of Sequoia couttsiae Heer; pinnules of Acrostichum lanzaeanum; and roots of Gyptostroxylon Conwentz. These are generally elements of temperate vegetation that became abundant during Upper Eocene times, underlining the deterioration of climatic conditions in southern England (Collinson et al., 1981). The plants could have grown on poorly-drained but slightly elevated areas on the landward side of coastal swamps (Fowler et al., 1973); however, some authors (Daley, 1972; Anderton et al., 1979) thought that they largely represent 'montaine' vegetation derived from upland areas bordering lowland coastal plains with tropical-like climatic conditions.

The angiosperms constitute the bulk of the warmth-loving plants. They are predominantly aquatic and sub-aquatic species, and include Chara, Limnocarpus, Stratiotes (water lettuce), Salvinia and Brasenia. Chandler (1961), grouping them as "gregarious genera and species", believed they indicate the existence of lowland freshwater ponds, sluggish rivers and lakes. The algae flora - Charaphyte - include Psilochara polita and Harrisichara vasiformis; they indicate very low energy water conditions (Feist-Castel, 1977).

Also common in the sediments are remains of land plants such as Rubus, Sambucus and Icacinaceae. They could have grown on, and been washed in from, banks of nearby rivers.

In general, the plants indicate an Upper Eocene palaeoenvironment of coastal alluvial flood-plains with open water, marshes and swamps. The abundance of temperate deciduous conifers and warmth-loving plants has arguably been shown (Daley, 1972) as suggesting the prevalence of a humid and warm sub-tropical climatic condition. The significant absence of tropical-forest mangrove taxa in the Upper Eocene contrasts sharply with the vegetation in Lower Eocene and much of the Middle Eocene times. In those periods, warmer climatic conditions prevailed and the vegetation predominantly had greater affinities to present-day vegetation in the tropics, although some 'extra-tropical' elements are not uncommon (Collinson et al., 1981).

1.4.4 Mineralogy

1.4.4A Clay Mineralogy

Gilkes (1966) undertook the investigation of the clay mineralogy of the Palaeogene Beds of the Hampshire Basin, and found that the clay mineralogy essentially comprised montmorillonite, illite, kaolinite, traces of chlorite and some undifferentiated mixed-layered phases. In the Upper Eocene sediments, illite and montmorillonite dominated the clay mineralogy, with illite often constituting more than 40% of the clay fraction. Kaolinite, however, occurs in very high amounts in the Barton Sand and the 'Lower Headon Beds' at Heatherwood Point and Totland Bay on the Isle of Wight. The clay minerals are believed (Gilkes, 1966; Perrin, 1970) to have been derived from exposed Pre-Tertiary rocks located to the west and north of the basin. Recently, however, Gilkes (1978) re-explained the high illite contents of clay fractions in sediments of the 'Lower Headon Beds' and the succeeding Oligocene sediments on the Isle of Wight as re-worked neoformed illites from very nearby sites. The author argued that illite neoformation could have occurred during dry periods within confined water-bodies, such as has been proposed in the Palaeogene sediments of the Paris Basin (Millot, 1970).

The other minerals observed by Gilkes (1966) in the clay fractions were quartz, feldspars, anatase, calcite, siderite, goethite, lepidocrocite and jarosite. They were not studied in detail.

1.4.4B Heavy Minerals

Following the pioneering works of Boswell (1923) and Groves (1931) on heavy minerals in southern England, Walder (1964) and Blondeau & Pomerol (1968) undertook detailed and systematic investigations of the heavy mineral assemblages in the Tertiary sediments. Walder worked on Isle of Wight sections, while Blondeau & Pomerol covered much of the Tertiary sediments of the Hampshire Basin and parts of the London Basin.

The heavy mineral content of the Upper Eocene sediments is dominated by zircon, tourmaline and rutile (Walder, 1964). These are largely granite-derived assemblages (Blondeau & Pomerol, 1967). Materials from metamorphic sources occur in smaller and very variable amounts. They include garnet, andalusite, glaucophane, kyanite, staurolite, sphene, brookite and epidote. Heavy minerals of probable authigenic origin include anatase and glauconite. Although the minerals are believed to be predominantly derived via land drainage systems (Walder, 1964), suggestions have been made (Blondeau & Pomerol, 1968) of the possible derivation of some materials from northern Britain and Continental Europe via the

'North Sea' and the westwardly transgressing Eocene seas in the Hampshire Basin.

1.4.5 Geochemistry

Probably the first of the chemical analyses on the Upper Eocene sediments were those of glauconites from the base of the Highcliffe Member at Highcliffe by Professor Livering (in Fisher, 1862). The glauconites, which were then called 'green colouring matter' were reported to be composed of 50·11% SiO_2, 25·04% Fe_2O_3, 6·12% Al_2O_3, 3·14 MgO, 5·17% K_2O and 10·02% H_2O. This shows the glauconites to be a high iron and moderate potassium-containing variety (cf. Burst, 1958; Borchart & Braun, 1963).

In work on radiometric (K-Ar) dating of the Palaeogene sediments in Britain, Odin et al. (1978) analysed glauconites from the base of the Highcliffe Member on the Isle of Wight. The mineral contains about 8% K_2O and yielded dates of 38·9 to 39·6 m.yrs for the Middle/Upper Eocene boundary. The dating seems to indicate a relatively uniform sedimentation rate of $\sim$ 2·5 cm/1000 yrs for the Eocene Succession of the Hampshire Basin.

Another geochemical study is that of Knight (1975), in which ten samples from the Naish Member at Barton-on-Sea were studied as part of a geochemical study of some Mesozoic and Tertiary diagenetic carbonates and their host sediments in southern England. The concretions analysed contained about 60-70% $CaCO_3$, and were enriched in manganese (600-1180 ppm), but depleted in hydrolysate trace elements (i.e. Rb, Pb, Ni, Ba and Zn) compared to the host clay sediments. Knight supposes that the concretions had an organic origin or that their formation was induced by remains of organisms.

Partial analysis of freshwater limestones in the 'Lower Headon' on Headon Hill has also been performed by Bumstead (in Edwards, 1967). These contain variable, but very high, amounts of calcium carbonate. The carbonate contents were commonly as high as 97%.

1.4.6 Geophysical Studies

One of the few published geophysical works is that of Dyer, Hamilton and Pingree (1969). The authors conducted seismic refraction shots across The Solent and obtained results that showed the Highcliffe and Naish Members as constituting a single seismic layer with the thickness decreasing westwards from the Isle of Wight to mainland Hampshire. This result is very much in agreement with the surface geology. The Barton Sand Formation and the fluvio-marine Solent Formation ~~sediments~~ constitute another integrated refracting layer, but with higher seismic velocity. The study also showed the Tertiary/Cretaceous unconformity boundary to be at about 500m depth.

1.4.7 Engineering Geology

Sea erosion and cliff-slumping are common and are causing environmental problems in coastal sections of the Palaeogene sediments. The necessity to protect the coastline and stabilise the cliffs has led to several geotechnical and engineering studies of the coast and cliffs. Work at Barton-on-Sea (i.e. Barton, 1973) has shown that several degradational processes are operative. The major one is the sliding of strata along bedding plane-shear surfaces. Seven of such developed shear-surfaces have been recognised (Barton, op.cit.) within the Highcliffe and Naish Members at Barton. Other degradational processes include scarp-slumping, mud-flows and the under-cutting action of streams. The combination and intensities of these processes vary from place to place such that, where substantial, the slumps may acquire inclinations of up to 20°, whereas lesser inclinations ($\lesssim 15^{\circ}$) are common in relatively stable places.

1.4.8 Derivation of Detritus

Having reviewed, in the preceding sections, most aspects of the known geology of the Upper Eocene succession, the derivation of the constituents may now be considered.

The sediments are essentially deposits of detritally-derived clastic materials and accumulations of biogenic fossil shells and plant matter. The derivation and distribution of the detritals would have depended on the tectonic movements within and around the Hampshire Basin, the Palaeogene palaeogeography and the interplay of marine transgression and regression.

During the Late Cretaceous and Early Tertiary, a series of tectonic movements in relation to the opening of the Atlantic Ocean Basin (Sutton, 1968) occurred in the European craton. One manifestation of the movements was the creation of the Hampshire Basin in southern England. Structural highs and landmasses adjoining the basin include: (i) the Cornubian highlands composed of metamorphosed Pre-Triassic rocks and igneous intrusives, which include (i) the kaolinitised Dartmoor Granites in south-west England; (ii) Mesozoic strata in Devon and Dorset, and also in south-west England; (iii) Permo-Triassic rocks to the north in the English Midlands; (iv) 'inverted' Pre-Tertiary sediments in the English Channel to the south; and (v) the Hercynian massifs of metamorphosed Pre-Triassic rocks and igneous intrusives in Britanny, the English Channel and in north-west France. These would have been the main sources of detritus to the Hampshire Basin. With warm and humid tropical-type climatic conditions prevailing, weathering could have been considerable in the region; whilst the detritus was predominantly water-borne in a drainage system that is believed to be dominated by an eastward-flowing Solent River (Fig.25; cf.West, 1980; Jones, 1981) with southward flowing tributaries.

Gilkes (1966) argued that illite and kaolinite were mainly derived from sources to the north and west, with much of the kaolinite possibly coming from kaolinitised granites in Cornwall. Chalk deposits exposed to the north and north-east of the basin were, however, believed (Gilkes, op.cit; Blondeau & Pomerol, 1964) to be the main sources of montmorillonite. The probable derivation of montmorillonite, in the sediments, from volcanic source materials has been given some thought (Gilkes, op.cit.), but could not be ascertained. This is surprising considering that volcanic materials erupted in the Early Tertiary Thulean igneous province, to the north, are commonly interbedded in the Tertiary North Sea sediments (Jacques & Thouvenin, 1975) and the Palaeocene - early Palaeogene sediments in the London Basin (Elliot, 1971; Knox & Harland, 1979). Although no occurrence of similar volcanic materials has been reported in the Palaeogene sediments of the Hampshire Basin, Gilkes (1966) has recorded the presence of clinoptilolite in the Middle Eocene Bracklesham Beds at Whitecliff Bay. Zeolites are common submarine alteration products of volcanic materials, although they may also form diagenetically (Stonecipher, 1978; Kestner, 1979).

The heavy mineral assemblages were also believed (Walder, 1964; Blondeau & Pomerol, 1968) to have been derived from the Cornubian Highlands to the west,the Mesozoic strata in the Midlands to the north and the Hercynian massifs to the south. In addition, Blondeau & Pomerol (1968) advanced the view of some derivation via the North Sea from areas further north in east England, Sweden and north France.

Intrabasinal tectonic movements are also believed to have influenced sedimentation in the Hampshire Basin (Fisher, 1862; Small, 1980). These and the contemporaneous regional tectonic movements could account for the following: the derivation of Lower Greensand chert pebbles in some 'Barton Sands' in the London Basin (i.e. Davis, 1939; Dewey, 1948); exotic chert pebbles in Dorset that were probably derived from the Cretaceous Lower Greensand, the Jurassic Purbeck Beds and other older sediments; the re-worked, decomposed flint pebble with foraminifera of Maestritchtian age in the late Middle Eocene Boscombe Sand (Curry, 1964). The source of the decomposed flint pebble was believed to be from 'inverted' Cretaceous sediment in the English Channel to the south of the Isle of Wight.

The intrabasinal movements would also account for the Pre-Eocene erosional Chalk surfaces, the re-working and re-deposition of earlier deposited Tertiary sediments, and the variations in thicknesses and attitudes of the Eocene sediments within the Hampshire Basin (Small, 1980; Jones, 1980). The possibility of intrabasinal movements and possible local exposures of the chalk have been emphasised further by the work of Plint (1982) on Middle Eocene deposits in the Hampshire Basin. Plint postulated the existence of localised chalk headlands from which flint pebbles were shed into the sea, to be re-distributed by longshore currents. These and earlier deposited Tertiary sediments would have been exposed on the up-thrown sides of monoclinal folds such as the Portsdown Anticline and Brixton Anticline (see Fig.1).

With the derivation of detritus mostly by mud-laden rivers draining elevated areas in the south-western parts of England and the English Midlands, coupled with the fluctuating incursions of the sea from the east, there was a shift in the nature of the sediments being deposited about a hinge that is now occupied by The Solent (Fig.1). To the west, the Basin was filled mainly by illite and kaolinite-rich, sandy and non-marine sediments; whereas to the east, most of the sediments were marine, more clayey and with clay minerals dominated by illite and smectite.

CHAPTER 2

SAMPLING AND DESCRIPTION OF THE UPPER EOCENE SUCCESSION

2.1 Sampling

In order to investigate detailed and systematic variations in the mineralogical and geochemical compositions of the Barton Clay Formation, Barton Sand Formation and the 'Lower Headon Beds', regarded as constituting the Upper Eocene succession in the Hampshire Basin (see Chapter 1, Section 3), representative sampling was carried out as follows.

2.1.1 Localities

Exposure of the Upper Eocene deposits are numerous in the Hampshire Basin, but it is only along the cliffs of mainland Hampshire and the Isle of Wight, that the whole succession is continuously exposed, and the stratotypes of the deposits are defined. The present studies have thus been devoted to the cliff sections.

Sampling was first carried out in the section between Highcliffe (SZ 188922) and Milford-on-Sea (SZ 280820) on mainland Hampshire (Fig.3) during the period of October 1978 to May 1979. Later, in December 1980 and January 1981, samples were collected from the easterly equivalents exposed on the cliffs at Alum Bay (SZ 304860) and Heatherwood Point (SZ 306854) in the west of the Isle of Wight (Fig. 3), and at Whitecliff Bay (SZ 860639) in the east (Fig. 4).

2.1.2 Factors affecting Sampling

Several problems were encountered in trying to obtain representative samples of the sediments. These included:

2.1.2A Inaccessible and unexposed sections

Some parts of the sections were obscured by vegetational growth, cliff slumping, cliff protection and construction work, and the placement of beach huts for holiday-makers. Of these the cliff slumping and vegetation were the most widespread and have been so for the greater part of the last two centuries (cf. Prestwich, 1847; Tawney & Keeping, 1883; Bujak, 1976). These problems may be avoided by using borehole samples; but such material was not available during the present study.

Fig.3 :Cliff Section of Palaeogene Sediments;Mainland Hampshire and Western-Isle of Wight.

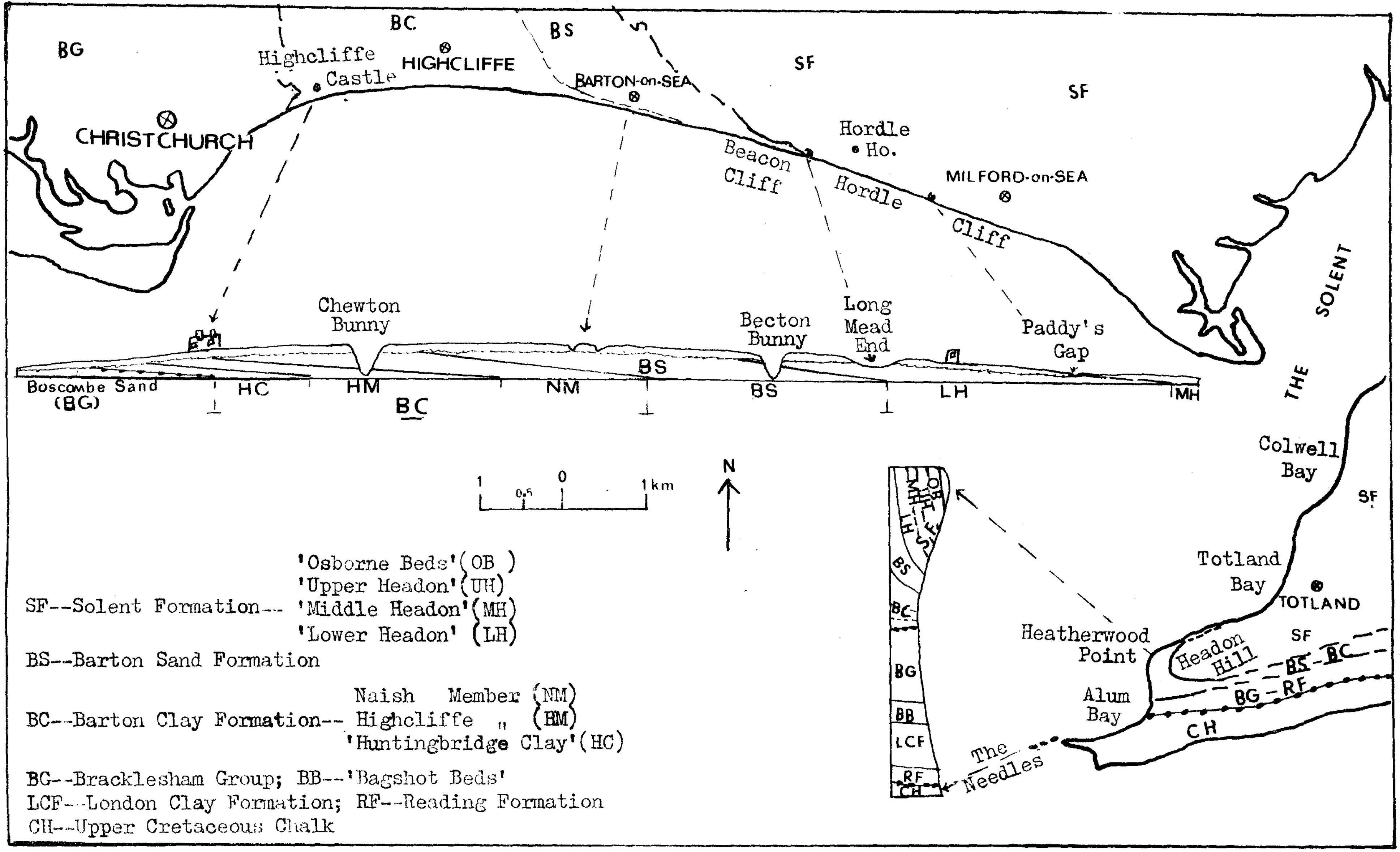
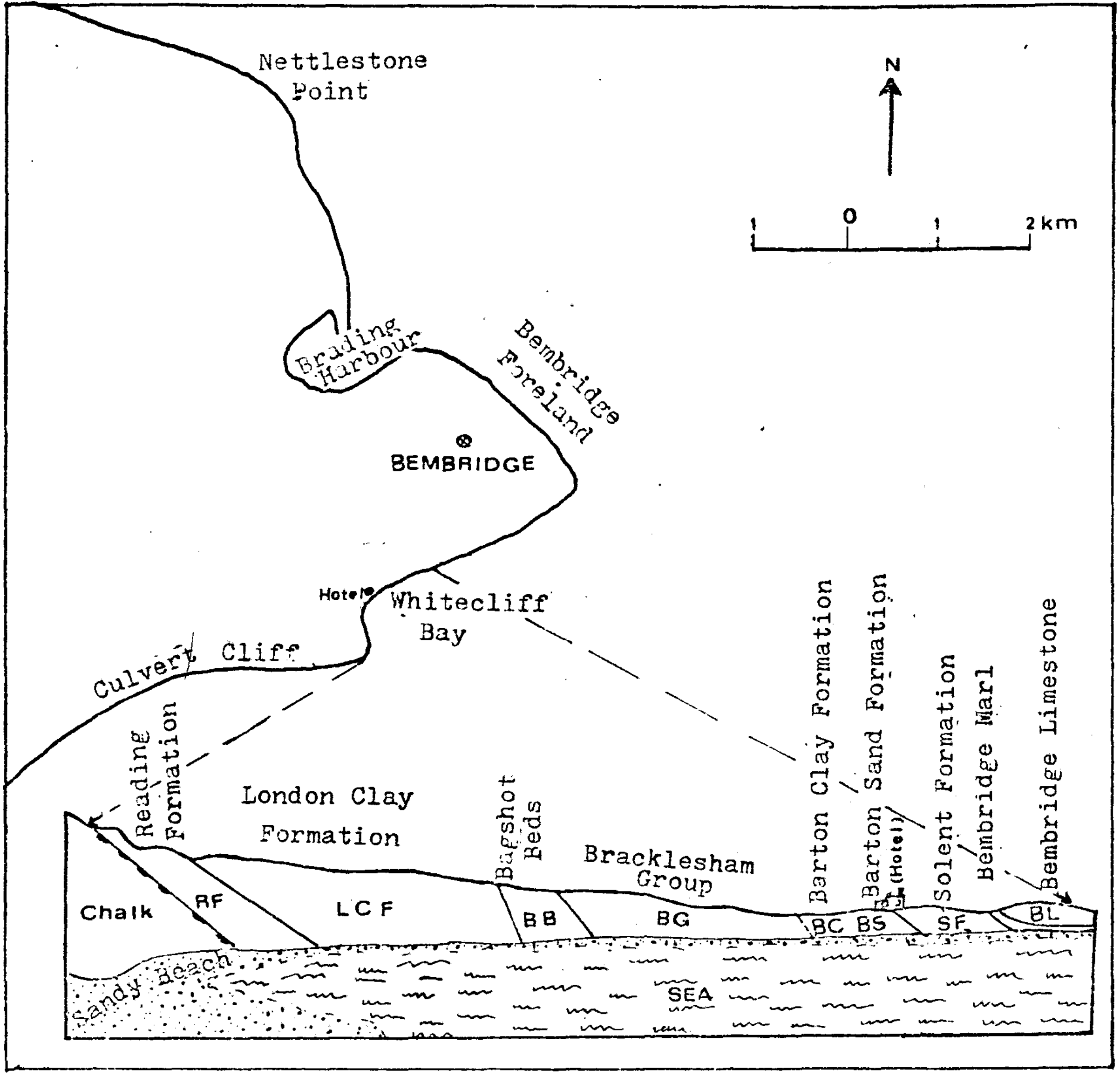


Fig.4 : Cliff Section of Palaeogene Sediments;Whitecliff Bay,Isle of Wight.



2.1.2B Weathering

Surface weathering of exposed sediments is common and substantially deep in places. The weathered sediments usually exhibit brownish to reddish coloration or are sometimes bleached. This bleaching is probably due to acidic solutions resulting from alteration, oxidation and hydration of constituents such as pyrite. Some fossiliferous horizons have been decalcified, and there are widespread occurrences of coatings of jarosite and selenite (gypsum) on exposed sediment faces.

During the present sampling exercise, the weathered positions were avoided by scraping off the weathered faces and/or digging as far as possible into fresh sediments. The effect of recent superficial weathering is particularly awkward in this study as many of the minerals produced by these processes (e.g. goethite, jarosite, gypsum, etc.) could also have resulted from similar processes contemporaneous with deposition. Attempts were made, particularly in the palaeosols, to distinguish between fossil and Recent processes.

2.1.2C Facies Changes

Facies changes are considerable in parts of the 'Lower Headon Beds' at Barton and Heatherwood Point. At these localities the arcuate shape of the coastline and the gentle, almost horizontal dip of the beds cause lengthy exposures of the sediments. Where lithological variation was substantial, sampling was performed to reflect the lateral changes.

2.1.3 Sampling Intervals

Depending on the thickness of the beds and their accessibility, samples were generally collected at intervals of 0·5 to 2m. However, wider sampling intervals were employed for the very thick Barton Sand Formation, whilst much closer intervals were necessary for sediments of the 'Lower Headon Beds' because they are often thinly bedded and/or rapidly change in lithology up the succession.

The succession at the different localities studied is shown in Figures 5, 6a & b, 7, with indications of the sample positions and numbers. They are described below.

2.2 Description of Sections

2.2.1 Mainland Hampshire (Highcliffe - Milford-on-Sea)

2.2.1A Barton Clay Formation

The pebble bed at the base of the Barton Clay Formation is exposed in a section some 200m west of Highcliffe Castle (SZ 199929). The bed is a brownish carbonaceous sand with scattered, rounded flint pebbles, and is 0·45m thick. A single chert pebble was also found in the bed. The pebble bed is underlain by a white, carbonaceous and bioturbated sand of the Boscombe Sands, one of the higher members of the Bracklesham Group (Plate 1). Occurring above the pebble bed is the Huntingbridge Clay. It is a 3m thick glauconitic sandy-clay and sparsely fossiliferous.

The Highcliffe Member is the 'Highcliffe Bed' of Gardner et al. (1888), and comprises the 'Lower Barton Beds A1, A2, A3 and B' of Burton (1929, 1933). The basal parts of the deposit are also exposed on the cliff section, west of Highcliffe Castle. Succeeding the Huntingbridge Clay is a 20 cm thick brownish-yellow clay-ironstone band. Along with a 20 cm thick glauconitic sandy-clay occurring immediately above it, the ironstone band constitutes the Nummulites prestwichianus Bed. The ironstone band, which is the 'foxy-red band' of Fisher (1862), was described as a 'glauconitic ferruginous loam or imperfectly formed ironstone' by Gardner et al. (1888), whilst Prestwich (1847) labelled it as 'tabular soft septaria'. Much of the 'Beds A1 and A2' in the section are overgrown and difficult to sample. 'Bed A3' is exposed east of Chewton Bunny (SZ 217932). It is more fossiliferous, with the occurrence of some thin shell-drifts. On the basal part of the cliff, on the eastern side of Chewton Bunny, a 0·45 cm thick purplish clay with an impersistent band of small (5-10 cm diameter) hard, greyish-white calcareous nodules was observed. The nodules were encompassed and separated by a softer, purplish-brown sideritic clay. This horizon may be one of a number of 'red marl' or 'red band' horizons said to be common within the Highcliffe Member, (i.e. Burton, 1933). 'Bed A3' becomes very sandy near the top and is succeeded by 'Bed B', a glauconitic sandy-clay that Gardner et al. (1888) referred to as the 'Pholadomya Bed'.

The Naish Member comprises the 'Middle Barton Beds C, D, E and F' of Burton (1933). The deposit is exposed, and was sampled, on the cliffs between Chewton Bunny and Barton-on-Sea.

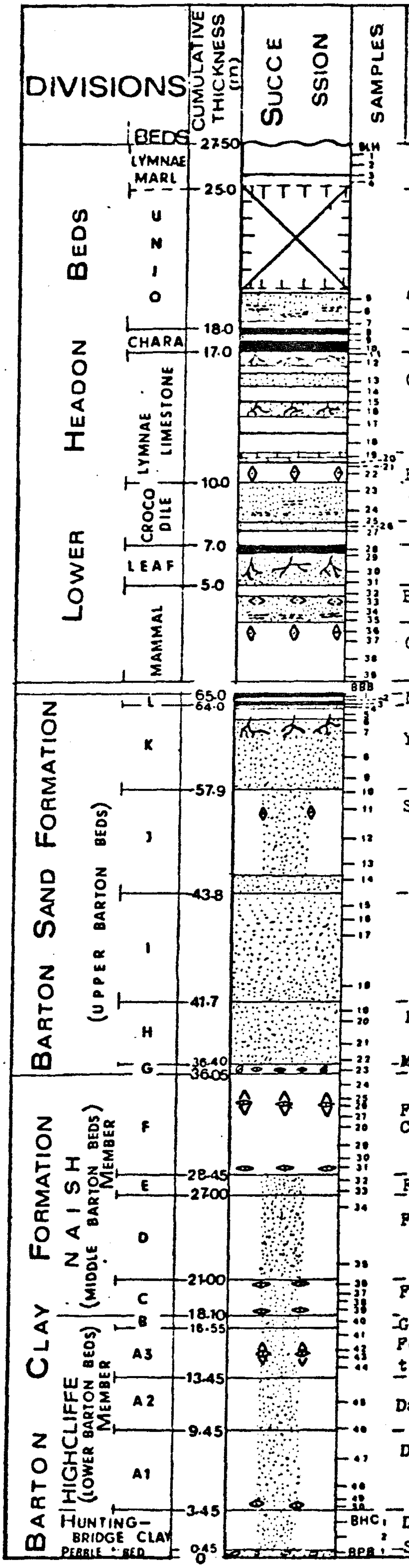
'Bed C' is the '<u>Voluta suspensa</u> Zone' of Gardner <u>et al.</u> (1888). It is a fossiliferous, glauconitic, green sandy-clay, with horizons of calcareous concretions conspicuously marking the base and top of the bed (Plates 2,3). The concretions are massive, spherical and oval shaped, varying from about 30 cm by 20 cm up to 100 cm by 50 cm. They are fine-grained, greyish-green, glauconitic and fossiliferous with fossil shells and carbonaceous materials. Some of the concretions are thinly encrusted with uncrushed fossil shells (Plate 6), which thus suggest penecontemporaneous exposure of the concretions on the sea-floor for a considerable length of time. The concretions also possess internal fissures that are filled with septarian calcite (Plates 4,5). The pre-compaction age of formation of the concretions is indicated by the deformation of the bedding planes of host sediment around the concretions (Plate 3).

'Bed D' is very sandy and uncompacted in its upper part, but clayey and glauconitic at the base. 'Bed E' is a drab (greyish) sandy clay with a basal seam of shells mainly composed of the bivalve <u>Ostrea plicata</u>. 'Bed F' is a brownish clay with numerous shell-drifts and calcareous concretions at the base and near the top. Those at the base are similar to the concretions in 'Bed C', whereas near the top the concretions form a continuous band encompassed by brownish sideritic clay.

2.2.1B <u>Barton Sand Formation</u>

The 'Barton Sands' consist of sediments believed (Curry, 1965; Murray & Wright, 1974) to have accumulated in the shallowing late-phase of the Barton Sea. The sediments are exposed between Barton-on-Sea and Becton Bunny (SZ 248927-254925) and comprise 'the Upper Barton Beds G, H, I, J, K and L' of Burton (1933). Change in the nature of the sea is first marked by a 0·45 cm thick mass of current-accumulated shell fragments. These are locally cemented by siderite into a brownish-red band - 'the Stone or Shell Band' of Burton (1929). The bed was only observed, during the current sampling, above a slumped terrace about 300m east of Chewton Bunny. It consists of concretionary clay ironstones at the base, and an upper part of alternating bands ($\lesssim$ 2 cm thick) of clays and shell drifts. The bed thins westwards, whilst eastwards the shell drifts thicken, so as to constitute the bulk of the bed. There are preserved trace fossils in the cemented parts of the 'Shell Band'. These comprise hair-like to millimetre-sized, mining-type escape burrows similar to those described

Fig.5 : The Upper Eocene Succession;Highcliffe-Milford on Sea,Mainland Hampshire.



LITHOLOGICAL DESCRIPTION

Fossilliferous mottled clays with a thin carbonaceous band

Unexposed series of clays and sands

Greyish-white sand with clay laminations and pockets of fossils; becomes ferruginous at top but underlain by a laminated clay

Lignites and brown sands with rootlets and shells

Goethitic sand underlain by alternating sands, clays and lignitic bands

Fossiliferous creamy-white 'Lymnae Limestone'; lignitic at base

Fossiliferous green clay with concretionary sideritic ironstone

White sands with clay laminations and pockets of shells at base

Fossiliferous carbonaceous clays separated by a brown sand and underlain by a green clay

Rootlets-bearing brown sand with a lignitic mud at top

Bright green clay underlain by a band of sideritic ironstone and greyish-white silty-sand with pockets of shells

Greenish clay with sideritic ironstone concretions at top but becomes carbonaceous at base

Mottled clay. lignitic at top and base

Yellowish and white sands with a thin green clay horizon, rootlets and pockets of shells at the top

Sparsely fossiliferous greyish sandy-clay with scattered sideritic nodules near the top; grades into a carbonaceous sand at the base

Bioturbated white sand

Fossiliferous greyish-blue sands(-the Chama Bed); becomes clayey towards the base

Masses of shells and greyish clay; siderite-cemented in places into 'Shell or Stone Band' with preserved trace fossils

Fossiliferous brownish-grey clays with numerous shell drifts. Calcareous concretions occur near the top and at base; the upper concretions being encompassed by a thin band of friable sideritised clay

Fossiliferous greyish sandy-clay

Fossiliferous sandy-clay; glauconitic at base but very sandy, mottled and carbonaceous towards the top

Fossiliferous, glauconitic sandy-clay with calcareous concretions at top and base

Glauconitic sandy-clay

Fossiliferous glauconitic sandy-clay with mottled sands at the top and an impersistent band of friable sideritised clay enclosing calcareous nodules

Dark-green glauconitic sandy-clay

Dark-green glauconitic sandy-clay with a sideritised ironstone band (-the Nummulites prestwichianus Band) at base

Dark-green glauconitic sandy-clay

Sand-supported flint pebble bed; brownish, loamy and carbonaceous by Cluff (1980) from shelf Palaeozoic shales in Illinois, U.S.A. There are also impressions of Chondrites Thallasnid and Lithodomus (identifications by P. Shelford - personal communication). The trace fossils depict the existence of shallow, aerobic shelf waters with low detritus deposition.

The 'Shell Band' is succeeded by the clayey basal part of 'Bed H' - the 'Chama Bed'. This bed is essentially a greyish-blue clayey-sand with ferruginised shells and casts of Chama squamosa. The more sandy upper part of the bed is exposed below the Golf Course, east of Barton-on-Sea.

Also exposed below the Golf Course is 'Bed I', an extensively bioturbated, largely unfossiliferous, white sand, believed to have been deposited in a shallowing very clear sea. Occurring above the white sand is a 1·4m thick, drab, carbonaceous clayey-sand constituting the basal part of 'Bed J'. The remaining part of 'Bed J' consists of a stiff, sparsely fossiliferous, greenish-grey sandy-clay, which is well exposed on the cliff faces on both sides of Becton Bunny. There are scattered small (~ 10 cm diameter) greyish-white sideritic nodules in the upper parts of 'Bed J' exposed in the lower reaches of the Beacon Cliff, east of Becton Bunny. 'Beds I and J', together, constitute the 'Becton Bunny Beds' of Gardner et al. (1888), while 'Bed J' is called the 'Olivella branderi Zone'. The foraminifera assemblage studied by Murray & Wright (1974) suggests the deposition of 'Bed J' to be in a brackish-water, estuarine or marsh environment.

The silting-up of the Barton Sea was completed with the deposition of 'Bed K', the 'Long Mead End Bed' of Gardner et al. (1888). This consists of about 6m of white and yellow sands with a brown clayey-sand at the base and a green mottled clay at the top. 'Bed K' is barren, except in its uppermost 2m, where mollusc fossil shells are current-concentrated into pockets. The dominant shells are those of the gastropod Batillaria concava. At Becton Bunny, this fossiliferous horizon was observed to have been decalcified, but equivalent horizons observed on the foreshore at Long Mead End are still fossiliferous. At the top of 'Bed K' is a 10 cm-thick, mottled green clay, which, in fact, may be part of a 'seat-earth' to the succeeding lignitic 'Bed L'. Within the green clay are rootlets, which also penetrate about 1m of the sand below. Rootlets are important pedogenic features (Brewer, 1964; Buurman, 1975) that would suggest the green clay and parts of the sand as having emerged, been colonised by plants, with the possible development of palaeosols. Other rootlet-bearing horizons occur higher up the succession, on Hordle Cliff and at Alum Bay.

'Bed L' is about 1m thick and consists of two bands of lignitic clays separated by a mottled brown clay with a few crushed fossil shells that are believed (Burton, 1929) to indicate brackish depositional conditions. The shells are mostly intimately mixed with carbonaceous materials and associated with mottled sand lenses and clays. The immediate seat-earth to the lower lignitic band is a thin, 2 cm thick, brown sand.

2.2.1C 'Lower Headon Beds'

The 'Lower Headon Beds' are exposed on Beacon Cliff and Hordle Cliff, respectively located to the west and east of the gap in the cliff at Long Mead End (SZ 262964) (Fig.3). The lower units are mostly exposed around Long Mead End, whilst the upper horizons can be seen to the east around Hordle House and at Paddy's Gap near Milford-on-Sea. The deposit was first divided into thirty-three units by Tawney & Keeping (1883). In 1888, Gardner et al. re-described the section with a smaller sub-division of thirteen units which were, either individually or as groups, assigned names. From the base, the units were named Mammal Bed, Leaf Bed, Crocodile Bed, Ironstone and Lymnean Limestone Beds, Chara Bed, Unio Bed and the Lymnean Marl. These latter descriptions were adopted by White (1915), Curry (1958), and also in the present study.

i) Mammal Bed

The Mammal Bed is exposed on Beacon Cliff. It is about 5m thick and mainly consists of greenish clays, silty sands and two horizons of sideritic clay-ironstones. The lower ironstone horizon is 3m from the base of the bed and is 'Bed 8' of Tawney & Keeping (1883). The ironstones are concretionary with similar size, shape and elongation to the calcareous concretions in the 'Middle Barton Beds' described earlier. The other ironstone horizon is a 5 cm thick band occurring about 1m above the concretionary ironstones. In between the ironstone horizons is a bluish-grey, silty sand with pockets of shells of the gastropod Viviparus lentus. A greenish-clay occurs below the ironstone concretions. It is sparsely fossiliferous and, towards the base, it becomes brownish-green with abundant lignitic and carbonaceous material. In the uppermost part of the Mammal Bed, and above the ironstone band, there is an unfossiliferous bright green clay. Tracing the Mammal Bed westwards from Long Mead End, most of the bed becomes obscured by cliff-slumps, but the upper parts were observed to have become very silty and more greyish. Edwards (1967), from floral and faunal studies, suggested that the Mammal Bed is a deposit of 'coastal fen-land waters' and probably represents various stages in a silting-up cycle from shoreline conditions.

ii) Leaf Bed

The Leaf Bed is 1·9m thick and consists of a 20 cm thick lignitic mud at the top, and a purplish-brown sand that gets siltier towards the base. The lignitic mud is 'Bed 10' of Tawney & Keeping (1883), and was only prominently exposed below a slumped terrace on the upper reaches of Beacon Cliff. It contains leaf remains, but impersistently thins out eastwards. Its immediate seat-earth is a 2 cm thick ferruginous brown sand. The purplish sand, constituting the bulk of the Leaf Bed, contains abundant carbonaceous material and numerous ramifying ferruginised rootlets. The floral content of the Leaf Bed has been of particular interest to many workers, including Chandler (1961), Edwards (1967) and Fowler et al. (1973). The assemblage suggests the prevalence of a brackish water to swampy environment, and a highly vegetated sub-tropical climatic condition.

Some 50m west of the gap, at Long Mead End, there is a large penecontemporaneous channel into the Leaf Bed and across the overlying Crocodile Bed. The channel is sandy and full of carbonaceous material. It was not studied in great detail in this investigation.

iii) Crocodile Bed

The Crocodile Bed was best exposed on the lower part of Hordle Cliff just east of Long Mead End. It mainly consists of a greyish-white sand which, towards the base, contains thin clay laminations and pockets of fossil shells comprising of Potamomya, Potamides and Corbicula. Mammalian remains, particularly crocodile bones and turtle carapaces are often found in the sands. Occurring below the sand are two thin, dark, carbonaceous plastic clays with comminuted shells. The clays are separated by a ferruginous brown sand. The brown sand and the plastic clays, together, constitute the Coprolite Bed of Gardner et al. (1888). A green clay, reported by earlier workers to occur below the Coprolite

Bed, was not observed in the present study due to slumping. Edwards (1967) regarded the Crocodile Bed as essentially a river-mouth sand deposit, with the mollusc assemblage suggesting slightly estuarine conditions.

iv) 'Lymnae Limestone (and Ironstone) Bed'

This bed is 6.6m thick and consists of green clays, purplish sands, sandy ironstones, a creamy limestone and three lignitic bands. They represent divisions 5, 6 and 7 of the sections made by White (1915), and were collectively designated the 'Lymnae Limestone Division' by Edwards (1971). At the base there is a concretional sideritic clay ironstone (Plate 10). This is 'Bed 16' of Tawney & Keeping (1883) or the Ironstone Bed of White (1915). The ironstone is succeeded by a fossiliferous green clay, followed by the creamy 'Lymnae' Limestone (Bed 17 of Tawney & Keeping or Division 6 of White, 1915). The limestone is 20 cm thick and contains abundant freshwater fossil shells of the gastropod Galba (Lymnae) longiscata. It has a basal lining of a thin, 1 cm thick, lignitic band. Succeeding the limestones are a series of green clays and purplish white sands with the other two lignitic bands. The uppermost of the lignitic bands and its underlying sand contain ferruginised rootlets. At the top of the bed occurs the other ironstone horizon. It is a 30 cm thick band of brownish-red, goethite-cemented and rootlet-bearing sand (Plates 11 and 12). In places, around Long Mead End, it is broken up into two 10 cm thick hardened bands separated by very ferruginous loose sands. Eastwards, the horizon becomes clayey and very sideritic. When traced further east to Hordle House, however, it is a brown ferruginous sand with mottled green clays. This contains yellowish pyritised rootlets (Plate 13) and small (~ 5 cm diameter) nodular gypsiferous bodies. The horizon is considered to be a relict of a fossil soil.

v) Chara Bed

The Chara Bed is about 1m thick and is mainly exposed on the Hordle House - Long Mead End section of Hordle Cliff. The section sampled around Hordle House consists, from the base upwards, of a thin ferruginous sand; a 35 cm thick lignitic clay; a 40 cm thick finely laminated and carbonaceous purplish-brown sand and, at the top, a 20 cm thick lignitic mud. The ferruginous sand at the base contains pockets of Polymesoda shells and pyritised and/or gypsiferous rootlets (cf. Plate 13). Pockets of Charaphyte nucules have also been reported from the sand (Tawney & Keeping, 1883; Edwards, 1967). The purplish-brown sand separating the lignitic horizons appears to be part of a sandy penecontemporaneous Channel-infill that cuts through the Chara Bed. The channel is not as carbonaceous as that cutting into the Leaf Bed on Beacon Cliff.

vi) Unio Bed

Much of this bed was unexposed during the present studies; only about 2m of its basal part was observed in the vicinity of Hordle House. The exposure consisted of a 60 cm thick fossiliferous, fissile, green clay at the base, followed by a 1m thick greyish sand with clay laminations and pockets of shells. Above the sand was a band of friable, sandy ironstone and a ferruginous sand.

vii) Lymnae Marl

This is the uppermost unit of the 'Lower Headon Beds'. It constitutes 'Beds 32 and 33' of Tawney & Keeping (1883) or Divisions 12 and 13 of White (1915). A 2m thick exposure of the bed was observed beside a footstair to the beach, some 300m west of Paddy's Gap. The section consists of a greenish-clay at the base, followed by a dark lignitic and shelly clay, and finally a mottled yellowish-green clay. The lignitic and shelly-clay comprises the 'Rodent Bed' of White (1915), from which rolled bones of vertebrates, especially rodent and serpents' teeth, have been reported. Common within the 'Lymnae Marl Division' are shells of Unio solandri and Galba (Lymnaea) longiscata.

viii) Younger Sediments

The Lymnae Marl, at the top of the Upper Eocene Succession, is unconformably overlain by a ferruginous, yellowish-brown sand full of shell debris. The sand marks the on-set of the marine transgression during which the 'Middle Headon Beds' were deposited. A few metres of the basal green clays of the 'Middle Headon' are exposed along the foreshore at Milford-on-Sea. Scattered small pods of sideritic ironstones occur within the clay.

Throughout the entire length of its exposure from Mudeford to Milford-on-Sea the sediments were capped, on the uppermost reaches of the cliffs, by up to 5-6 cm of Plateau Gravel, a Pleistocene superficial deposit. These gravels are thought to be channel deposits of an eastward flowing 'Solent River' (White, 1915; West, 1981).

2.2.2 Alum Bay - Heatherwood Point, Isle of Wight

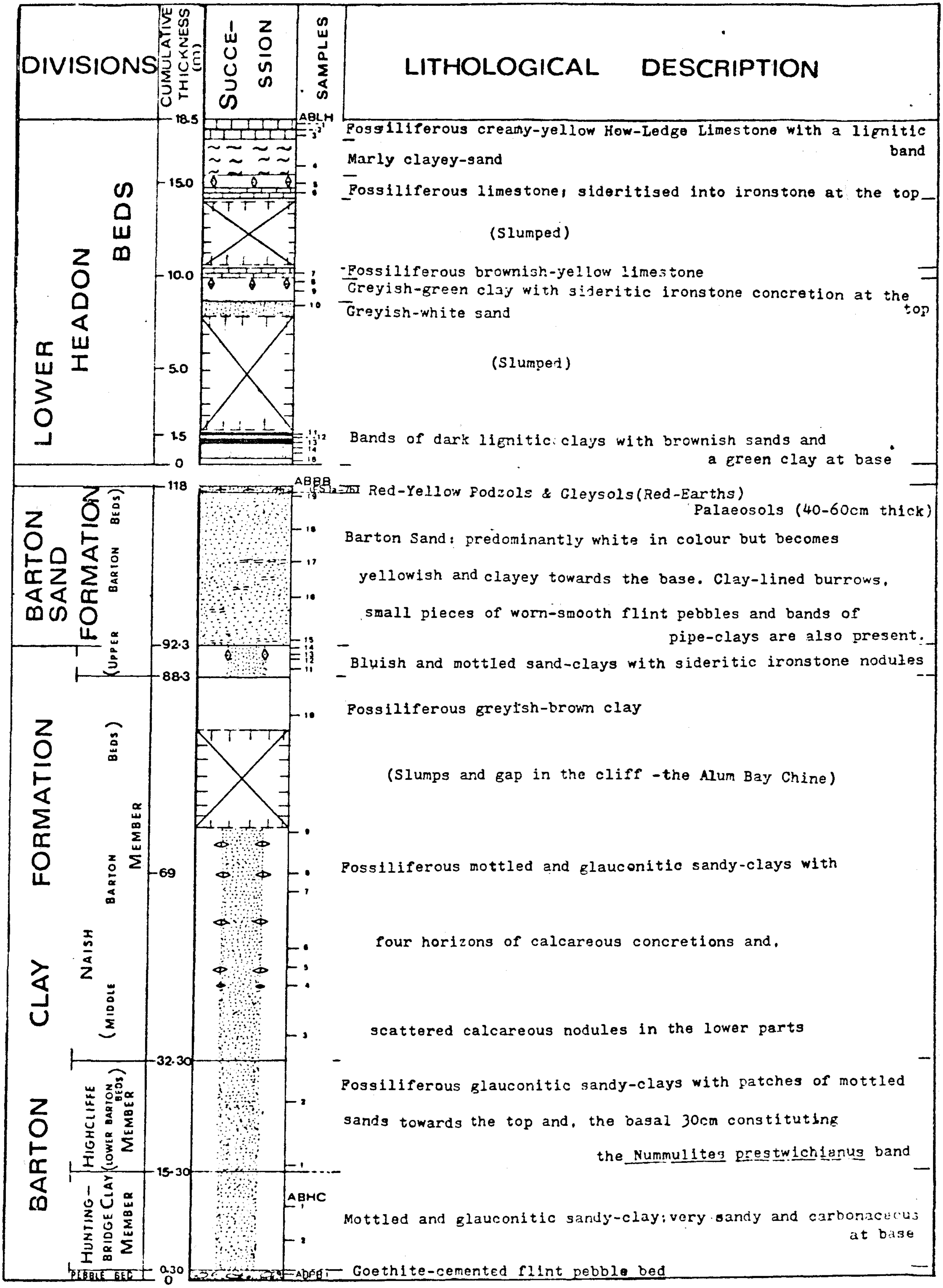
Alum Bay is situated on the western part of the Isle of Wight, and is separated from Milford-on-Sea by a 7 km stretch of The Solent (Fig. 3). The Belemnitella mucronata Zone of the Upper Cretaceous Chalk forms the southern end of the Bay; the part of it that juts into the sea is known locally as 'The Needles'. The Palaeogene deposits succeed the Chalk northwards, with the Reading Formation at the base and the 'Bembridge Limestone' at the top. The 'Lower Headon Beds' and younger deposits mainly outcrop on Headon Hill, at the northern end of Alum Bay, and continue northwards along the cliff from Heatherwood Point to beyond Colwell Bay.

The sediments from the Chalk to the top of the Barton Clay Formation are steeply inclined and have an E-W strike; the dip, however, decreases rapidly from the base of the Barton Sand Formation to become near-horizontal at the base of the 'Lower Headon Beds', at around Heatherwood Point. The Upper Eocene succession at this locality was studied and sampled with reference to the sections given by Prestwich (1846), Bristol (in Forbes, 1856), White (1921), Curry (1958) and Bujak (1976). Details of the succession (Fig.6a,b) are as follows.

2.2.2A Barton Clay Formation

This deposit constitutes 'Bed 29' of Prestwich (1846) and, as on the mainland, the succession commences with a pebble bed. The bed is 30 cm thick, brownish-red, and comprises sands and flint pebbles cemented by goethite. The pebbles are mostly rounded to sub-rounded, and occasionally flattened. Many of them possess goethite-filled or lined surface cracks. This pebble bed was correlated with that on mainland Hampshire by Fisher (1862), who also considered the pebble beds to be a beach deposit marking the onset of the Barton Sea transgression. He further thought that the bed formed the bottom of the Barton Sea for a long period, during which little sediment deposition occurred. The deposition of the bed was considered to be indirect evidence for low scale, intermittent subsidence emergence of the Hampshire Basin during the Eocene.

Fig.6a: The Upper Eocene Succession,Alum Bay-Heatherwood Point;Isle of Wight.



In the present study, the pebble bed at Alum Bay is considered to constitute the goethite-indurated horizon of a palaeosol profile. The bed is underlain by a ferruginous, yellowish sand and non-marine rootlet-bearing lignites and plastic clays belonging to the Middle Eocene Bracklesham Group.

The Huntingbridge Clay that succeeds the pebble bed is a 15m thick, drab-green, mottled sandy-clay; very sandy and full of plant debris in the basal part, but glauconitic and sparsely fossiliferous at the top. At the base of the succeeding Highcliffe Member is the Nummulites prestwichianus Bed - a dark-green, glauconitic and fossiliferous sandy-clay. The rest of the deposit is also generally glauconitic and fossiliferous, although towards the top there are mottled horizons with patches of greyish sand lenses. The succeeding Naish Member may be sub-divided into four units. The lowermost unit is made up of mottled sandy clays with numerous sand lenses, with abundant carbonaceous material and scattered calcareous nodules. These nodules are greyish-white with diameters of about 3 cm to 6 cm. The next unit of the division consists of mottled sandy clays, fossiliferous and glauconitic sandy clays, and four horizons of calcareous concretions. The concretions are also glauconitic and dark green. They are similar to those in equivalent horizons at Barton, except that they lack the calcite-filled septarian fissures. Also many of the exposed concretions are weathered, with thin layers of lustrous selenite on the weathered surfaces. The third unit of the deposit comprises a fossiliferous brown clay; this is separated from the earlier sediments by a 15m wide gap in the cliff - the 'Alum Bay Chine' (SZ 306854), through which access to the beach is gained (Plates 14 & 15). The uppermost part of the Naish Member comprises the basal 4m of the 'Upper Barton' of Gardner et al.(1888). It is made up of mottled, bluish-green clay with sand lenses and two, 3-6 cm thick, bands of nodular sideritic ironstones. When traced down the cliff onto the foreshore, each of the ironstone bands, which are about 1m apart, is further split into two bands to give a lenticular outline to the enclosed unsideritised clay. White (1921) and Murray & Wright (1974) have correlated these ironstones with the Shell Band ('Bed G') at Barton, whilst the underlying and overlying mottled sandy clays have been respectively equated to the top of 'Bed F' and the 'Chama Bed (Bed H)' at Barton.

2.2.2B Barton Sand Formation

The Barton Sand Formation at Alum Bay wholly comprises a white sand.

The deposit is the 'Headon Hill Sand' of Prestwich (1846), the 'Upper Bagshot Sand' of Bristow (in Forbes, 1856) and the 'Barton Sand' of White (1921). Inland occurrences of the sand on the Isle of Wight are said to have been quarried for glass-making (Webster, 1816). A few metres of the basal part of the 'Barton Sand' are yellowish and clayey, whilst the upper part is capped by a variegated, brownish-red, goethitic palaeosol.

Although at first sight featureless, in fact the Barton Sand contains several interesting features that include Liesegang rings (Plate 16); small, friable, goethitic hollowed sand-moulds of plant stems and roots; pipe clays; clay-lined burrows; carbonised plant matter; and small flint pebbles.

The Liesegang rings probably formed in situ by iron segregating from mobile, iron-rich pore waters, but their time of formation could not be ascertained. The derivation of the goethitic sand moulds is also difficult to ascertain without further detailed knowledge of their petrology and mineralogy. These two features were most common in the lower parts of the Barton Sand. However, a few were observed in some of the mottled sand lenses in the Barton Clay, lower down in the succession.

The pipe clays (Plate 17) occur as discontinuous lenticular seams within the sands at levels of 3m and less above the beach level, at about 30m south of Heatherwood Point. They are greyish-green and plastic, with thicknesses of 3 cm to 6 cm. The pipe-clays often have thin films of dark lignitic or carbonaceous material at the top or base. Similar pipe-clays occur sporadically throughout the Palaeogene succession in the basin, and are exploited as ball-clays in Dorset (see Gilkes, 1966). Similar, but thicker, deposits occur in the cyclic fluvio-lacustrine Oligocene sediments of the Petrockstow Basin, north Devon (Freshney, 1967). The pipe-clays have probably settled in ponded water bodies on flood-plains with little or no current agitation.

The carbonaceous matter occurs mostly as very small ($< 0{\cdot}5$ cm) disseminated macerated aggregates in the sands. They would have been derived as debris from nearby vegetated lands. The flint pebbles are few and widely disseminated. They are generally well worn and flattened with long axes less than 2 cm, and may well have been re-worked from older Tertiary sediments.

The clay-lined burrows occur mostly in the lower parts of the Barton Sand. They are thought (Daley & Edwards, 1973) to resemble burrows of certain living crustaceans and annelids which inhabit well-sorted sands in littoral zones and on tidal-creek point bars. Their occurrence in the Barton Sand would thus suggest that deposition occurred close to mean sea-level.

2.2.2C Palaeosols

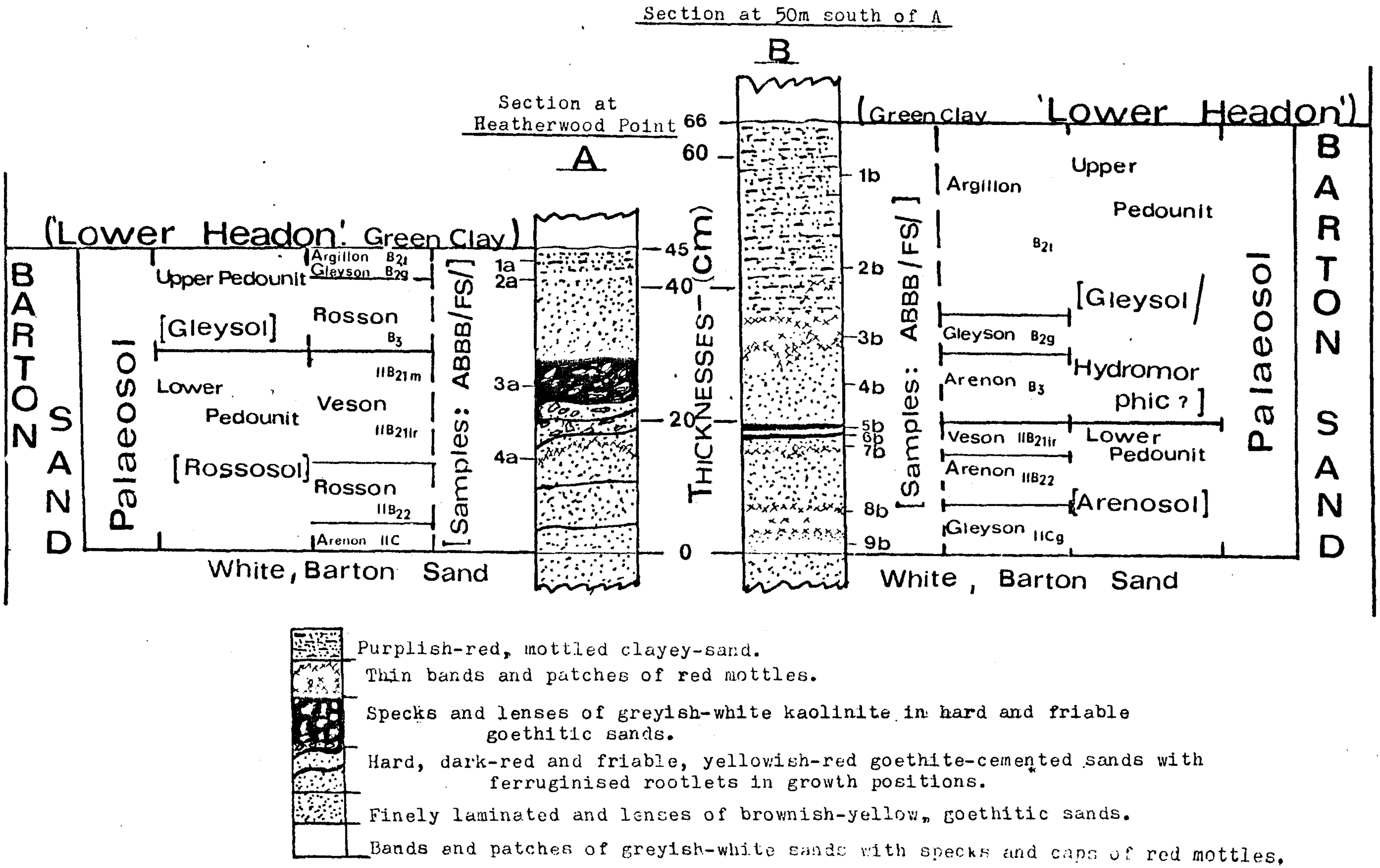
The top of the Barton Sand is marked by a ferruginous, brownish-red and yellowish horizon. At the time of sampling, access to the horizon was limited to Heatherwood Point, and a section some 50m further south. The sections observed (Plates 18 and 19) are considered to be palaeosols of the red-yellow sub-tropical to tropical podzol type (Benemma, 1962; Hunt, 1972; Buurman, 1980b) and are shown in Figure 6b. The horizon may be related to the numerous podzolic-lateritic palaeosols occurring in the Tertiary rocks of western Europe (Pomerol, 1964; Van den Broek and Van der Waals, 1967; Freytet, 1971; Muckenhausen, 1973; Buurman, 1980; and Isaac, 1981 & 1983).

Using the pedological characterisation contained in U.S.D.A. (1967) and Fitzpatrick (1971), tentative identifications of the palaeosol horizons have been made. These can only be regarded as approximate because of their long post-depositional history; they could, among other things, have been subjected to contemporaneous erosion and diagenetic alteration.

The two soil sections observed are shown in Figure 6b ; each is made up of two pedounits, which are incompletely preserved soil profiles. The lower pedounit consists entirely of thinly laminated sands, whereas the upper pedounit, although mostly sandy, has a relatively clayey top. In the upper pedounit the thin laminations become obliterated upwards, so that in the uppermost clayey horizon no lamination is visible.

The palaeosol Profile B, south of Heatherwood Point, is about 66 cm thick. It consists of a lower pedounit comprising a gleyson (IICg), arenon (IIB3) and veson ($IIB2_{ir}$) in ascending order; whereas the upper unit comprises an arenon (C), gleyson (B2g) and argillon ($B2_t$). The gleysons are horizons with thin bands, patches and lenses of greyish or bluish-white, pallid sands. They show red mottles, which consist of scattered specks of goethite, which are often concentrated into thin wavy bands or channels.

Fig.6b: Profiles of the Barton Sand Palaeosols, Heatherwood Point-Alum Bay



Purplish-red, mottled clayey-sand.

Thin bands and patches of red mottles.

Specks and lenses of greyish-white kaolinite in hard and friable goethitic sands.

Hard, dark-red and friable, yellowish-red goethite-cemented sands with ferruginised rootlets in growth positions.

Finely laminated and lenses of brownish-yellow, goethitic sands.

Bands and patches of greyish-white sands with specks and caps of red mottles.

The arenons are brownish-yellow, uncemented, goethitic, finely-laminated sands. The veson is composed of loosely cemented or friable brownish-red goethitic sand that grades upwards into hardened, dark red goethitic bands with red mottles. Plant remains are very common in the veson and there are numerous rootlets in growth position (i.e. Plate 20). These rootlets are generally elongated, hollowed tubes with knobbly ends. They measure between 2 and 5 cm in length, and 0·2 to 0·6 cm in diameter. They possess a thin (∼ 0·5 mm) dark-coloured wall, rimmed externally by a thin layer of red mottling. The hollows of many of the rootlets are filled with brownish and reddish, loosely agglutinated, sand grains, with red mottling and, sometimes, dark red goethite concentrates. The sand grains and mottles in the veson can be seen to 'swirl' round the rootlets or to 'collapse' against the root walls - these are 'drag' features that have resulted as roots forced their way through the soils. The argillon consists of a mass of purplish-red and mottled clayey or silty sands, with some thin lenses of greyish and yellowish-brown sands. The colour is deep purple in the lower part of the argillon, but pales towards the top. The argillon is firm and plastic when wet but friable when dry.

At Heatherwood Point, the Palaeosol Profile A (Plates 18a,b) was observed. The profile is about 45 cm thick, more sandy than Profile B, and possesses a thicker lower pedounit. There is no gleyson at the base of the lower unit; rather, the lowest horizon is a thin (2 cm) thick yellowish sand arenon (IIC). This is succeeded by a yellowish-red goethitic sand, the rosson (IIB22); and it in turn by a veson, which is made up of friable yellowish-red goethite-cemented sand with mottles ($IIB21_{ir}$), and hard, dark red goethitic bands (IIB21m). Vesicular greyish-white flint-like kaolinite occurs within the veson (Plates 18c,d) The kaolinite occurs as small lenses and specks, generally irregularly disposed, although it shows some tendency to concentrate along bedding planes. Most of the lenses are less than 3 mm in length; only a very few exceed this, achieving a maximum length of 1 cm.

The upper pedounit of Profile A also consists of a 10 cm thick rosson (C) with a very thin < 1 cm greyish-white pallid band (B2g); and a mottled, purple clayey sand - the argillon ($B2_t$).

Common to both the arenons and rossons in Profiles A and B are small lenses and patches of greyish-white sand. These could be eluviated patches in the soils. From the above descriptions, the lower pedounit at Heatherwood Point may be classed as a Rossosol which, to the south, grades into an Arenosol. The upper pedounit may be a Gleysol or, in broader terms, a Hydromorphic soil. Detailed descriptions of these soil classes are given in Fitzpatrick (1971).

2.2.2D 'Lower Headon Beds'

At the time of sampling, much of the 'Lower Headon Beds' between Alum Bay and Colwell Bay was poorly exposed because of cliff-slumps. It was only at Heatherwood Point that the deposit was exposed and studied. The exposure consists of three sections, separated from each other by slump terraces. Immediately overlying the Barton Sand Palaeosols is the 30 cm thick green clay basal bed of the 'Lower Headon Beds'. The clay has a sharp but slightly wavy and undulating (erosional) contact with the palaeosol below. It is succeeded by a 90 cm thick purplish and greyish sand; and two lignitic clays, 5 cm and 10 cm thick respectively, separated by a brown sand.

The second exposure occurs about 5m higher than the lower one, and consists of a 20 cm thick fossiliferous limestone underlain by a 15 cm thick band of greenish sideritic ironstone concretions. The ironstones are encompassed and underlain by a 1·15m thick plastic green clay. The clay is, further, underlain by a white sand, only 1m of which was exposed.

The third section contains the uppermost sediments of the division. The sediments consist of earthy-brown and creamy-yellow fossiliferous limestones with lignitic bands; a 2·50m thick sandy marl; and a 20 cm thick sideritic ironstone. This ironstone is a sideritised shelly limestone. Some of the primary lime-mud enclosed within some fossil shells appears to have been preserved, unaltered (Plate 22). The uppermost sediment is the How Ledge Limestone, a 1·50m thick creamy-yellow limestone with a 10 cm thick lignitic band occurring at about 50 cm from the top. These limestones contain abundant Galba(Lymnae) longiscata.

Succeeding the 'Lower Headon sediments', above another slumped terrace, are the fossiliferous brown clay basal beds of the Oligocene 'Middle Headon Beds'.

2.2.3 Whitecliff Bay, Isle of Wight

Sediments exposed along the cliff at Whitecliff Bay (SZ 638857-639860-660870) are similar to those exposed at Alum Bay - Headon Hill. In addition, a younger Oligocene sediment, the Bembridge Marl, is also exposed. The sediments (Fig. 4) are vertical or steeply inclined; only in the 'Bembridge Limestone and Marl' does the dip change rapidly to near horizontal eastwardly. The Upper Eocene succession (Fig. 7) has been studied with reference to the sections given by Prestwich (1846), Gardner et al. (1888), Curry (1958) and Stinton (1971).

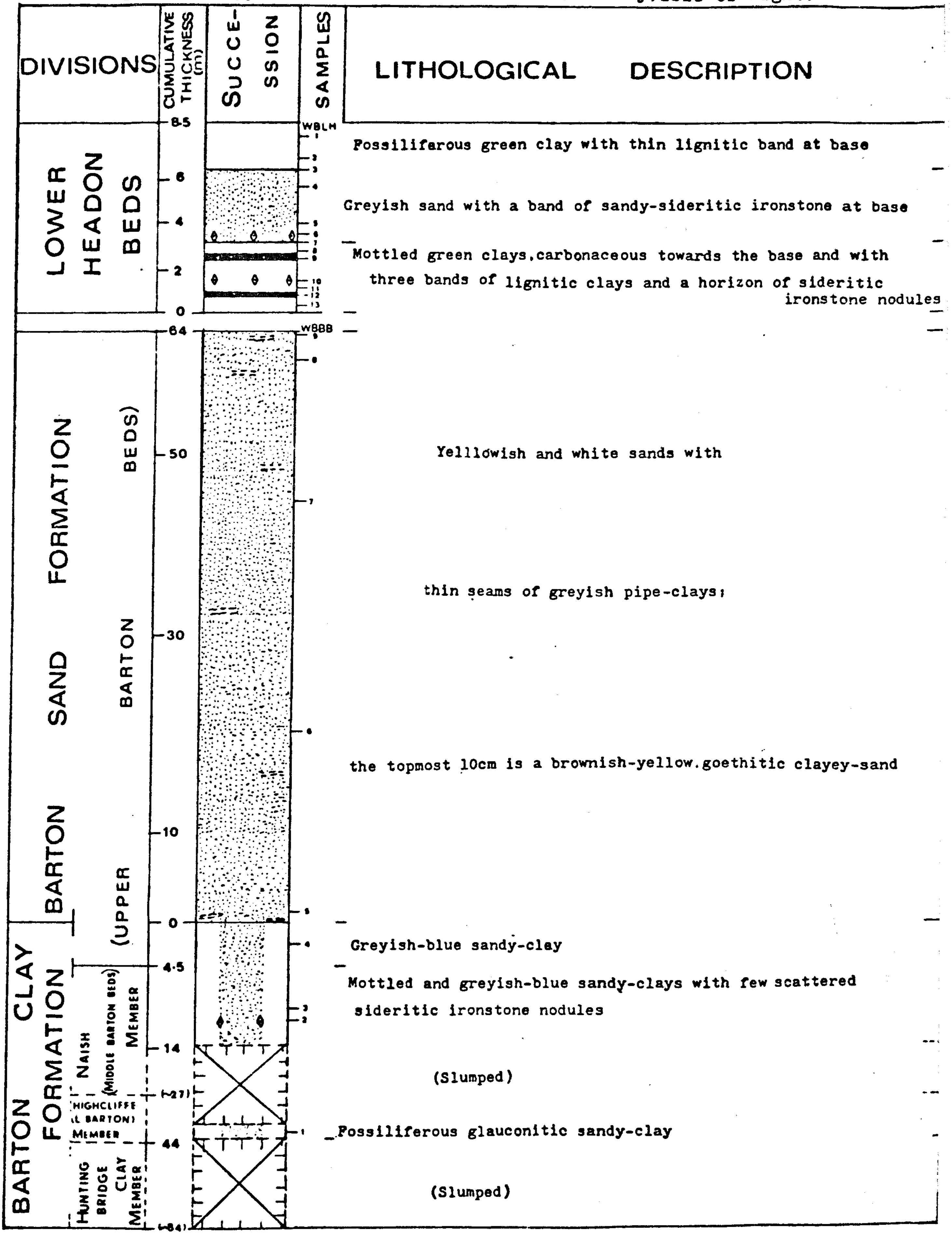
2.2.3A Barton Clay Formation

There is no pebble bed at this locality, but the Huntingbridge Clay and most of the equivalents of the Highcliffe and Naish Members, that together constitute 'Beds 16-19' of Prestwich (1846), were obscured by cliff slumps. Only a small section of part of the Highcliffe Member was exposed. This was just south of where a zig-zag foot-stair and path descend onto the beach. It consists of about 1m of very fossiliferous, glauconitic sandy clay. Also, about 15m of the upper part of the Naish Member was exposed in a cliff face behind a beach-hut (Plate 23). The first 10m of the section consists of mottled sandy clay with sand lenses, pyritised shell casts, and a horizon with scattered ironstone nodules. The nodules are sideritic, brownish-red and sub-spherical with diameters of 3 cm to 6 cm. The uppermost 5m consist of a greyish-blue sandy-clay with ferruginised casts of mollusc shells. It has been equated to the 'Chama Bed' at Barton (Gardner et al., 1888).

2.2.3B Barton Sand Formation

The Barton Sand at Whitecliff Bay (Plates 23, 24) is wholly sandy and consists of 63m of thick yellowish and white sands. The deposit constitutes the 'Headon Hill Sand' (Bed 30) of Prestwich (1846) or the 'Barton Sand' of White (1921). At the base of the Barton Sand there are thin iron-pan bands with some geothitic sand-moulds of plants similar to those described from the Barton Sand at Alum Bay. Also, there are thin seams of greyish pipe-clays and clay laminations in the middle and upper parts of the sands. Towards the top, the Barton Sand becomes more yellowish, and its top is marked by a 10 cm thick, loamy, yellowish-brown, goethitic clayey sand (Plate 24). This loamy sand may also have been part of a

Fig.7 :The Upper Eocene succession, Whitecliff Bay, Isle of Wight.



Possiliferous green clay with thin lignitic band at base

Greyish sand with a band of sandy-sideritic ironstone at base

Mottled green clays, carbonaceous towards the base and with three bands of lignitic clays and a horizon of sideritic ironstone nodules

Yelllowish and white sands with thin seams of greyish pipe-clays; the topmost 10cm is a brownish-yellow, goethitic clayey-sand

Greyish-blue sandy-clay

Mottled and greyish-blue sandy-clays with few scattered sideritic ironstone nodules

(Slumped)

Possiliferous glauconitic sandy-clay

(Slumped)

fossil soil, laterally equivalent to that at Alum Bay.

2.2.3C 'Lower Headon Beds'

The tops of the Barton Sand and the 'Lower Headon Beds' were well exposed half way down a footpath to the beach behind the Whitecliff Bay Hotel. The section (Plate 24) was less affected by weathering, vegetational growth and cliff slumps than that on the beach side of the cliff.

The 'Lower Headon Bed' is 8·5m thick and consists of green clays, four lignitic bands, two ironstone horizons, and a 3m thick greyish sand. At the base there are very carbonaceous green clays, including a 30 cm thick very lignitic clay. The other lignitic clays are thinner, being between 3 cm and 10 cm thick. Most of the fossils in the clays occur as crushed and poorly preserved shells. The lower ironstone horizon occurs 1·5m from the base, and is nodular, with nodule sizes of about 20-30 cm by 10-15 cm. The ironstones are enclosed within a mottled green clay matrix (Plates 24, 25). These ironstones possess outer foliated layers and crusts of brownish-yellow or red goethite with coatings of orange-brown lepidocrocite. Their inner sideritic layer is white when freshly broken, but turns reddish-brown on only a few days' exposure. There is also a hollowed centre, although with no 'clay rattle' such as that described by Childs et al. (1974) in some ironstones from New Zealand. No fossil remains occur in the hollow centre either. The second ironstone band occurs at the base of the greyish sand, 3·5m from the base of the Lower Headon division. The band is a 15 cm thick, brownish-red and sandy sideritic ironstone. The top of the section is marked by a green clay. This is succeeded by a brown clay with a mass of marine shells, which marks the base of the 'Middle Headon Beds'.

CHAPTER 3

EXPERIMENTAL

The laboratory investigations were essentially designed to give detailed mineralogical, petrological and geochemical information on the Upper Eocene sediments (Figs.5-7), in the hope of elucidating their petrogenesis. The techniques employed included mineralogical analysis by X-ray diffraction; petrological analysis by optical and scanning electron microscopy (SEM); chemical analysis by X-ray fluorescence spectrometry, β-probe spectrometry, atomic absorption spectrometry and infra-red gas-analysis, as well as conventional wet geochemical methods. These are described in greater detail below.

For most analyses, other than clay mineralogy and the microscopic investigations, finely-powdered material was used. This enabled reproducible splits to be made for separate analysis. Each sample was oven-dried at approximately 80°C for 4-6 hours, quartered, and one split was ground in a small Tema-mill for 10 minutes. For very sandy samples, a longer grinding period of 20 minutes was required for satisfactory size-reduction. The resulting finely-divided powders were stored in small plastic bags until required.

The compositional data of the analysed sediments were then statistically analysed by computer, using Fortran programmes.

3.1 Mineralogical and Petrological Investigations

3.1.1 X-ray Diffraction

Mineralogical analysis of the samples was mainly performed by X-ray diffraction. The use of X-ray diffraction is based on the fact that each crystalline substance has its own characteristic ordered atomic structure which diffracts X-rays in a distinct pattern. The method is non-destructive and requires only small amounts of material. Details of many of the procedures and sample preparation techniques are given by Klug & Alexander (1974).

In the present investigations, a Philips P.W. 1050/25 diffractometer, equipped with a proportional counter, was employed to study both the clay and bulk sample mineralogy. The former usually involved the use of oriented smear mounts, whilst random powder mounts were usually used for the latter. The radiation employed in diffraction studies in this research was CuKα (1·5418Å) generated at 36 KV and 24 mA, and Ni-filtered. Identification of mineral phases was based on the J.C.D.P.S. diffraction data index and the diffraction patterns listed in Grim (1968) and Brindley & Brown (1980).

3.1.1A Clay Mineralogy

The clay minerals were generally studied as oriented smears of < 2 µm fraction of the sediments. This is because clay minerals are generally platy and their basal reflections are enhanced in oriented mounts, thus making their identification simpler.

i) Sample Preparation

About 1g of sediment was mechanically disaggregated and dispersed in distilled water using an ultra-sonic vibrator. Carbonate and lignitic sediments were first treated with 1M HCl and 30% H_2O_2 respectively, and washed free of excess reagent with distilled water. These treatments remove carbonate minerals and organic matter whose presence in large amounts may obscure or greatly reduce the reflection intensities of the clay mineral phases. The disaggregated and dispersed sample slurry was allowed to stand for a minute or two to allow particles of sand to coarse-silt size to settle, and the suspension removed. The obtained suspension was further dispersed with ultrasonic treatment and a few drops of 10% Calgon [$NaH(PO_4)_3$] , a dispersing agent, were added. After thorough dispersion, particles of size greater than 2µm were allowed to settle at a rate of 1 cm/45 min. in accordance with Stokes' Law for particles settling under gravity (Jackson, 1969). The resulting suspension was decanted and a few drops of 10% $MgCl_2$ were added to flocculate the -2 µm clay fractions. The clay was concentrated by centrifuging, and excess $MgCl_2$ was removed by washing twice with distilled water. The clays were partially air-dried into pastes, and then lightly and evenly smeared onto glass slides. Smearing provides a better spread of the clays and avoids particle-size differentiation that arises when drops of clay suspensions are dried (Gibbs, 1965).

A set of three smear mounts was made for each sample. On air-drying, one was left untreated, the second was treated with ethylene-glycol at 60°C for two hours in order to solvate expandable clay minerals, while the third was heated at 350°C for two hours to remove interlayer water and collapse the expandable clay minerals. The untreated smear mounts were scanned from 2-40° 2θ, whilst the glycolated and heated smears were scanned from 2° to 18° 2θ. The diffraction traces were recorded at an angular velocity of $2^\circ 2\theta$ per minute using 1° aperture slits, a time constant of 1 second and, depending on intensity, count rates of 1×10^3 to 4×10^3 cps (counts per second). Typical diffraction traces of the smeared clay fractions are shown in Figures 8, 9, 10.

ii) Phases Identification

Clay minerals are generally identified on the basis of their basal 00ℓ reflections. Full details are given in Brindley & Brown (1980). The clay minerals identified in the Upper Eocene succession consist of:

a) Smectite - an expanding phase having a 14·5Å reflection that expanded on glycol treatment to 17·5Å, but which collapsed to 10Å on heating. On the basis of electron microscopy, Gilkes (1966) suggests that the smectite is probably the dioctahedral montmorillonite variety.

b) Chlorite - shows a 14Å reflection. This is only clearly observed in the glycolated and heated smears - and then only in a limited number of samples.

c) Illite - shows basal reflections at 10Å, 5Å and 3·3Å that do not change on glycolation or heating. In glauconitic samples, the illite phase would include some glauconite, an iron-rich micaceous mineral.

d) Kaolinite - having reflections at 7·2Å and 3·6Å not affected by glycolation or heating at 350°C. Since chlorites also possess reflections of these d-spacings, a slow scan of the 3·6Å reflection was made on chlorite-containing samples, in the manner suggested by Biscaye (1964), but no resolution into two peaks was obtained. Therefore, it was taken that very little, if any, contribution was made by chlorite to the 7·2Å peak, Consequently this could be utilised for the quantitative estimation of kaolinite.

Samples of some lignitic sediments possess a peculiarly broad 7·2Å reflection that tails in the high d-spacing direction (i.e. Fig. 10b). The reflection becomes enhanced on glycolation, persists on heating to 350°C, but completely collapses at 550°C. It is presumed that halloysite is present in the samples, and causes the tailing 7·2Å.

Fig.8: Diffraction Traces of Oriented Clay (-2µm) Fraction of Sample BBB27

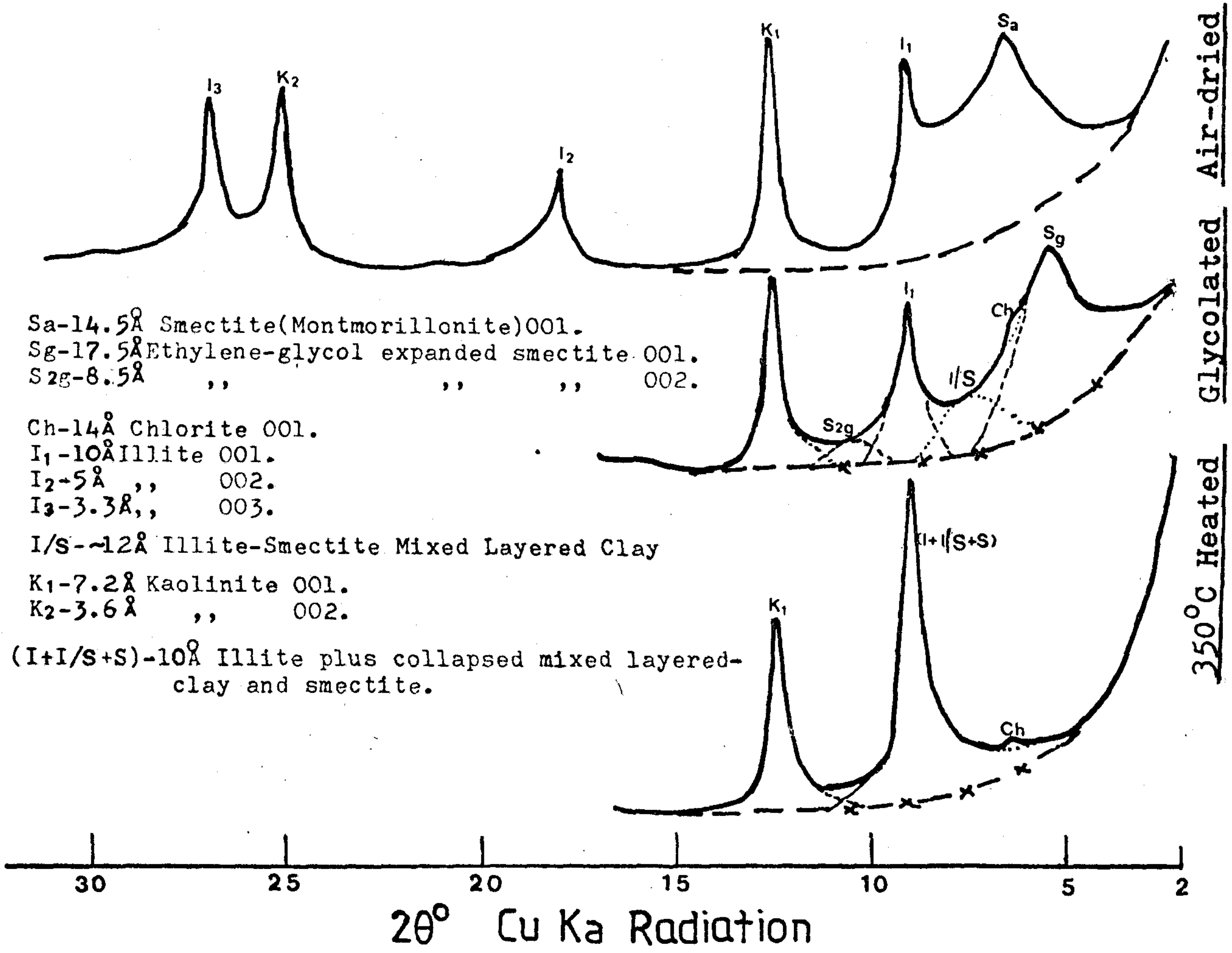


Fig. 9: Sketch of Diffraction Traces of Clay Assemblages in the Barton Clay and Barton Sand Formations; Alum Bay, Isle of Wight.

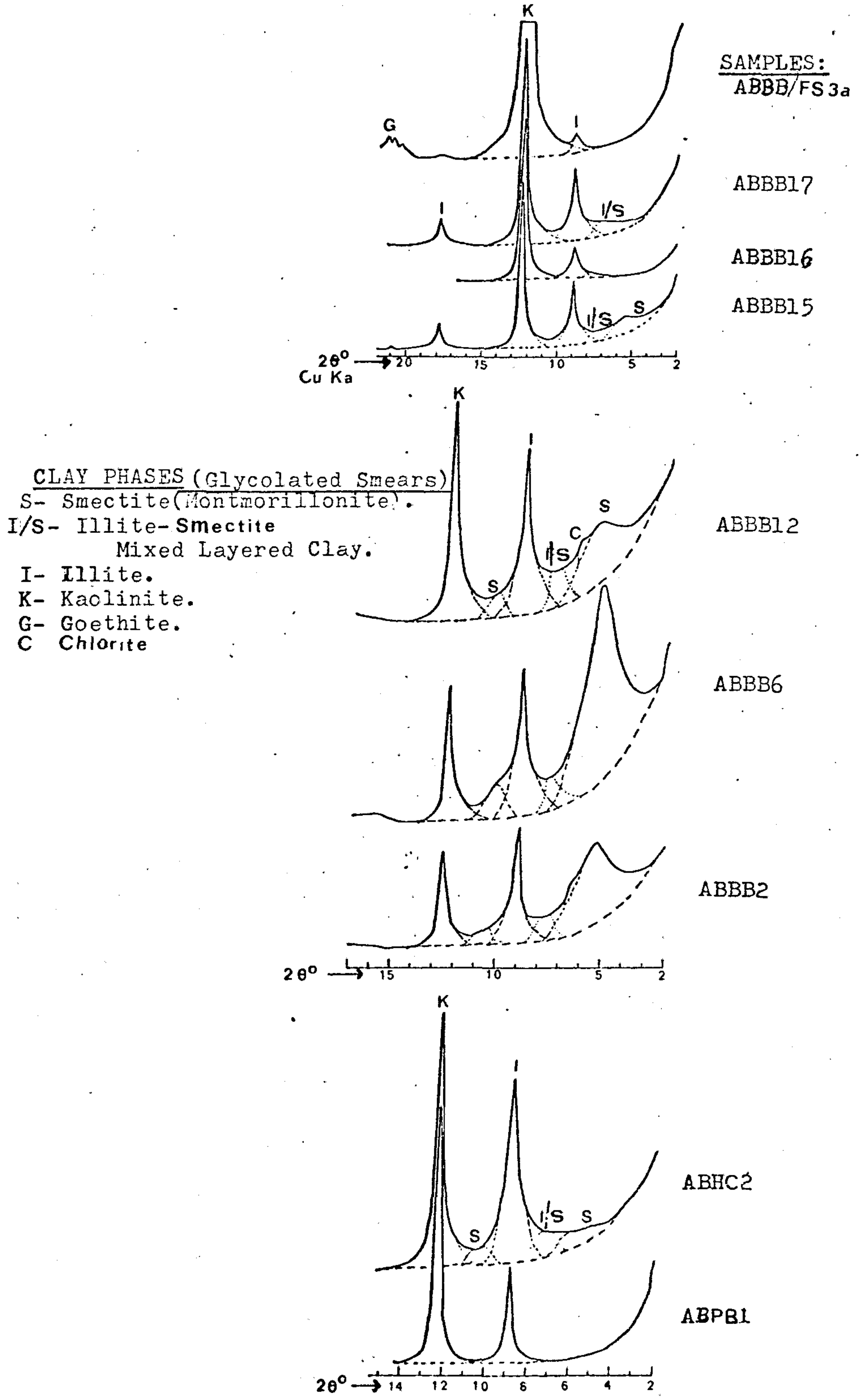
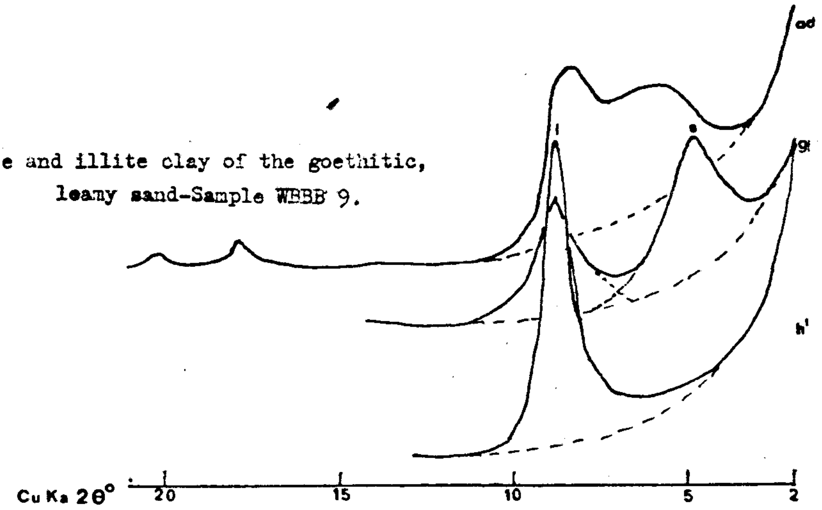
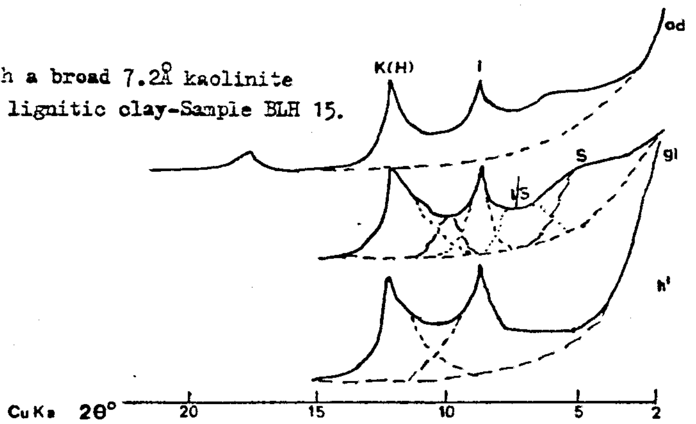


Fig.10: Diffraction Traces of Uncommon Clay Assemblage in the Upper Eocene Succesion

a) smectite and illite clay of the goethitic, loamy sand-Sample WBBB 9.



b) clay assemblage with a broad 7.2Å kaolinite (+halloysite?) from lignitic clay-Sample BLH 15.



c) clay assemblage with a 11.4Å hydroxy—chlorite from lignitic clay-Sample BBB 1.

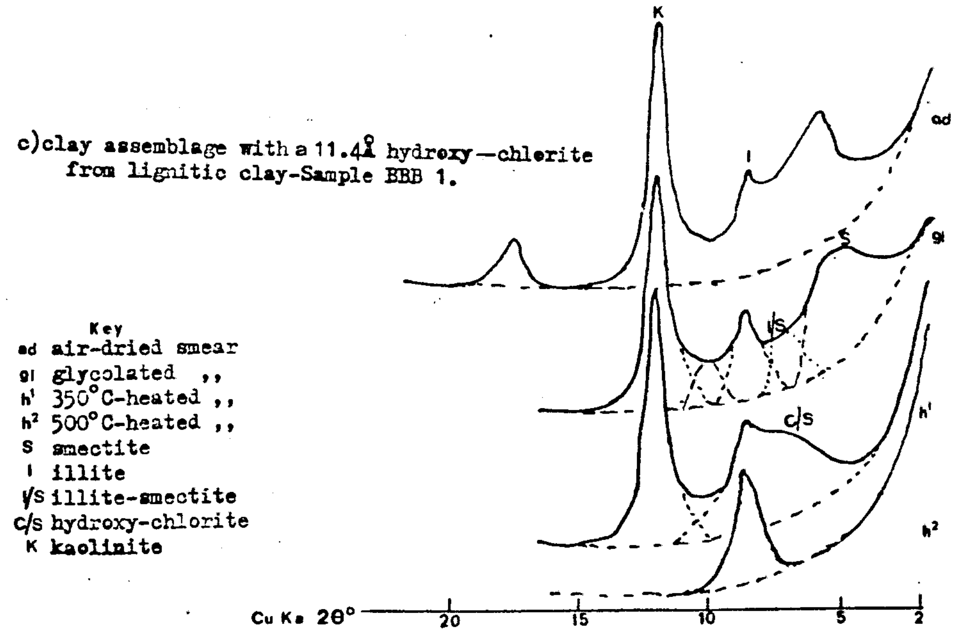


Fig.11: Illustration of 'Constructed Background' For Smeared-Clay Reflection

(Sample BBB 41)

Semi-Quantitative Estimation

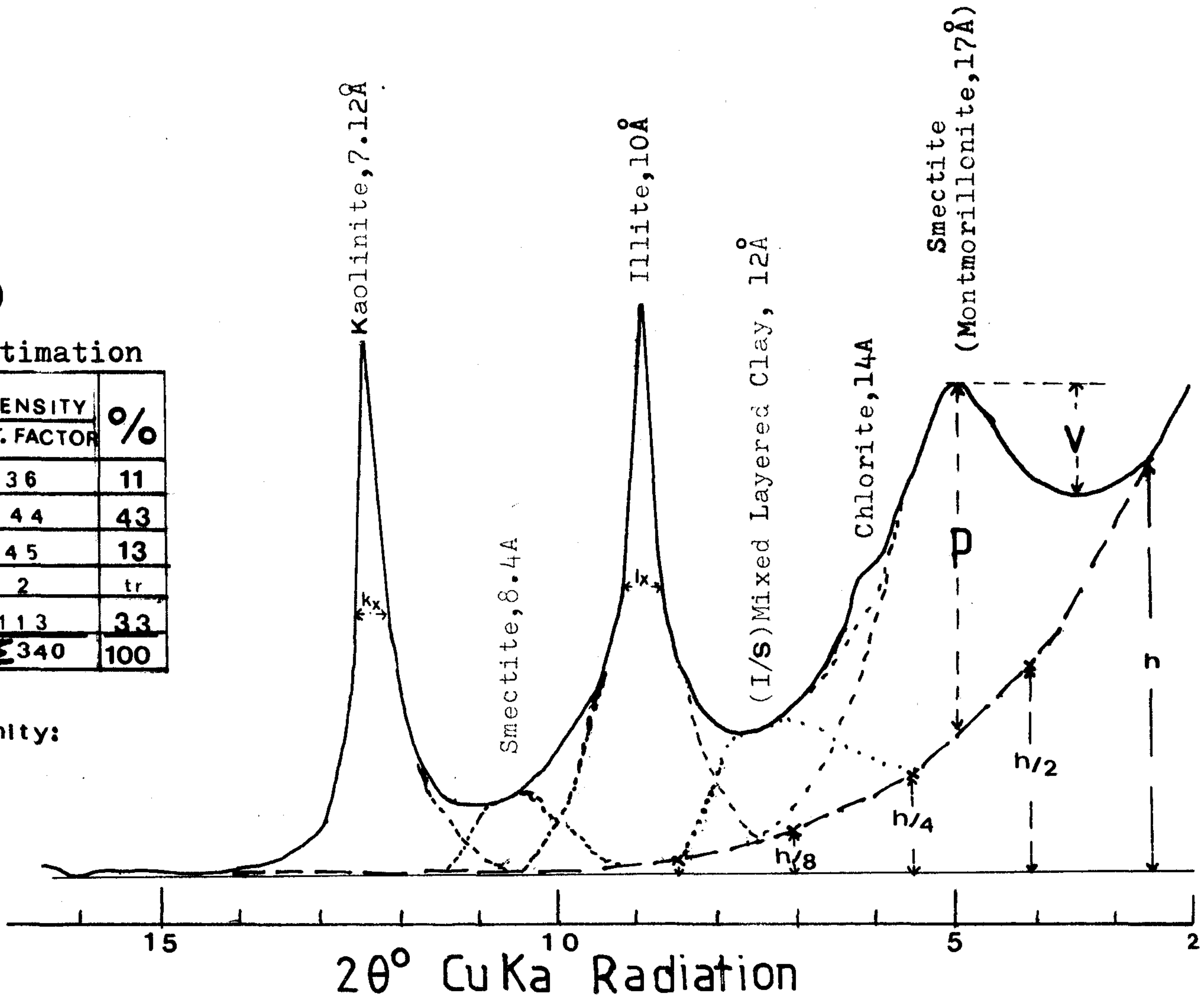
Phase	INTENSITY (Weighed Peak Area)	INTENSITY / INT. FACTOR	%
Kaolinite	109	36	11
Illite	144	144	43
Illite - Smectite Mixed - Layer	68	45	13
Chlorite	4	2	tr
Smectite	260	113	33
		Σ340	100

Smectite Crystallinity:

v/p = 17/57

= 0.3

K_x — Crystallinity Indices(2θ°)
I_x — of Kaolinite & Illite



e) Mixed Layer 1. Illite-Smectite : is assigned to the broad peak centred around 12Å on glycolated smears. The reflection collapses to 10Å on heating.

f) Mixed Layer 2. Chloritic Hydroxy-interlayers: are believed to be responsible, in some carbonaceous samples, for a 14Å reflection that partially expands to 17Å on glycolation, incompletely collapses to 11·4Å on heating at 350°C (i.e. Fig.10c), but collapses completely at 550°C.

iii) Crystallinity Indices

Towards consideration of the probable mode of derivation of the clay minerals, attempts were made at estimating their degradation in terms of crystallinity indices. The estimations made were based on the principle that the lesser the crystallinity of a given mineral phase, the broader are its reflections (Klug & Alexander, 1974), although it is appreciated that other factors can affect peak width.

a) Kaolinite and Illite: The 7·2Å and 10Å reflections were employed for kaolinite and illite respectively. The peak widths at half peak heights (heights above background) were measured on glycol-treated smears, expressed in degrees 2θ and utilised as the estimates of index of crystallinity for the minerals.

b) Smectite: The method adopted by Biscaye (1965), using the 17·5Å smectite reflections in glycolated smears, was employed. This involved measuring the peak height (P) above the background and the depth of the 'valley' (V) on the high d-spacing side of the reflection (i.e. Fig.11). The ratio V/P was calculated, for each sample, and recorded as the crystallinity index for smectite. Since the absolute peak area (or abundance) of the smectite may affect the value obtained by this method, Biscaye (1965) cautioned that the obtained crystallinity index should be employed only as a 'good first approximation'.

iv) Quantitative Estimation

Attempts at estimation of clay minerals in sediments were initiated in earnest by Johns, Grim & Bradley (1954). From their efforts and many others since, it was realised that the intensities of the basal reflections of the clay phases are not simply proportional to the absolute amount of clay present because of the angular spread of the reflections, overlap of very close reflections by two or more phases, and the effects of the X-ray scattering functions of the various layered structures. Biscaye (1965) has also shown that, apart from variations between diffractograms due to X-ray diffractometer conditions, the nature of the sample mount has significant influence on the relative intensities of the clay mineral reflections. Factors involved include smear thickness, degree of preferred orientation, and variations in crystallinity and chemical composition. Because of these factors, most estimations of clay minerals in smear mounts are rather crude and are based on rough relative intensity factors for the various phases with respect to the intensity of the 10Å illite (001) reflection. In the present study the reflections and intensity factors used were those given by Biscaye (1965) and Weir <u>et al</u>. (1975). They were, however, adjusted to take into account the 1° slits used in this study. The reflections and factors are listed below:

Table 2 Clay Phases and Intensity Factors

	Clay Mineral Phase	Reflection Å	Intensity Factor
Glycolated:	Smectite	17·5	2·3
	Chlorite	14	1·5
	Illite-Smectite	12	1·5
	Illite	10	1
	Kaolinite	7·2	3
350°C	Collapsed Smectite Collapsed Illite-Smectite Illite	10	1
	Chlorite	14	1·5
	Kaolinite	7·2	3

One of the main sources of uncertainty in the semi-quantitative analysis of clays is the background position, particularly at low angles. In order to aid reproducibility, an objective technique for background estimation was employed. Using the diffraction trace of the glycolated clay smear of Sample BBB-41 (Fig. 11) as an example, the background is obtained as follows.

Assuming that the background deviates from the trace at $2\cdot5^{o}2\theta$, and later flattens out with the trace at around $12\cdot5^{o}2\theta$, a straight-line background was projected from $12\cdot5^{o}2\theta$ to the low-angle region. Then, the vertical height, h, from the projected line to the trace at $2\cdot5^{o}2\theta$ is measured and subsequently halved geometrically at $1\cdot5^{o}2\theta$ intervals to obtain the background 'coordinates'. The coordinates - h/2 at $4^{o}2\theta$, h/4 at $5\cdot5^{o}2\theta$, h/8 at $7^{o}2\theta$ and h/16 at $8\cdot5^{o}2\theta$ - are joined as a smooth curve meeting the straight-line background at around $12.5^{o}2\theta$. The curve is the 'best fit' background to the chart-recorded reflection of the clay smear mount.

The same procedure is carried out for the heated smear traces except that the height, h, is taken at $3\cdot5^{o}2\theta$. Then the integrated peak areas of the reflections were estimated in terms of peak area by square-counting, and divided by the appropriate intensity factor. These were summed up and normalised to 100%. The estimation of the phases in the glycolated smear of Sample BBB-41 is given in Figure 11 as an example. Since all the clay mineral phases were individually estimated on glycolated smears, it was these values that were used in later discussions. The estimates from the heated smears were used for comparison. The values were generally within 20% of each other, which is quite acceptable given the problems of clay mineral estimation. The real accuracy of these determinations, however, is extremely difficult to estimate. Indeed, a study by Heath and Pisias (1979) on some N. Pacific sediments, using 10% Talc as an internal standard and statistically treating the data, suggests that the factors used for clay mineral quantification may be out by as much as four times. The authors further indicate, as do many other workers on clays, that clay mineral estimations with the clay phases normalized to 100% do not often reflect the real abundance of the minerals in sediments. However, within a given suite of sediments containing varying proportions of the same minerals, the values will reflect the changes in the relative concentrations of a given mineral from sample to sample.

The clay mineralogy of the samples from Upper Eocene sediments is given in Tables 8a - h, and their stratigraphic variation is shown in Figure 22a-c. The crystallinity indices of the kaolinite, illite and smectite phases are also contained in the tables, whilst only that of the smectite is plotted in the figures.

3.1.1B Bulk Sample Mineralogy

Randomly-oriented powder mounts were employed for the study of the general mineralogy of the bulk samples as well as for more detailed studies of some of the constituent phases. The powdered samples were loaded into aluminium cavity-mount holders, supported by a glass slide. Care was taken to avoid undue pressure causing preferred orientation. The samples were scanned from 2 to 65°2θ under the same diffraction conditions employed for the clay mineralogy, except that the recording of the trace was at a slower angular velocity of 1°2θ per minute. A typical diffraction trace of the powdered samples is shown in Figure

i) Identification and Quantitative Estimation of Mineral Phases

The mineral phases identified comprised clay minerals, quartz, potash and sodic feldspars, aragonite, calcite, siderite, pyrite, anatase, gypsum, goethite, lepidocrocite, jarosite and traces of apatite.

Quantitative estimation of the minerals is based on the relationship between the concentration of the minerals and their reflection intensities (Klug & Alexander, 1974):

$$W_i = K_i I_i \bar{\mu} \qquad (1)$$

where W_i = weight per cent of phase i in mixture;

K_i = constant which depends upon the geometry of the apparatus, etc. and varies from phase to phase and reflection to reflection;

I_i = intensity of a specific reflection belonging to phase i not overlapped by another reflection;

and $\bar{\mu}$ = the mass absorption (or average mass attenuation) coefficient of the mixture.

Various methods of dealing with the mass absorption problem have been summarized by Klug & Alexander (1974) and Brindley (1980). The method adopted in the present studies is essentially that of Schultz (1964), as modified by Burnett (1974). The approach is similar to that described previously for the clay minerals, in that the total of crystalline phases is normalized to 100%. For a given component, i, its weight percentage, W_i, in a mixture of n components is given by:

$$W_i = 100\ K_i I_i / \sum_{n}^{i=1} (K_i I_i) \qquad (2)$$

where K_i is called the intensity factor and will be constant for a particular mineral reflection in samples analysed under the same diffraction conditions. A suitable mineral reflection is one of reasonable intensity that can be isolated or resolved satisfactorily from other adjacent reflections. For some minerals it is difficult to find a suitable reflection meeting such criteria, particularly in multiphase mixtures, where reflections of different phases often overlap each other. In some minerals such as siderite or feldspar, the existence of two or more phases may be manifested, in diffraction traces, as asymmetrical or very closely spaced, overlapping reflections. There is no set procedure for dealing with these problematic reflections; each must be dealt with in the most appropriate manner. In the present study, two approaches were employed for the estimation of the intensity factors, K_i.

a) Quartz-Mineral Mixture: In this method, 50/50 mixtures of quartz and the minerals whose intensity factors were to be estimated were prepared, and run as random powders. From (2) above, for mineral phase (i) and quartz (q),

$$\frac{W_i}{W_q} = \frac{K_i I_i}{K_q I_q} \qquad (3)$$

or,

$$K_i = I_q / I_i \qquad (4)$$

The 3·34Å reflection was chosen as standard, and conventionally defined to have an intensity factor of 1. Ideally, pure phases extracted from the sediments should be employed; but, with the exception of aragonite, goethite and lepidocrocite, it was not feasible to extract pure minerals from the Upper Eocene sediments of the Hampshire Basin. Therefore standard materials from outside the sediments were employed. Prior to being used, the monomineralic purity of each material was ascertained by X-ray diffraction. The phase composition (and hence purity) of the standard feldspars was pre-determined by the cell parameter determination method of Wright (1964). As a measure of intensities, peak areas rather than peak heights were employed, because peak areas are less liable to errors due to changes in crystallinity of minerals. However, peak heights were

Table 3: Mineral Constituents and their Intensity Factors

Mineral	Reflections	(Å)	Intensity Mode	Standard Material	Intensity Factor
Aragonite	(111)	3·40	Peak Area	Aragonitic Shells *	4·76
Anatase	(101)	3·51	" "	Spec.Pure TiO_2	2·50
Calcite	(104)	3·03	" "	Dog-Tooth Calcite Crystal	1·52
Clays		~ 4·56	Peak Height	Clays *	90
		~ 2·56	" "		139
Feldspars (Potassic)	(002)	3·24	Peak Area	Orthoclase Xal (Or > 96%)	3·75
(Sodic)	(002)	3·18	" "	Albite Xal (Or < 3%)	2·72
Fluorite	(111)	3·15	" "	Spec.Pure CaF_2	0·66
Goethite	(110)	4·18	Peak Height	Goethite *	70
Gypsum	(020)	7·56	Peak Area	Satin Spar, Purbeck Bed, S.England	4·76
Jarosite	(113)	3·08	" "	Jarosite, Ingleton, Engl.	4·76
Lepidocrocite	(020)	6·27	" "	Lepidocrocite *	2
Pyrite	(200)	2·71	" "	Pyrite Xal Lake District, England	2·08
Quartz	(101)	3·34	" "	Rock Quartz Crystal	1
Siderite	(104)	~ 2·82	Weighted Peak Area	Siderite *	9·17

* Materials obtained from the Upper Eocene succession of Hampshire Basin.

used for goethite because of the broad nature of its reflections.

The most intense reflections of aragonite and feldspar are the only reflections of the minerals generally observed in the sediment samples, and hence have to be calibrated. Because the reflections occur very close to the 3·34Å quartz reflection, their intensity factors with respect to calcite or fluorite were estimated. These were then corrected to that of 3·34Å quartz.

No suitable standard materials could be obtained for the clay minerals whose estimations in the bulk samples were collectively identified as 'total clay'. Nor was there a suitable standard for the siderite, whose reflections were asymmetrical, and suggestive of being made up of substituted or mixed siderite phases. For these, a different approach was needed.

b) Calibration Curve: The intensity factors of the total clay and siderite were determined by the construction of calibration curves, shown in Figures 13,14. For the clays, ten samples representing different lithologies were randomly selected, and their 'total clay' obtained by difference. The 'absolute' quartz contents of the selected samples had, in an earlier and separate experiment, been determined by the pyrosulphate fusion method of Trostel & Wynne (1939); and the quartz values employed to obtain the abundance of non-clay phases, as described in the other method above. For the siderites, only sideritic samples were used; with the siderite amounts being determined by acid digestion and infrared gas analysis. The peak heights of the common non-basal reflections of the clay phases were employed as the clay intensities. Two such reflections, the 2·56Å and 4·56Å, were determined; the first was the most intense and present in almost all samples and is thus employed for discussion, whilst the second was for comparison. In the case of the siderites, 'weighted' peak areas (square counting) were employed for the asymmetrical reflections. The inverse of the slopes of the calibration curves gives the required intensity factors.

The standard materials, the reflections employed and the intensity factors obtained are listed in Table 3. The percentage of each mineral phase present in each sample was calculated by multiplying the intensities (I_i) by their intensity factors (K_i), summing these up $[\Sigma(K_iI_i)]$ and

Fig.12 :Sketch of Part of Typical Diffraction-Trace of Powdered-Samples

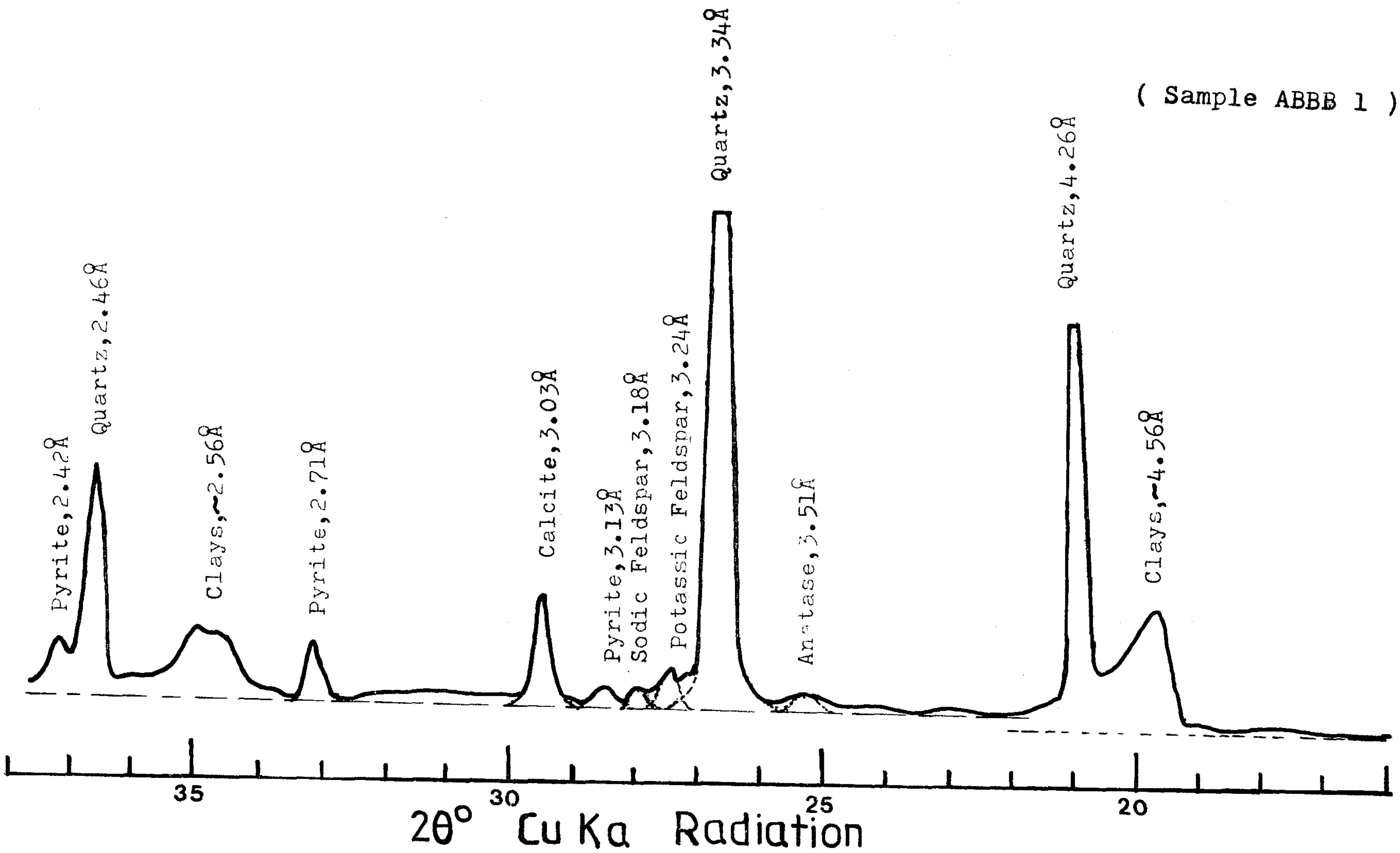


Fig.13: Calibration Curves For Clay Minerals

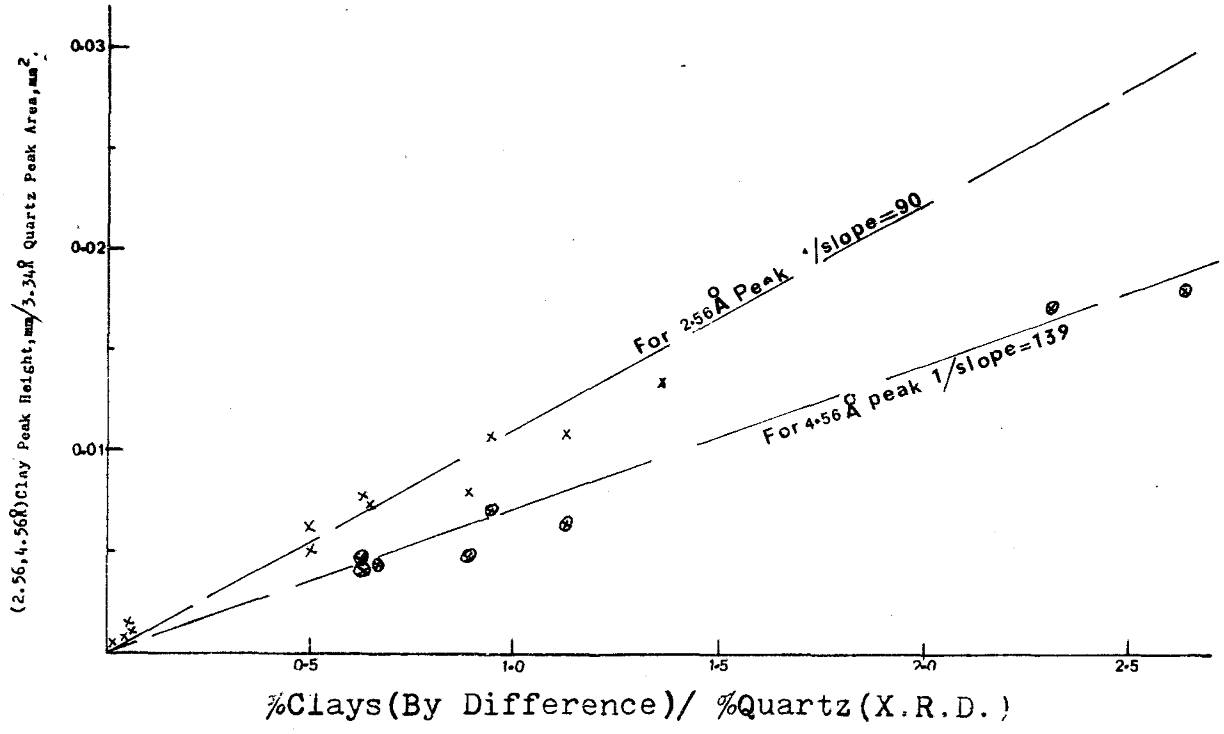
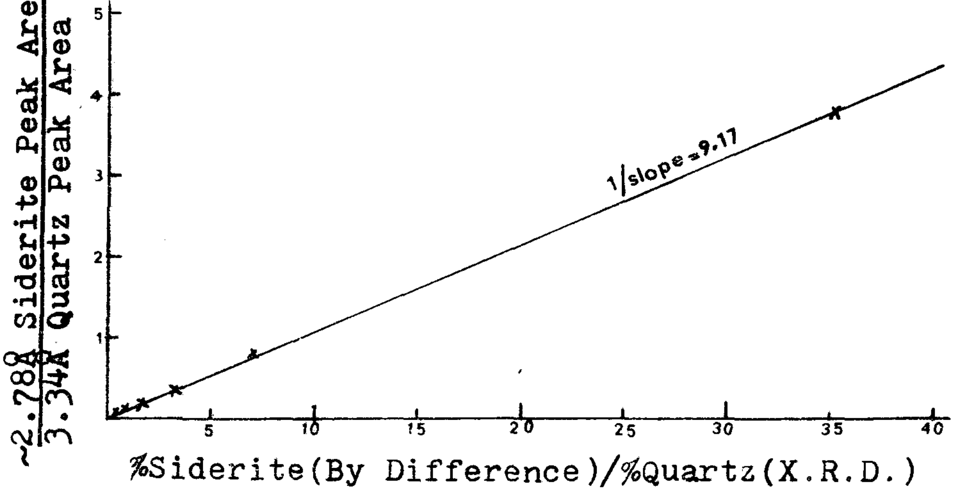


Fig.14: Calibration Curve For Siderite



normalizing to 100%. The phases present in the diffraction trace of Sample ABBB-1 are shown in Figure 12, and their estimation shown in Appendix 2, as an example.

ii) Precision and Accuracy of Estimations

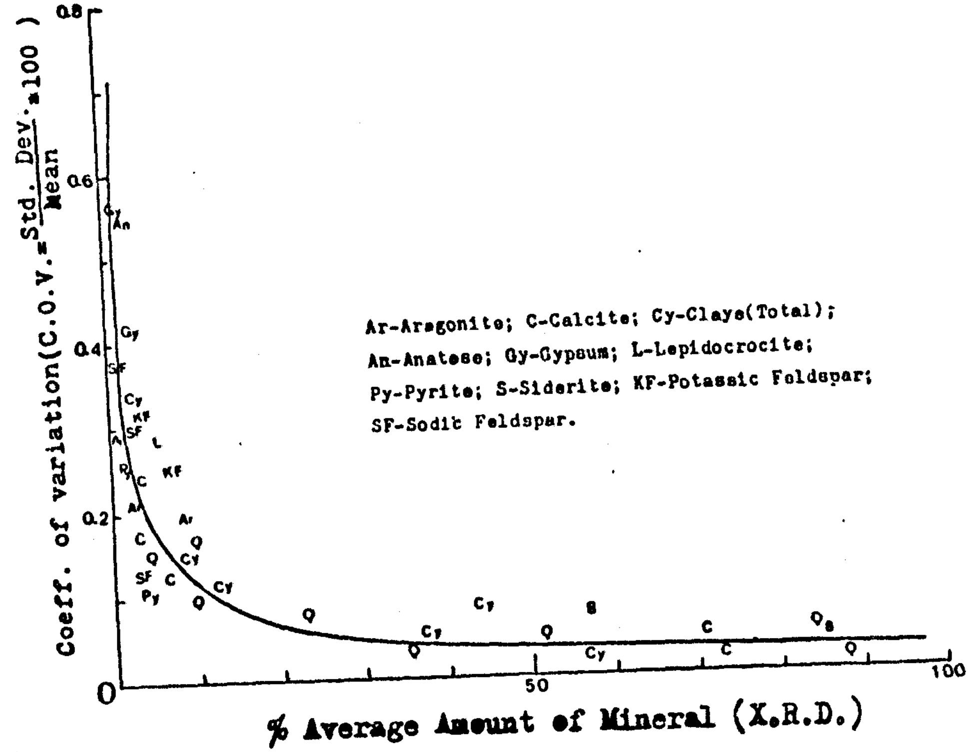
The precision of the mineralogical analysis by X-ray diffraction was determined from the values obtained for five separate splits of eight randomly selected samples of different lithologies. The coefficients of variation of the constituent minerals and the mean of their estimates were calculated for each sample and plotted against each other (Fig.15). This facilitated comparison with similar plots made by Schultz (1964) and Burnett (1974). The values obtained compare very well, as follows:

Mineral Estimates in Sample	Precision
a) >50%	± 4%
b) 50 - 20%	± 10%
c) 20 - 5%	± 20%
d) <5%	Variable poor, ± 20% to about ± 60%

The 'total clay' estimates obtained for the 4·56Å clays reflections were generally close and often within 10% of estimates from the 2·56Å reflections. It is thus in order to employ the 4·56Å alone for discussion, as it is the only reflection of the clays present in most samples.

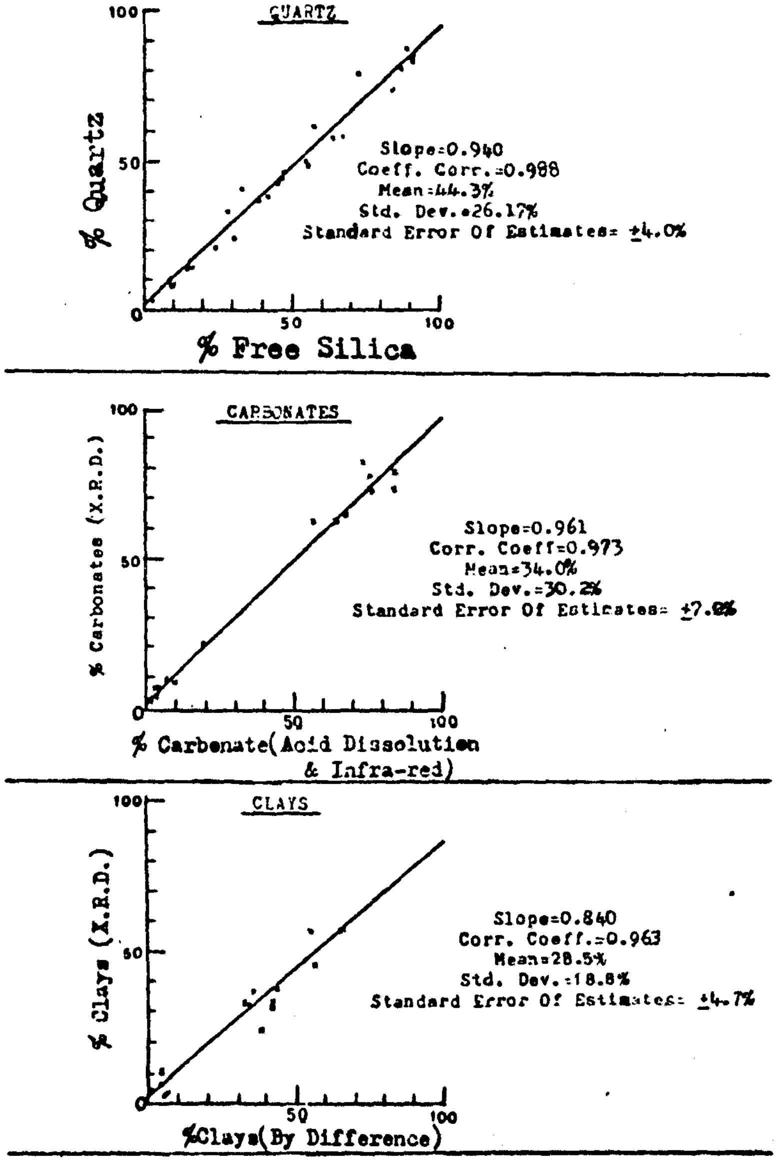
The greatest problem was in the estimation of apatite and anatase phases. In all samples the intensities of the apatite reflections were very small, broad, and apatite is thus considered to occur in trace amounts. Although the anatase reflections are resolvable, the X-ray diffraction estimates of the mineral were aubsequently found to be about four times in excess of the chemically determined TiO_2 contents of the samples. The high diffraction estimates could have been due to error in the intensity factor determined from 'Analar TiO_2', or more likely to over-estimation of the reflection intensities. This is because the major peak lies very close to broad peaks of nearby 3·5 - 3·6Å clay mineral reflections. Because of this, the anatase estimations were rejected in favour of the chemically determined TiO_2. This would be a better measure of the TiO_2 phase(s) in the samples, although

Fig.15: Precision Curve For Minerals Estimates By X.R.D.



Ar-Aragonite; C-Calcite; Cy-Clays(Total);
An-Anatase; Gy-Gypsum; L-Lepidocrocite;
Py-Pyrite; S-Siderite; KF-Potassic Feldspar;
SF-Sodic Feldspar.

Fig.16: Accuracy Plots For Quartz, Carbonates, Clays.



Slope=0.940
Coeff. Corr.=0.988
Mean=44.3%
Std. Dev.=26.17%
Standard Error Of Estimates= ±4.0%

Slope=0.961
Corr. Coeff=0.973
Mean=34.0%
Std. Dev.=30.2%
Standard Error Of Estimates= ±7.0%

Slope=0.840
Corr. Coeff.=0.963
Mean=28.5%
Std. Dev.=18.8%
Standard Error Of Estimates= ±4.7%

some titanium might be present in solid solution in other minerals.

It should also be stated that X-ray diffraction estimates of the mineralogy do not include X-ray amorphous organic matter and possible amorphous iron-oxides and/or hydroxides. However, organic matter was determined from CO_2 measurements using an infra-red gas analyser. Details of this are given later.

Some estimations of the accuracy of the mineral estimates by X-ray diffraction were determined by comparison with those obtained by other analytical methods. Three mineral phases - quartz, the carbonates and 'total clay' - were independently determined in some randomly selected samples of different lithologies.

Taking the quartz as the predominant resistate phase present in the samples, the free-silica contents were chemically obtained by the pyrosulphate fusion method of Trostel & Wynne (1939). The method involved dissolving the fused samples in hot distilled water and digesting with NaOH. The free silica settles out of, and is quickly filtered from, the digested solution. The free silica values obtained were plotted against normalised quartz estimates. From the plot (Fig.16a), some idea of the accuracy of the quartz estimation by X-ray diffraction is given by the calculated standard error of estimate. The accuracy thus obtained for the quartz phase was ±4·0%.

Independent estimates of the carbonate minerals were determined by acid dissolution and infra-red gas analysis. Details of the analytical procedures are given in the next section. The estimates obtained were plotted against the normalised X-ray diffraction estimates (Fig.16b) and a ±7% standard error of estimate was obtained as a measure of accuracy for the carbonate minerals.

As previously stated, 'total clay' was determined by difference. In order to establish the reasonableness of using these estimates, a plot (Fig.16c) of the ultimate estimates by diffraction against the estimates by difference was made. A very good accuracy of ± 4·7%, comparable to that of quartz, was obtained, although previous work suggests that this is probably an under-estimate of the clay accuracy.

The bulk sample mineralogy of the Upper Eocene succession investigated is given in Tables 7a-g, whilst the stratigraphical variations are shown in Figures 20a-c.

3.1.2 Optical Microscopy

3.1.2A Thin-Section Petrography

The Upper Eocene sediments possess different degrees of coherence, so three different thin sectioning procedures were employed as follows:

i) Relatively well-compacted and cemented sediments such as calcareous concretions, sideritic ironstones, the goethite-indurated pebble bed and palaeosol horizons, and other hard materials such as pebbles and rootlet bodies, were cut into small chips of sizes 0·5 to 1 cm thick and 2 to 5 cm long, using a diamond saw. These chips were polished, using carborundum powders, on glass plates. After polishing, washing and drying on a hot plate, the chips were then mounted onto warmed glass plates using Lakeside 70° cement resin. The mounts were further ground to about 30 μm thickness.

ii) The friable and less compacted sediments were cut into chips and impregnated with a mixture of araldite resin and hardner (EPO-TEK 301 A&B, marketed by Logitech Ltd. of Scotland) in vacuum for two days. The thin sections of the impregnated samples were then made in the manner described above for the harder sediments.

iii) The third thin-sectioning procedure adopted was that of West (1966). This was used for the soft, clayey sediments, and involved the use of araldite to mount flat-ground samples onto glass slides. The grinding was done using coarse and fine-polishing sandpapers and warm frosted glass plates. Further grinding of the sample mounts was done until a thickness of about 5 mm was achieved. The mounts were then soaked in water for about thirty minutes, during which much of the sediment broke away. A fine hairbrush was then gently used to clean the section face in water. The sections were drained dry and studied.

The prepared thin sections were studied using a Vickers' binocular microscope and a Zeiss polarising microscope. Photomicrographs of samples were taken with a camera attachment on the latter. Some of the carbonate sediments were studied as stained thin sections. The staining was carried out as follows:

3.1.2B Thin-Section Staining

On preparation, some of the thin-sections of the carbonate sediments were stained with a solution of Alizarin red-S and potassium ferricyanide using the procedure described by Lindholm and Finkelman (1972). Staining solution was freshly prepared by dissolution of 1g Alizarin red-S and 5g potassium ferricyanide in 1 litre of 0·2% HCl (998 ml distilled H_2O & 2 ml conc.HCl). The sections, pre-etched in 2% HCl for about 20 seconds, were then immersed in the staining solution for about 4 minutes. The stained sections were washed with water, care being taken not to touch by finger or hit with direct water-jet, which could cause peeling of the stained layer. The stained sections were drained ~~dry~~ but studied moist under polarising microscopes. Then, using the plot of % FeO vs stain colour of Lindholm & Finkelman (1972) as a guide, an idea of the ferroan nature of the observed carbonate minerals was obtained.

3.1.2C Grain Mounts

Clove oil and cooked Canada Balsam were used to mount the unlithified sandy sediments and other granular materials. Clove oil mounts were used for rapid, brief studies, whilst Canada Balsam mounts were useful for photomicrographs and could be stored. The grain-mounts were also studied with the Vickers' and Zeiss microscopes.

3.1.3 Electron Microscopy

Scanning electron microscopy (SEM) was employed to study selected samples and materials. An International Scientific Instruments, ISI-60A, was employed. It was fitted with a camera for photomicrographs, and an EDXRF (Energy-dispersive X-ray fluorescence) spectrometer fitted with a lithium-drifted silicon detector for chemical analysis of materials under scan. Details of the principles of SEM and applications of EDXRF are contained in many publications, including those of Gard (1971), Long (1977) and Zulliger & Steward (1977).

The sample materials were air-dried and cut into small, flat, 2-5 mm thick pieces. Care was taken to avoid touching or scratching the freshly-cut faces. The pieces were then mounted onto aluminium stubs with graphite or silver emulsions. The mounts were either carbon or gold-coated under vacuum before being scanned and studied.

3.2 Geochemical Investigations

3.2.1 Major Element Analyses

3.2.1A Major Element Composition by β-Probe Spectrometer

Major element analysis of the samples was carried out on a β-Probe (Telsec β-300) Spectrometer. The instrument employs the principle of electron excitation to generate the characteristic X-rays of the elements. These are crystal-dispersed and measured with a flow counter. The measured intensities are computer-processed and the results listed as weight per cent oxide. Calibration of the instrument was performed using standard rocks genetically and compositionally similar to those found in the present study. The elements analysed were - Si, Ti, Al, Fe(Total iron), Mg, Ca, Na, K, P and S.

i) Sample Preparation

a) Raw Samples - Oven dried (110°C, 2 hrs) powdered samples were mixed with graphite in a 9:1 proportion (i.e. 1·8g sample to 0·2g graphite) in a Tema pot for 15 minutes. The mixtures were then pelleted onto lead discs. The graphite and lead disc ensured that the samples were electrically conductive, in order to prevent severe drift due to charging of the sample surface by the electron beam.

b) Fluxed-Bead Samples - Some samples, such as the lignitic clays, when prepared as above, cracked up under the high vacuum of the excitation chamber and the high temperature caused by the electron beam. In order to overcome this, such samples were made into glass beads by fluxing 0·40g of oven-dried (110°C) powder with 2g of lithium meta-borate in a pre-weighed platinum crucible. On cooling and weighing, the loss in weight was recorded as % Loss on Ignition (%LOI) and the difference made up with more flux. Then the sample was re-heated and the final bead was crushed and mixed with graphite in a 9:1 weight proportion. The resulting mixtures were pelleted onto lead discs and analysed. The bead procedure was also employed for materials for which only small quantities were available, or samples whose water and carbon-dioxide contents were not to be determined.

Calibration statistics of the β-Probe analyses, as obtained for the standard rocks, are given in Table 4. Some idea of the accuracy of the analyses is given by the standard error of estimate, which is dependent not only on the particular element, but also on the concentration

Table 4: Calibration Statistics - Major Elements by β-Probe Spectrometer

	Elements	No. of Standards	Mean %	Concentration Range %	Standard Error of Estimate (% S.E.E.)
Carbonate Rocks [Raw Samples]	SiO2	28	1·15	0·00 - 2·83	0·069
	TiO_2	34	0·083	0.00 - 0·61	0·020
	Al_2O_3	37	1·57	0·00 -16·00	0·062
	Fe_2O_3	40	0·49	0·00 - 2·02	0·068
	MgO	40	11·20	0·00 -21·59	0·627
	CaO	40	38·50	13·30 -56·03	0·673
	K_2O	25	0·044	0·00 - 0·09	0·005
	P_2O_5	31	0·029	0·00 - 0·08	0·007
Sedimentary Rocks [Raw Samples]	SiO_2	30	51·21	28·29 -65·39	1·99
	TiO_2	24	0·739	0·35 - 1·06	0·033
	Al_2O_3	27	16·19	7·24 -23·58	0·804
	Fe_2O_3	24	5·56	3·20 - 8·73	0·224
	MgO	24	2·11	1·27 - 4·50	0·172
	CaO	24	4·36	0·47 -11·86	0·266
	Na_2O	21	0·92	0·10 - 3·43	0·030
	K_2O	30	3·36	0·74 - 7·93	0·046
	P_2O_5	27	0·190	0·08 - 0·37	0·0067
Silicates [Beads]	SiO_2	30	55·03	28·29 -76·20	0·704
	TiO_2	31	0·67	0·038- 2·72	0·033
	Al_2O_3	32	13·73	0·44 -23·58	0·387
	Fe_2O_3	30	7·26	1·40 -16·97	0·319
	MgO	32	5·55	0·03 -43·30	0·235
	CaO	32	4·71	0·31 -13·30	0·130
	Na_2O	30	2·68	0·04 - 8·92	0.135
	K_2O	33	3·17	0·01 -15·34	0·086
	P_2O_5	32	0·188	0·01 - 0·94	0·020

Standard Error of Estimate (X)(S.E.E.) = $S.D_{(x)} \sqrt{1-r^2}$

where r = Correlation coefficient

$S.D_{(x)}$ = Standard deviation of element concentration values range. In terms of percentage error, the accuracy is between 1% and 6% of the estimated values. The accuracy, is, however, poor for very low ($< 0{\cdot}1\%$) concentrations such as the values of P_2O_5 and TiO_2 in most sediments, particularly the calcareous ones.

The amounts of some elements in the analysed samples were given as extrapolated values, because they are greater than the upper limit of the concentration range of the calibrated standards. This was the case for Fe_2O_3 in very ferruginous and sideritic sediments; K_2O in glauconitic sediments; and SiO_2 in the sands. However, the accuracies listed in Table 4 are believed to be reasonably similar for the higher extrapolated estimates, since they are within 50% of the upper limit of the standards' concentration range.

Sulphur, S, was analysed independently of the other elements and the calibration was performed using known amounts of specpure sulphur.

Major element compositions of the analysed sediments of the Upper Eocene succession are given in Tables 15a- g , and their stratigraphic variations shown in Figures 29a - c. The recorded Fe_2O_3 values are those remaining after correction has been made for the FeO determined by the procedure described below.

3.2.1B FeO Determination

The FeO contents of the samples were determined by the wet chemical method of French & Adams (1972). The method involved digesting 0·25g of oven-dried samples with hot 5 ml HF - 5 ml H_2SO_4 acid mixtures; and, after flushing with up to 200 ml boric acid solution, titrating against 0·05N ceric sulphate solution, using N-phenylanthronolic acid as indicator. FeO equivalent to the volume (ml) of ceric sulphate that gives the end point (a faint pink colour that persists for about 30 seconds) for each sample was recorded as the amount of ferrous iron present in that sample.

3.2.1C H_2O Determination

H_2O was determined by the sodium tungstate fluxing method of Shapiro & Brannock (1955b). 1g of raw sample powder was mixed with 2g of anhydrous sodium tungstate ($NaWO_4.2H_2O$) in a Pyrex tube fitted with a one-hole stopper. The mixture, at the closed end of the tube, was fused and the water released was absorbed onto a pre-weighed filter-paper placed within the upper part of the tube before heating. The upper part of the tube was kept cooled by ice contained in a polyethylene jacket, with the freezing point of the ice being kept depressed by the addition of some NaCl or NH_4Cl. After fusion and cooling, the filter-paper was removed and quickly transferred into a small pre-weighed glass tube with cover. The gain in weight of the filter paper, expressed as a percentage of the sample weight analysed, was recorded as the % Total H_2O, i.e. combined and adsorbed H_2O.

The adsorbed H_2O was obtained from the difference in weight of 1g raw sample powder before and after drying at 110°C for 4 hours. Then deduction of the adsorbed H_2O from the Total H_2O was made to obtain the structural H_2O. Repeat determinations were made for each sample, and the average values recorded as % H_2O in Tables 15a - g.

3.2.1D CO_2 and Organic-C Determinations by Infra-red Gas Analysis

The infra-red gas analyser employed for CO_2 measurement was BINOS 1, marketed by Leybold-Haraeus Ltd., London. The instrument is a non-dispersive infra-red photometer measuring CO_2 gas within the range of short and medium infra-red (up to 15 mµ) absorption bands. CO_2 released by the samples could either be due to organic matter (Organic-C CO_2) or carbonate minerals (Carbonate CO_2) or to both organic and carbonate constituents (Total CO_2). These are determined as follows:

i) Total CO_2

Total CO_2 was measured by weighing 0·02g of oven-dried powdered sample into a silica boat and heating it in a furnace held at 870°C. This temperature ensures complete oxidation of all organic matter and decomposition of the carbonate minerals. With the aid of oxygen gas-flow (a flow rate of 200 cc/min was used) the released CO_2 was fed into the 1-litre ~~capacity~~ measuring chamber of the analyser. The measured concentration was recorded and compared with that of Analar $CaCO_3$, used as a standard with 100% $CaCO_3$; 43·97% CO_2 or 12% C. The Total CO_2 obtained is the carbon-dioxide estimate recorded in the chemical compositions (Tables 15a - g).

ii) Carbonate CO_2

Carbonate CO_2 was obtained by treating 0·01g of sample, weighed into a glass boat, with phosphoric acid. The acid treatment was carried out within an enclosure at an elevated temperature of 125°C, in order to facilitate faster reaction and prevent retention of evolved CO_2 in the solution. The evolved CO_2 was fed into the measuring chamber and the measured concentration was again recorded and compared to the Analar $CaCO_3$ standard.

Repeat measurements of standard Analar $CaCO_3$ showed that the infra-red gas analyser possessed a precision of about ± 3% and ± 4-5% for the furnace and acid methods respectively. The accuracy of the CO_2 estimates was believed to be within the percentage limits of the precision.

iii) Organic-C

Different procedures were adopted for the Organic-C estimation depending on the presence, type, and amounts of carbonate mineral present, as observed by X-ray diffraction.

a) Non-Carbonate Samples - For samples with no carbonate minerals, the CO_2 estimates obtained are entirely due to organic matter. They were converted to, and recorded as, % Organic-C.

b) Low Carbonate Samples - For samples containing 10% or less carbonate minerals, the Organic-C contents were obtained from the difference in the total CO_2 and carbonate CO_2 determinations. This procedure was not employed for samples with higher carbonate contents because the small differences involved led to considerable variations in Organic-C estimates. This would have resulted from the relatively poor precision of the infra-red analyser. In fact, this procedure was not employed for sideritic samples because it was observed that carbonate CO_2 measurements were inaccurate as a result of insoluble iron-phosphate formation preventing complete acid attack.

c) Sideritic and Calcitic Samples - Sideritic and highly calcitic samples were first digested in hydrochloric acid (hot and cold 1M HCl respectively) to dissolve the carbonate minerals. The acid insoluble residues of the samples were then combusted in the furnace, and the % Organic-C calculated from the measured CO_2 and adjusted to the weight of the digested samples.

Although it was convenient to obtain the Organic-C of carbonate-containing samples from their acid insoluble residues, Robert, Palacas & Frost (1973) have warned that such Organic-C values should be considered as minimum values. The authors observed that up to 44% of the organic matter present in such samples could be dissolved during the acid treatment. The Organic-C contents of the samples are given in the tables (Tables 7a - g) showing the bulk sample mineralogy.

3.2.2 Trace Element Analysis

Trace element analysis was carried out with a Philips P.W.1212 X-ray fluorescence spectrometer (X.R.F.). Boric-acid backed pressed pellets (Norrish & Chappell, 1977) of the powdered samples were prepared and used. The samples, within the spectrometer sample chamber, were bombarded with X-rays from tungsten (W), molybdenum (Mo) and chromium (Cr) X-ray tubes. The W-tube was used to determine Mo, Nb, Zr, Y, Sr, Rb, Ti, Ni, Mn, Cr and V; the Mo-tube was used for U, Th, Pb, As, Zn and Cu; whilst the Cr-tube was used for Ba, I, Ce and La.

The characteristic X-rays emitted by the elements were crystal-dispersed and measured with flow and/or scintillat~~ing~~on counters. The measured intensities were computer-corrected for mass absorption and compared with calibrated standard materials. The results are expressed and recorded in parts per million (ppm). The detection limits of the elements and the calibration statistics of the standard materials are given in Table 5. All estimates below the detection limits of the elements are recorded as not present (n.p.). The standard errors of estimates, when expressed as % of mean estimates of the calibrated standards, indicate accuracies in the range of ± 6% to ± 20%. In absolute ppm, errors in the estimates of elements in the analysed samples are small, being similar to the detection limits or small multiples of them. The absolute error is, however, very substantial for Ti and Mn. This may be due to the wide range of concentrations in the calibration standards.

The trace element compositions of the analysed samples are given in Tables 25a - g, and their stratigraphical variation shown in Figures 44a - f.

3.2.3 Acid Digestion

Acid digestion of the carbonate sediments was performed in order to determine the acid-soluble contents of the samples, as well as to obtain the non-carbonate acid-insoluble components for mineralogical and

Table 5 Calibration Statistics - Trace Elements by X.R.F.

Tube	Elements	Lower Detection Limit(ppm)	No.of Calibrating Standards	Mean (ppm)	Standard Error of Estimate (S.E.E.) ppm
Tungsten, W	Ti	4	36	4746	483
	Rb	6	31	153	15
	Sr	8	29	223	17
	Y	5	24	51	9
	Zr	5	31	185	21
	Nb	5	19	18	3
	Mo	4	9	33	6
Tungsten, W	V	1	24	106	14
	Cr	4	7	100	9
	Mn	4	29	915	82
	Ni	2	30	220	29
Chromium, Cr	Ba	6	28	597	64
	I	3	5	39	2
	Ce	13	20	92	21
	La	22	32	62	16
Molybdenum, Mo	U	5	13	29	4
	Th	4	23	91	17
	Pb	5	23	66	10
	As	6	7	77	4
	Zn	5	27	99	12
	Cu	5	24	38	6

Detection Limit = $2\sqrt{2/m} \times \sqrt{Rb/Tb}$

and Standard Error of Estimate (S.E.E.) = $S.D.(\gamma)\sqrt{1 - r^2}$

where M = slope in counts/sec/ppm

Rb = background in count/sec

Tb = time for background counts in seconds

S.D.(γ) = standard deviation of element concentration values

r = correlation coefficient

chemical studies. This enabled them to be compared with surrounding clastic host sediments.

A sufficient amount (50-500g) of sample needed to give between 5 and 10g of acid insoluble residue was oven-dried ($60^{o}C$ for 4 hours) and hand-ground in a pestle and mortar to pass through a 500 μm sieve. This particle size ensured representative sampling and complete acid attack of the carbonates.

Calcitic and aragonitic samples were digested with cold 1M HCl, whilst sideritic samples were digested in hot 1M HCl on a hot ($90-100^{o}C$) plate for 1-2 hours. The hot acid treatment was needed for siderite because of its resistance to attack by cold mineral acids. For all samples, digestion was enhanced by occasional stirring and decantation of spent acids. When effervescence ceased the suspension was vacuum-filtered through a pre-weighed filter paper, using a Buchner Funnel. The retained and insoluble residue was washed three to four times with distilled water, dried at $110^{o}C$ for about 6 hours and then weighed with the filter paper. The difference in weight, expressed as a percentage of the sample weight digested, was recorded as % acid insoluble residue in Tables 18, 23 and 24. The acid insoluble residues were then subjected to the various analytical procedures employed for the normal samples, as described above. The trace element contents were, however, not determined. The analytical data for the analysed insoluble residues are given in Tables mentioned above.

3.3 The Investigation of Glauconitic Grains and Carbonate Minerals

The experimental procedures described in the preceding sections were primarily concerned with the chemical and mineralogical composition of the sediments under investigation. There are, however, some constituents of sedimentological and diagenetic significance whose characterisation required additional analytical procedures. The materials concerned are the glauconitic grains occurring in parts of the Barton Clay; biogenous (fossil shell) calcite and aragonite; lime-mud calcites in the limestones; diagenetic calcites in the calcareous concretions; and siderites in the ironstones. These were studied as follows:

3.3.1 Glauconitic Grains

A) Separation

About 100g of five selected glauconitic sediment samples from the three sampling localities described in Chapter 2 were disaggregated by gentle crushing, soaking in distilled water and ultrasonic treatment. They were then wet-sieved, retaining a 'coarse' ($\gtrsim$ 500 μm) and a 'fine' ($<$ 500-125 μm) fraction. These fractions were washed free of clays and finer materials and dried at 60°C. They were then passed through an isodynamic magnetic separator operated at 0·3 - 0·7 amps, in order to separate the paramagnetic glauconitic grains. Separation was repeated several times, at successive current increments, to ensure complete separation, and avoid biased selection of the more iron-rich grains (cf. Odin, 1969). The separated grains were then viewed under a binocular microscope and all non-glauconitic grains, such as black lustrous pyrite, brownish or yellowish iron-oxides and greyish clay aggregates, were removed.

B) Petrological and Compositional Analysis

Each of the obtained glauconitic grain fractions was first studied petrologically under light and electron microscopes for their microtextures. Then X-ray diffraction traces of oriented and powdered (hand-ground) mounts were obtained in order to characterise the mineral and deduce the expandable layer content. The diffraction conditions were as for ordinary sediment samples described in Section 3.1.1. The (060) reflection position was established by slow-scanning the powdered samples at a rate of $\frac{1}{8}^{\circ}2\theta$ per minute over the $58\text{-}65^{\circ}2\theta$ range. Major element chemical compositions were obtained by β-Probe spectrometric analysis of fluxed bead samples (Section 3.2.1A). FeO was determined by HF - H_2SO_4 acid dissolution followed by titration against $Ce(SO_4)_2$ (Section 3.2.1B).

Sketches of the typical diffraction traces of the glauconies (<u>sensu</u> Odin & Matter, 1981) are shown in Figures 26a,b; whilst the chemical compositions and structural formula are given in Table 12.

3.3.2 Fossil Shells

A) Separation

Shells from ten horizons representing various lithologies and stratigraphical variation were separated by water-soaking, ultrasonic treatment and gentle disaggregation of selected sediments. Extraneous materials were cleaned off the shells with jets of distilled water and repeated gentle ultrasonic treatment. The shells were then oven-dried at 60°C for 4 hours, and hand-ground into fine powder, suitable for analysis.

B) Composition and Purity

Diffraction traces of the powder mounts were obtained, and utilised for determining the aragonite-calcite contents. The determination involved the use of the ratio of the intensities of 3·39Å aragonite and 3·03Å calcite reflections and the aragonite/calcite intensity ratio versus % aragonite calibration curves of Lowenstram (1954). The magnesian nature of the calcite phase, where present, was also determined from the position of the 3·03A (112) calcite reflection, using the plot of composition versus d-spacings of the $10\bar{1}4$ reflections of Fe-Mg-Ca carbonates (Fig.17).

Chemical purity of the shells was determined by β-Probe spectrometer analysis of the major elements using fluxed bead samples. The Sr contents of the shells, as well as the Mg, Fe and Mn contents of some of them, were determined by atomic absorption spectrometry (AAS) analysis of HCl-acid digested samples. The instrument used was a Hilger and Watts Atomspek H1550. Details of the instrumental conditions are given in Table 6. The compositions of the shells analysed are shown in Table 14.

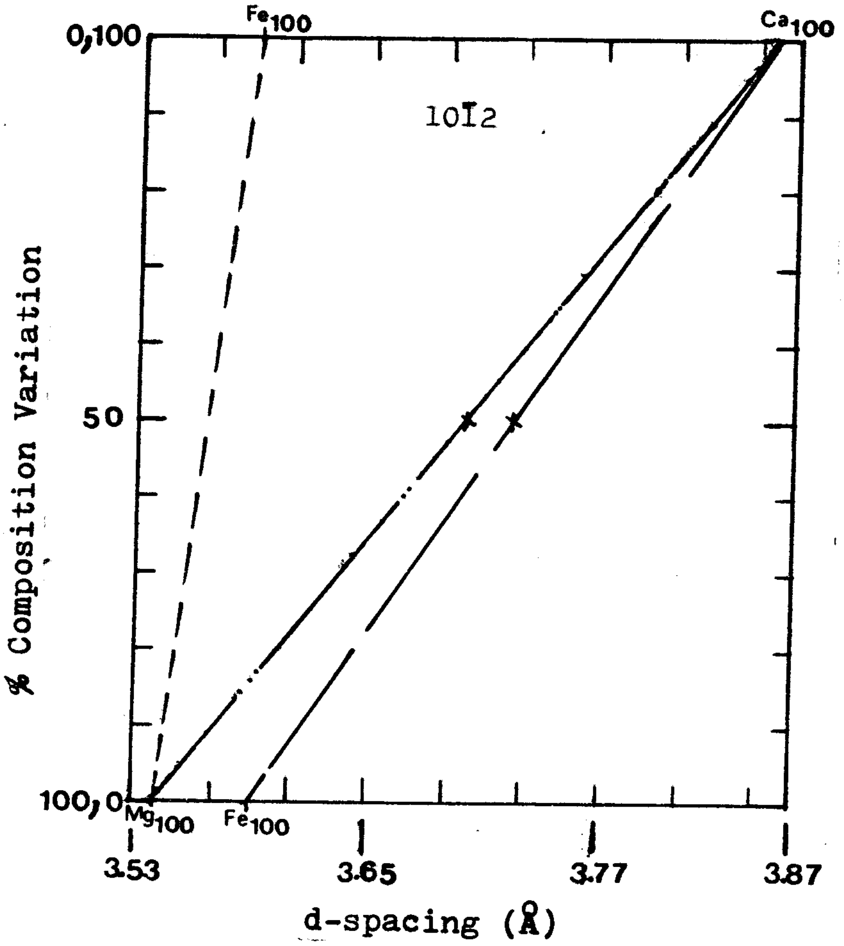
3.3.3 Siderites and Non-biogenous Calcites

Siderites and non-biogenous calcites occur mainly in the carbonate sediments. However, because of their intimate mixing with clastic materials and fossil shells in the largely fine-grained sediments, attempts to separate them for investigation were virtually impossible. It is possible, however, using the bulk samples, to determine the phase compositions by X-ray diffraction and atomic absorption spectrometry (AAS) of HCl acid-leachates.

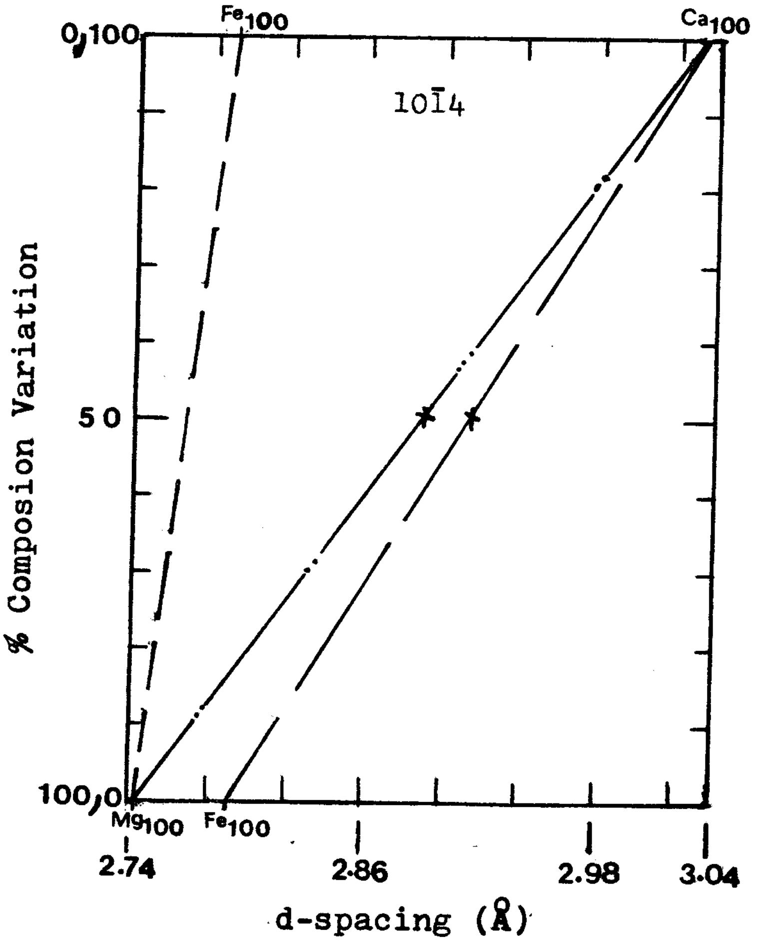
3.3.3A X-ray Diffraction Determination

The use of X-ray diffraction for phase analysis is based on the assumption (Végards Law) that variations in the d-spacings of particular reflections of Fe-Ca-Mg carbonates are related to ionic size, and vary linearly with composition. Plots of such variations were constructed for the $10\bar{1}2$ and $10\bar{1}4$ reflections (Fig.17) using the d-spacings adopted from Graf (1961) and Brindley & Brown (1980). The d-spacings of the end members are:

Fig.17 :Plot of Composition and d-spacing of Ca, Fe and Mg Carbonates



$CaCO_3$---3.86Å
$FeCO_3$---3.59Å
$MgCO_3$---3.538Å
$Ca_{0.5}Fe_{0.5}CO_3$---3.723Å
$Ca_{0.5}Fe_{0.5}CO_3$---3.698Å



$CaCO_3$---3.035Å
$FeCO_3$---2.79Å
$MgCO_3$---2.742Å
$Ca_{0.5}Fe_{0.5}CO_3$---2.914Å
$Ca_{0.5}Fe_{0.5}CO_3$---2.889Å

Phase Compositions	Reflection and d-Spacings (Å) $10\bar{1}4$	$10\bar{1}2$
$Fe_{1.0}CO_3$ (Pure Siderite)	2·79	3·59
$Fe_{0.5}Ca_{0.5}CO_3$	2·914	3·723
$Ca_{1.0}CO_3$ (Pure Calcite)	3·035	3·86
$Ca_{0.5}Mg_{0.5}CO_3$	2·889	3·698
$Mg_{1.0}CO_3$ (Pure Magnesite)	2·742	3·538

The $Fe_{0.5}Ca_{0.5}CO_3$ and $Ca_{0.5}Mg_{0.5}CO_3$ are theoretical solid solution phases with 'projected' d-spacings.

Powder mount diffraction of the carbonate samples was performed, and the $10\bar{1}4$ and $10\bar{1}2$ reflections were scanned at a slow rate of $\frac{1}{8}^{\circ}2\theta$/minute and a time constant of 8 seconds. The peak positions (d-spacing, Å) of the reflections were corrected with respect to the 3·343Å (101) reflection of quartz that was present in each sample studied.

The calcite phases possess unsplit reflections whose analysis was straightforward. The siderite reflections, on the other hand, are mostly unsymmetrical, and are shifted from the theoretical pure siderite position. They appear to be composed of two or more overlapping reflections of dissimilar intensities. Although there is some uncertainty as to whether the phases are discrete and/or compositionally continuous, the siderite reflections have been resolved into two individual phases using the procedure employed by Pearson (1974a) for siderites in some English Carboniferous sediments. These showed similar overlapping reflections. The procedure involved repeated constructions of each individual reflection until they became symmetrical and unchanging with further reconstruction. The resulting phases are labelled Φ_1 and Φ_2, the former being the higher d-spacing phase (Fig.18). The peak heights of the resulting resolved reflections were measured, and the proportional percentage of each peak height was calculated and taken as the relative per-cent intensity for that phase. Then the d-spacings of each phase were used to calculate the lattice parameters, a_o and c_o, by using the lattice formula for hexagonal cells:

$$1/d^2_{hk\ell} = (h^2 + hk + k^2)A + \ell^2 C$$ (Klug & Alexander, 1974).

The results of the X-ray diffraction analysis of the phases are

Fig.18: Sketch of Resolved Peaks Constructed for the 10$\bar{1}$4 Reflection of Substituted-Siderite (-Sample ABBB 13)

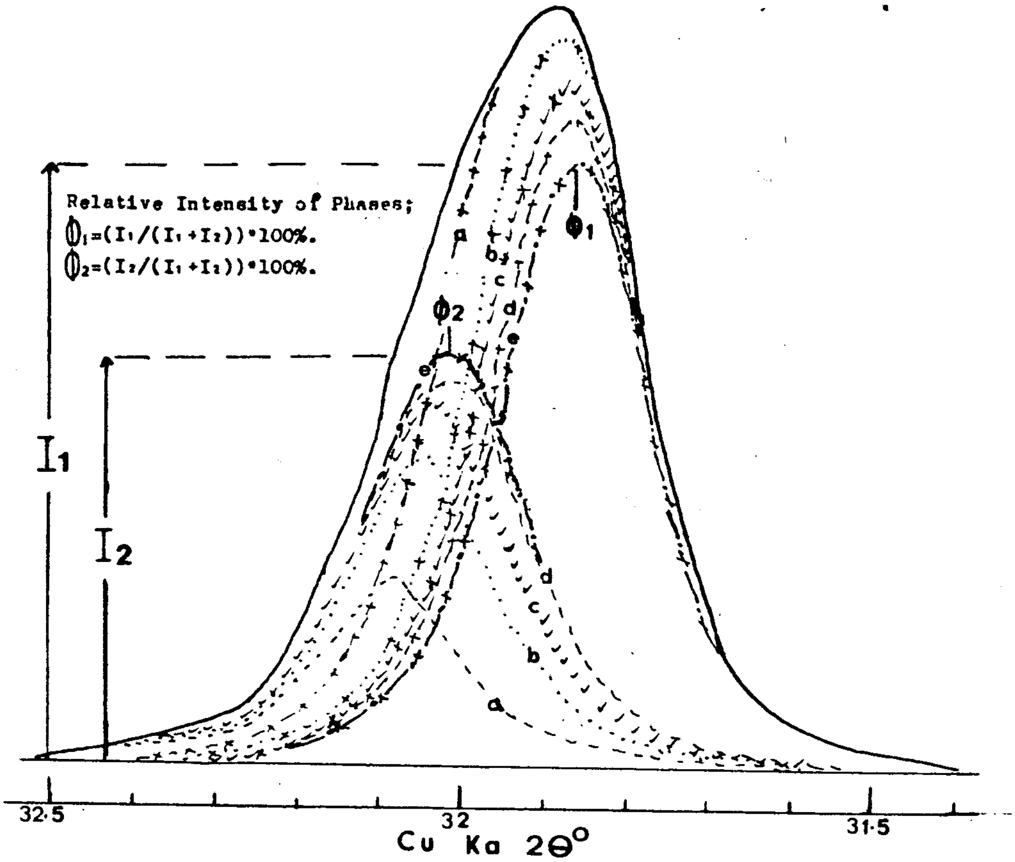
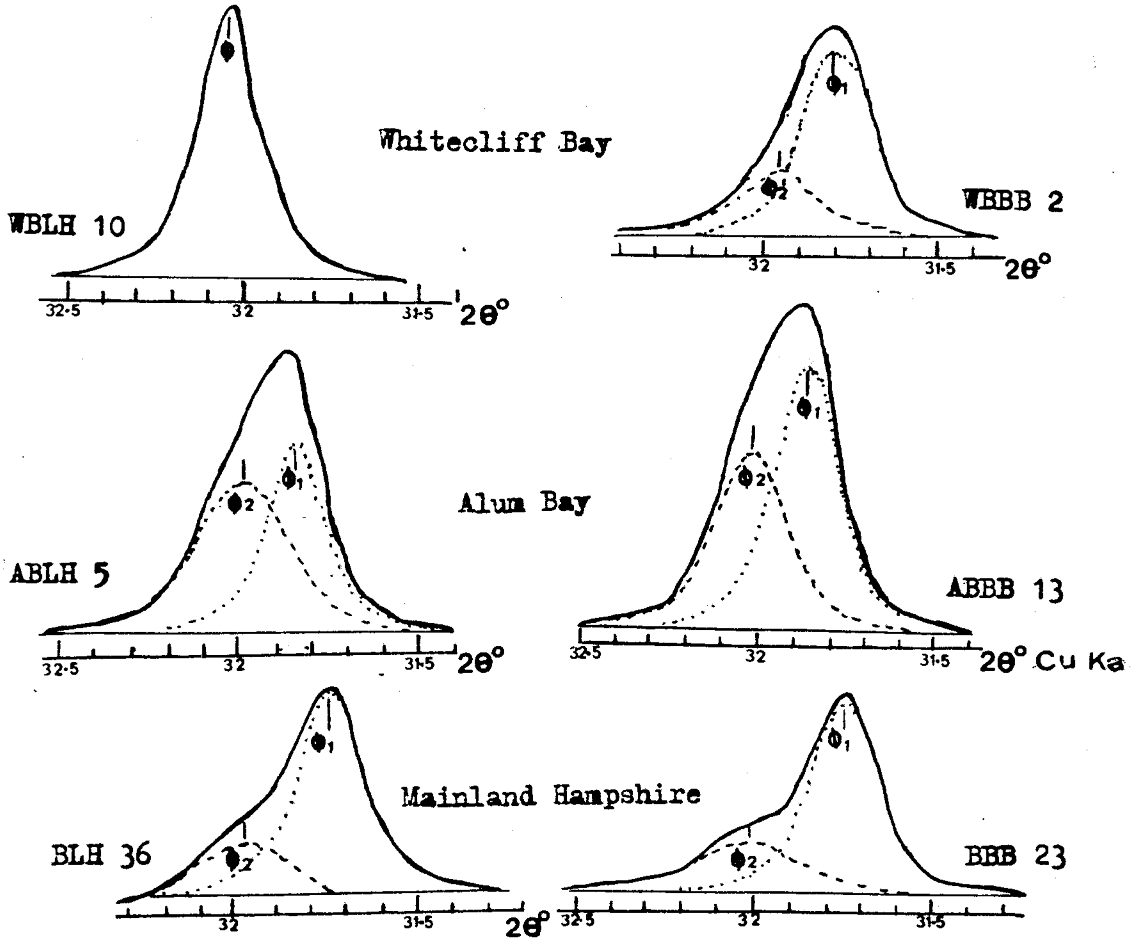


Fig.19: Typical Resolved Peaks of 10$\bar{1}$4 Substituted-Siderite Reflections



given in Table 19, while typical resolved reflections of the siderites under study are shown in Figure 19.

Although the XRD method allows each of the resolved phases to be assessed relative to the other, the method is nevertheless liable to be misleading. This is because the shift of the siderite reflections from that for the pure phase depends on the nature of the substituting ion. For example, the shifts due to Mg^{2+} and Ca^{2+} occur in opposite directions. The substitution of 0·99Å Ca^{2+} for 0·74Å Fe^{2+} causes increased cell dimensions of the siderite crystal, and hence a shift in the higher d-spacing direction. The opposite is the case with the smaller (0·66Å) sized Mg^{2+}, whose relative shift per ion is much smaller. Hence the estimation of Mg in a dominantly Ca-substituted siderite is virtually impossible. The same applies to Mn^{2+} which, on substituting for Fe^{2+}, produces only small lattice changes.

The shifts of the siderite reflections under study are mostly to the high d-spacing side of pure siderite. Chemical analysis suggests the predominance of Ca^{2+}-substituted phases and that Mg^{2+} and Mn^{2+} are low. Much of the shifts will most probably be due to the Ca^{2+}. The composition of the resolved phases is expressed as mol% $(Fe+Mn+Mg)CO_3$ and mol% $CaCO_3$; with Fe>>>Mg and Mn (Table 19). The 'composite' phase composition was then obtained for each siderite sample. The Fe and Ca contents in each of the phases, for the $10\bar{1}4$ and $10\bar{1}2$ reflections, were multiplied by the appropriate relative intensity of the phase. These were then combined and the average content of each of the elements in the carbonate was obtained and recorded as the composite composition.

One important difficulty of the XRD method concerns the lower limit to the sample's absolute siderite content found necessary for satisfactory resolution of the two reflections. These were ~10% for the $10\bar{1}4$ reflection and ~30% for the $10\bar{1}2$ reflection. Therefore only partial resolution was possible for ironstones with < 50% siderite contents. The results are particularly tenuous for ironstones BBB50 and BLH22 with ~10% siderite contents. The two samples have, therefore, not been included in the discussion of the phase compositions in Chapter 14.

3.3.3B Determination by AAS Analysis of Acid Leachates

The principle of this method involves taking the carbonate minerals into solution with acid and analysing the leachate for soluble Fe, Mg, Ca and Mn, and then deriving the molecular formula of the mineral. The procedure employed was a modification of that used by Pearson (1974b).

Depending on the pre-determined carbonate content of the samples, a slightly excess volume of 0·1M HCl was used to digest 0·1g of the powdered sample on a hot sand-bath for about 30 minutes. It was hoped that little, if any, silicate minerals would be taken into solution in the short time used for digestion and by the use of low strength acid. However, in order to correct for dissolved silicates, two non-carbonate containing samples (one clayey, the other sandy) were also treated with acid. After digestion, the sample suspensions were filtered through fine filter paper and washed several times with distilled water. The collected filtered solutions were made up to 100 ml with distilled water after 2 ml conc.HNO_3 had been added. The solutions were analysed for Fe, Mn, Ca, Mg and Al with an atomic absorption spectrophotometer - Atomspek H1550. The instrumental conditions are given in Table 6; and an accuracy of ±5% of the estimations was obtained from HNO_3-based standard solutions employed for calibration. Corrections were made for element contributions from dissolved silicate phases. These are obtained by multiplying the dissolved Al contents of the carbonate samples by the ratios of each of Fe, Mg, Mn, Ca:Al contents of the non-carbonate samples. After correction, the elements were converted to their equivalent CO_2; and the proportion of each in the 'total-equivalent CO_2' was calculated and recorded as the mol% element carbonate (Table 20).

The samples, however, generally contain micro- and macro-sized biogenic $CaCO_3$ which could not be physically separated during sample preparation. Attempts to correct for this in the AAS-obtained compositions, using the X-ray diffraction estimates of the biogenic carbonates, proved unsatisfactory. The biogenic abundance is low, < 10%; but the precision of their estimation is poor (see Section 3.1.1B). The XRD-obtained mol% $CaCO_3$ was thus employed as a more accurate estimation. Estimations obtained for the calcareous concretion and limestone samples are assumed to be insignificantly affected by the low (< 2%) dilution from the biogenic calcites. Then the XRD obtained composite $(Fe+Mg+Mn)CO_3$ was split in proportion of the CO_2-equivalent of the acid soluble wt% Fe, Mn and Mg. The recast XRD data is given in Table 21 and mainly employed for discussion. It was also used for the triangular plot of $(Fe,Mn)CO_3$ - $CaCO_3$ - $MgCO_3$ (Fig.36) showing the spread of the carbonate phase compositions.

Table 6: Analytical Conditions for Acid-leachates Analysis by Atomic Absorption Spectrophotometer

Element	Working Range μg/ml	Sensitivity μg/ml	Detection Limit μg/ml (at 1000 dilution)	λ^* nm
Fe	1 - 20	0.06	0.004	248.3
Mg	0.05 - 1	0.005	0.005	285.2
Ca	0.3 - 10	0.03	0.0001	422.7
Mn	0.3 - 5	0.03	0.0008	279.5
Al	10 - 200	1.0	0.005	396.2

*Analysis by flame emission using Air/Acetylene flame, except Al, for which N_2O/Acetylene flame was used.

3.4 Data Statistics

Working on about 200 samples and determining about 60-80 components (or variables) of each sample led to the production of over 13000 data points. Therefore, in order to establish the variations and relationships between the analyses, and also the range in the sediment compositions, the compositional data were statistically analysed with a computer. The computer employed was Cromemco Z-2D, a table-top computer, and Fortran programs written by T. Clayton (unpublished, 1982) of the Geology Department, University of Southampton, England. Summary statistics and correlation coefficients of data sets, for sediments of different divisions, localities and lithologies, were calculated and employed for discussions.

CHAPTER 4

QUARTZ, FELDSPAR, CLAYS AND OTHER DETRITAL MINERALS

4.1 Introduction

Clastic sediments constitute about 95% of the Upper Eocene succession of the Hampshire Basin. These sediments, described in Chapter 2, include the flint pebble beds at the base of the succession at Highcliffe and Alum Bay; marine glauconitic sandy clays, mottled clays and sands, and brown clays of the Barton Clay Formation; sand deposits of the Barton Sand Formation with some clay horizons; and non-marine sands, clays and lignitic clays of the 'Lower Headon Beds'. Although there are numerous palaeontological studies (i.e. Burton, 1933; Edwards, 1967) and some broad studies of the clay mineralogy (Gilkes, 1966) and heavy minerals (Walder, 1964; Blondeau & Pomerol, 1968), there are no known previous detailed investigations of the sediments compositions.

In this chapter the distribution of detrital constituents of the clastic sediments is discussed. The bulk mineralogical compositions of the sediments are given in Tables 7a - g, and stratigraphically plotted in Figures 20a - c. Quartz, feldspars and clay minerals are the dominant detrital materials in the sediments. The heavy minerals, observed, but not estimated, include garnet, rutile, staurolite, tourmaline and zircon. Flint pebbles also occur, but are restricted to a few horizons. The derivation of the detrital materials is considered along with their sedimentological significance.

4.2 Quartz

Quartz is present in all the sediments studied, although its abundance varies from trace amounts to 95% (Tables 7a - g). In the sand deposits of the Barton Sand Formation and 'Lower Headon Beds', quartz varies from 67% to 95%, averaging 83 ± 6%. These are much higher than the 65% quartz reported for average sandstones (Blatt et al., 1972). Those sands, particularly the Barton Sand and the sand matrix in the pebble bed at Highcliffe, which are characterised by > 80% quartz, would be quartz-sands (cf. Blatt et al., 1972; Pettijohn et al., 1972).

The quartz contents of the clayey sediments are more variable. The lignitic clays and the marine brown clays contain less than 30% quartz compared to between 40 and 60% quartz in the silty- and sandy-clays that

Table 7a :Mineralogical Composition of the 'Lower Headon Beds', Mainland Hampshire.

	BULK SAMPLE MINERALOGY (%)													
BLH	Quartz	Total Clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepidocrocite	Goethite	Organic C
1	78·8	12·5	8·2	0·5					1·0					0·8
2	46·4	38·9	7·7	1·7	5·1				0·9					1·7
3	40·0	40·0	4·3	1·2	4·4			4·2	0·8	5·7				3·2
4	52·9	19·8	4·9	3·5	4·6	5·4		1·0	0·9	7·8				1·1
5	32·4	28·6	4·5	0·7	14·9		2·0	tr					17·1	0·3
6	84·6	7·2	7·1	1·1										-
7	25·0	42·5	5·3	1·4	16·6	4·9			0·7	2·4	0·8			1·8
8	53·2	37·0	4·7						0·9		4·7			1·9
9	83·2	9·5	3·8	2·0				tr						0·4
10	47·2	46·5	3·7	0·8					1·1	1·7				2·7
11	45·0	19·9	2·3	2·4	7·4			21·3		1·9	tr			0·6
12	69·7	10·7	P				3·3					6·9	10·0	0·3
14	54·8	38·2	2·2	3·2				0·6	1·1	tr				-
15	54·2	45·4	2·7											0·9
16	83·9	10·2	4·5	0·7	0·7				0·9					0·2
18	53·3	40·5	4·4	1·1	0·7				0·9					0·4
19	9·8	7·8			72·1	7·5				2·2				0·6
20	33·5	47·0	4·0		4·3	4·5			0·7	1·3				4·8
21	63·3	29·8	4·3	1·8	0·1			0·9	0·8					0·6
22	65·4	9·7	5·7		8·9		10·3							0·2
24	87·8	5·9	6·7											0·3
25	28·4	53·1	6·0		9·4			1·6	0·8	1·5				1·9
26	89·6	2·9	6·6	0·7						0·2				0·4
27	29·5	51·1	8·6		8·6				0·7	2·0				1·2
28	21·9	65·8	4·7	2·3				2·7	1·3	2·5				2·1
29	88·3	7·0	4·4	2·2					0·4	0·2				0·4
30	84·1	6·7	9·7						0·5	P				0·6
31	78·3	14·3	2·9	1·1					1·2	0·9				0·5
32	41·9	51·2	5·3	1·8					1·1	tr				0·4
33	54·3	4·7	4·0	2·5	2·5		32·1		0·5					0·2
34	84·3	9·6	4·4	1·1	0·4									0·2
35	83·9	3·8	10·0	0·9	0·4				0·6	1·0				1·5
36	3·1	9·5			4·4	tr	82·2							0·2
37	50·4	37·9	6·9	1·2	2·3			1·4	1·0					0·1
39	43·1	49·4	4·1	1·0				2·2	1·0	0·4				2·5

Table **7b** Mineralogical Composition of the Barton Sand Formation, Barton-on-Sea

	BULK SAMPLE MINERALOGY (%)												
	Quartz	Total Clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepido-crocite	Goethite	Organic C
BBB														
1	14.7	62.4						2.7	0.3	0.4				19.5
2	55.5	30.8	4.4	2.1					1.1	4.2				1.6
3	21.9	60.6	2.5					1.8	0.6	**tr**				13.0
4	81.0	6.5	11.5											0.5
5	56.3	33.0	8.1	2.6				2.4	0.6	0.8				1.1
6	82.3	6.0	10.3	1.4										0.4
8	88.2	2.2	5.9	**tr**				0.8			1.3			0.5
9	74.1	10.8	12.6	1.1					0.4					0.3
10	64.5	24.8	8.1	1.8	0.3				0.7		0.5			0.8
11	12.3	18.2					69.5							0.3
12	51.9	34.0	8.4	0.7				3.4	0.8	1.8				1.0
13	43.9	42.2	10.0	1.8				2.3	0.8	1.5				1.0
14	81.8	11.8	6.3											0.4
16	84.0	3.8	10.4	0.7										0.4
18	86.8	2.9	10.2											—
20	83.2	5.3	11.4							**tr**				0.3
22	65.3	21.4	11.0							**2,3**				0.4
23	7.9	**30.7**	2.4		1.3	2.4	58.3							0.5

Table 7c: Mineralogical Composition of the Barton Clay Formation, Mainland Hampshire.

BULK SAMPLE MINERALOGY (%)

	Quartz	Total Clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepidocrocite	Goethite	Organic C
BBB														
24	22.8	65.1	4.4		5.1			5.9	0.9	2.6				1.4
25	7.9	13.6	0.6		76.2	1.2				tr				0.3
26	15.6	31.3			6.3		44.7			2.2				0.6
27	21.3	59.5	2.7	1.3	5.8	1.6		5.8	0.9	2.3				1.6
30	26.3	51.7	7.7	2.1	3.9	4.0		3.6	0.8	2.3				1.1
31	7.2	10.2			81.9					0.6				0.3
32	34.1	48.3	5.0	1.8	4.2			5.5	0.8	1.1				1.3
34	50.5	40.0	6.2		0.7			2.2	0.7	0.4				1.0
35	37.5	54.0	4.0	1.8	0.7				0.8	2.0				1.0
36	11.8	13.0	1.9		72.6			tr		0.8				0.4
37	39.1	51.9	5.5		0.7				0.8	2.9				1.1
39	6.6	9.9	tr		82.3					1.2				0.5
40	37.3	46.6	9.7		0.7			2.9	0.6	2.2				1.2
41	59.8	33.7	3.3	0.5				1.1	0.9	1.5				0.8
42	14.6	17.5	tr		65.3					2.4				0.4
43	20.7	43.3	2.8			2.5	29.9							0.6
44	29.8	57.4	4.1	1.3	0.4				0.8	2.1				0.6
45	40.3	48.4	5.5	2.5					0.9		3.3			0.7
46	34.0	53.8	4.9	2.3							4.9			0.9
47	48.6	49.4									3.7			0.8
48	44.9	48.1	4.1	2.9					0.8		2.0			0.8
49	39.1	50.7	3.7		0.6						8.0			0.6
50	34.3	48.7					10.8		0.6	2.6		3.5		0.7
BHC														
1	24.0	58.4	6.5		1.2					2.0	7.8			0.7
2	49.0	46.0	1.8	2.1					0.5	0.7				0.7
BPB														
1	80.6	11.6	6.3	1.5										0.6

TABLE 7d: Mineralogical Compositions of the 'Lower Headon Beds', Heatherwood Point, Isle of Wight

	BULK SAMPLE MINERALOGY (%)													
	Quartz	Total Clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepido-crocite	Goethite	Organic C
ABLH														
1	tr	tr			87·8	12·2								0·2
2	5·2				74·2	20·6								0·9
3	tr	tr			97·1	2·9								0·1
4	29·8	13·5	2·2	1·0	50·5	3·0								0·2
5	8·6	7·6			3·3	2·4	77·5							0·1
6	1·4	tr			81·8	16·7								0·5
7	8·0	tr			66·7	75·3								0·3
8	9·1	tr					90·6							0·1
9	65·6	27·4	6·0	1·2					0·8					0·5
10	77·9	15·9	5·7	0·6					1·0					0·2
11	12·0	52·8	1·3					5·0	0·3					23·4
12	80·1	13·8	5·6	0·5					0·3					0·4
13	44·9	19·7	1·7					2·2						17·4
14	93·2	tr	4·7	2·2										0·3
15	85·9	7·9	4·9	1·3										0·5
16	32·4	59·5	6·2	2·0					0·9					0·5

Table **7e** Mineralogical Composition of the Barton Sand Formation and Palaesols, Alum Bay.

	BULK SAMPLE MINERALOGY (%)													
	Quartz	Total Clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepidocrocite	Goethite	Organic C
ABBB/FS														
1a	81.0	15.5	3.5											
2a	61.9	24.5	2.3										11.2	
3a	39.5	15.4											44.1	
4a	88.0	3.5	1.8										6.7	
ABBB/FS														
1b	76.8	10.0	3.3	1.5									8.6	
2b	77.9	12.3	4.2										5.6	
3b	78.9	5.8	3.5	1.8									10.9	
4b	83.2	2.6	5.2										9.0	
5b	77.4	4.0	5.5	2.7									10.4	
6b	65.1	5.5											29.4	
7b	83		3.7	1.9									11.5	
8b	92.8	6.7	2.9	0.7									3.7	
ABBB														
19	95.2		3.3	1.5										0.4
18	92.5	2.1	5.4											0.1
17	31.4	66.1	1.7	0.8										0.2
16	91.7	2.2	3.6	0.9										0.1
15	84.4	7.3	8.3											0.4

Table 7f Mineralogical Composition of the Barton Clay Formation, Alum Bay

	BULK SAMPLE MINERALOGY (%)													
	Quartz	Total Clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepido-crocite	Goethite	Organic C
ABBB														
14	50.1	36.5	5.8	1.8				3.1	0.9	1.2	1.4			0.9
13	4.0	11.8	3.2				79.8			tr				0.2
12	41.7	51.1	3.7	0.8				2.7						0.9
11	33.6	57.4	5.5	2.2					0.9	1.4				1.6
10	38.9	40.3	5.8	1.6	11.0				0.8	2.6				1.2
9	71.1	17.4	5.8					5.5	0.7	0.3				0.8
8	15.3	11.1	3.2		70.4									0.2
7	62.3	29.0	6.5							2.2				0.8
6	40.3	50.3	3.5	2.7				3.2						0.6
5	10.8	12.2	2.2	1.1	72.0	1.1				0.7				0.3
4	11.8	18.5			69.8					tr				0.2
3	60.2	30.5	2.9	1.2				4.8	0.9					0.8
2	48.5	40.3	4.8	2.0	2.3				0.8	2.2				0.8
1	40.6	46.2	3.8	2.5	4.2				0.6	2.9				1.0
ABHC														
1	63.7	28.7	4.2	2.1					0.7	0.8				0.7
2	73.7	21.4	3.8						0.7	1.0				0.9
ABPB														
1	67.4	12.4											20.5	0.2

Table 7g: Mineralogical Composition of the Upper Eocene Succession, Whitecliff Bay.

	BULK SAMPLE MINERALOGY(%)													
	Quartz	Total clay	Potassic Feldspar	Sodic Feldspar	Calcite	Aragonite	Siderite	Gypsum	Anatase	Pyrite	Jarosite	Lepidocrocite	Goethite	Organic C
WBLH														
1	26·4	62·3	4·8	1·9	4·7				0·8					1·0
2	29·0	45·7	5·1	2·3	6·6				0·8				10·5	0·7
3	41·6	39·0	3·8	1·1					0·8				14·2	0·8
4	77·2	16·7	6·3						1·0					0·3
5	79·6	14·0	6·7						0·8					0·1
6	37·7	6·5	8·7				47·1							0·2
7	23·2	66·8	3·5	1·4				4·7	0·9					2·5
8	47·9	44·3	7·9						0·8					0·6
9	15·0	38·2	2·6					12·0		0·8				31·2
10	3·8	tr					96·2							0·1
11	54·6	37·8	5·4						1·0					0·6
12	23·0	70·7	4·1					2·7	0·8					1·9
13	27·6	57·4	4·7	1·8					0·8				7·9	0·4
WBBB														
9	67·0	14·9	8·1										10·1	0·3
8	78·2	5·0	8·7										3·9	0·3
7	81·1	8·7	10·2											0·3
6	79·1	9·0	9·5											0·2
5	81·1	10·0	9·0											0·1
4	59·5	27·3	11·0							2·2				0·7
3	59·5	23·9	15·8						0·7	0·7				0·4
2	24·4	15·5	10·0				48·9			1·4				0·2
1	30·0	49·4	8·2	4·7	5·1				0·6	2·6				0·6

Fig.20a : Stratigraphical Variation of Bulk Sample Mineralogical Composition; Highcliffe-Milford on Sea, Mainland Hampshire.

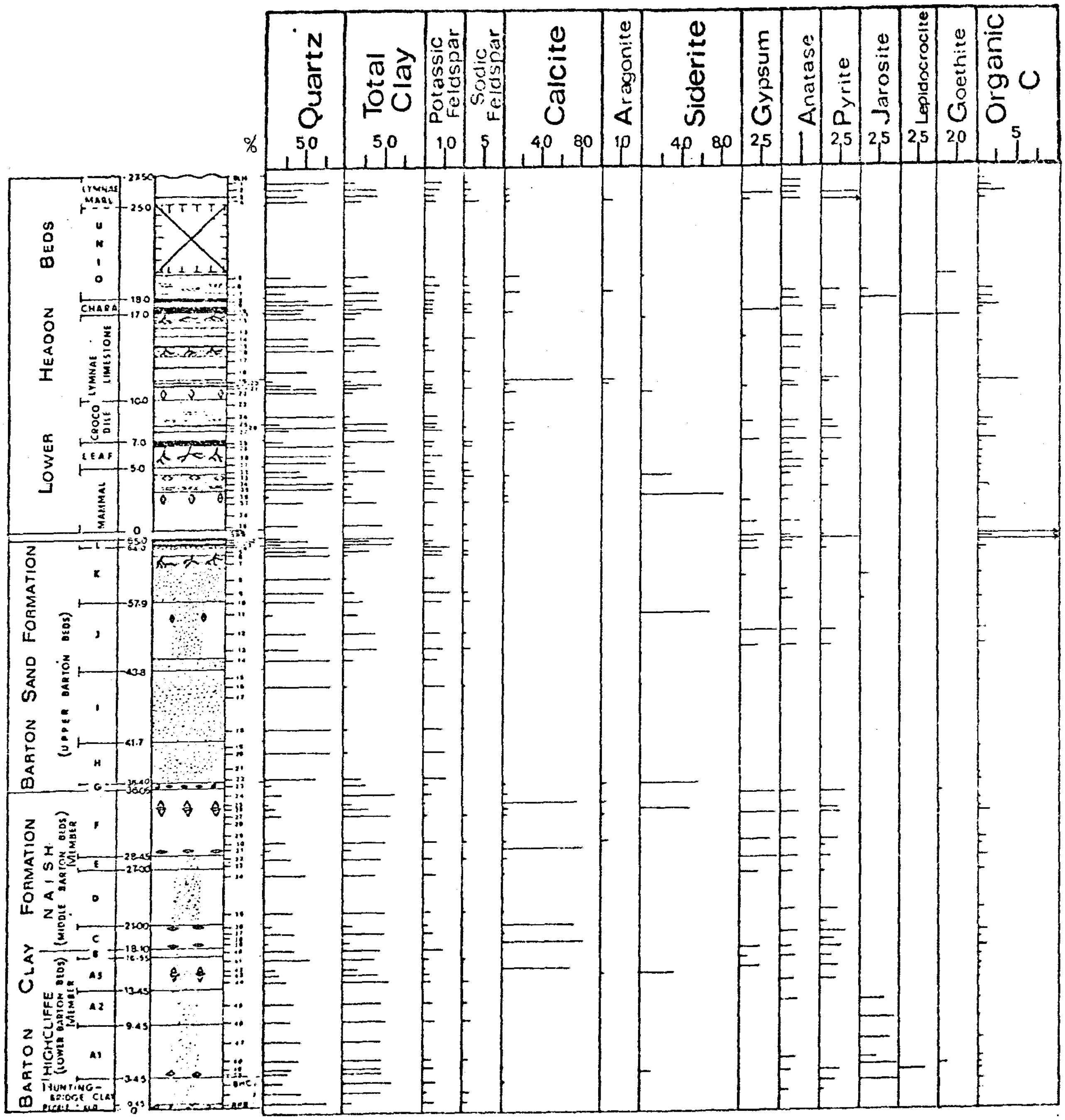
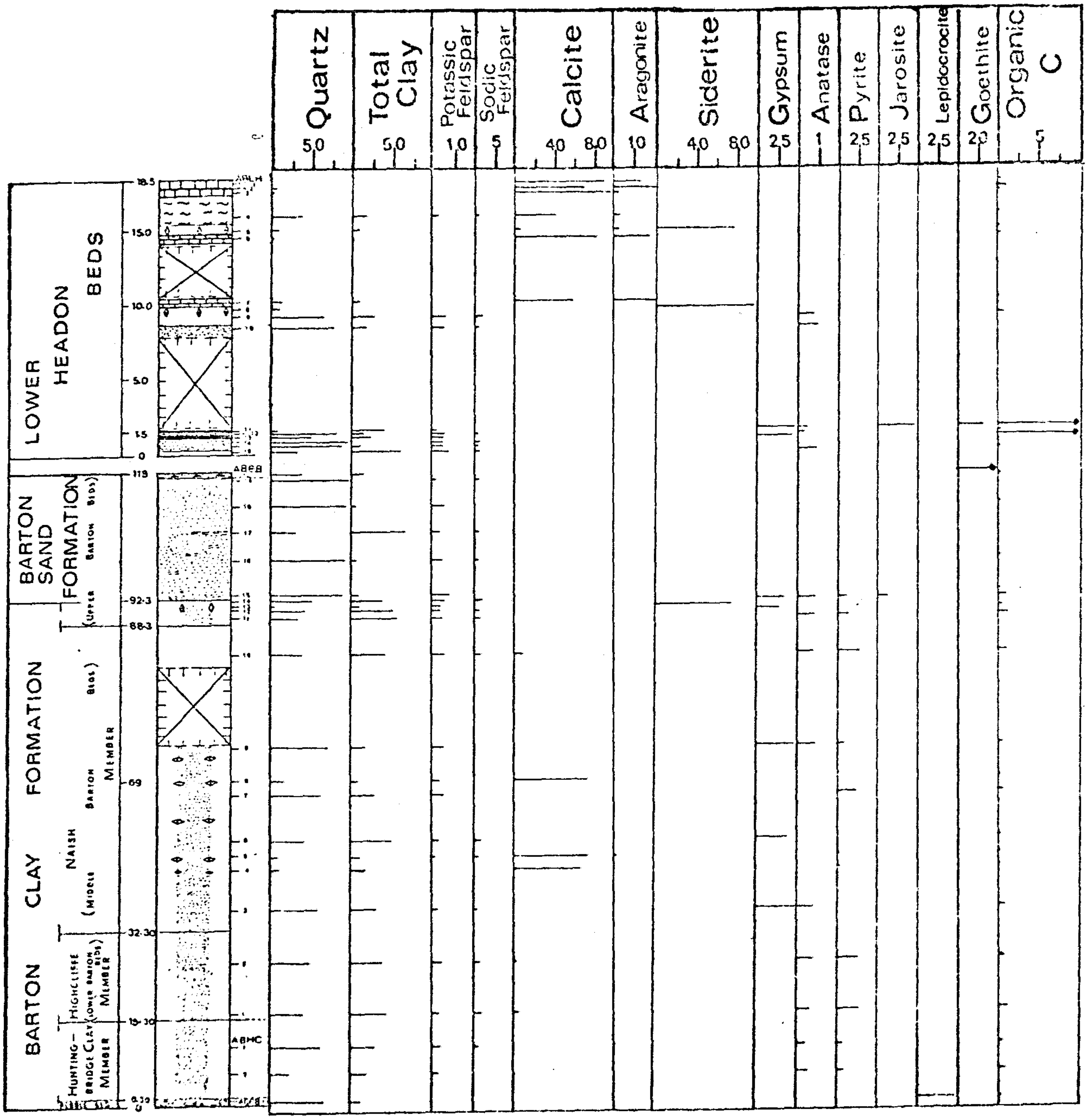


Fig.20b :Stratigraphical Variation of Bulk Sample Mineralogical Composition; Alum Bay-Heatherwood Point, Isle of Wight.



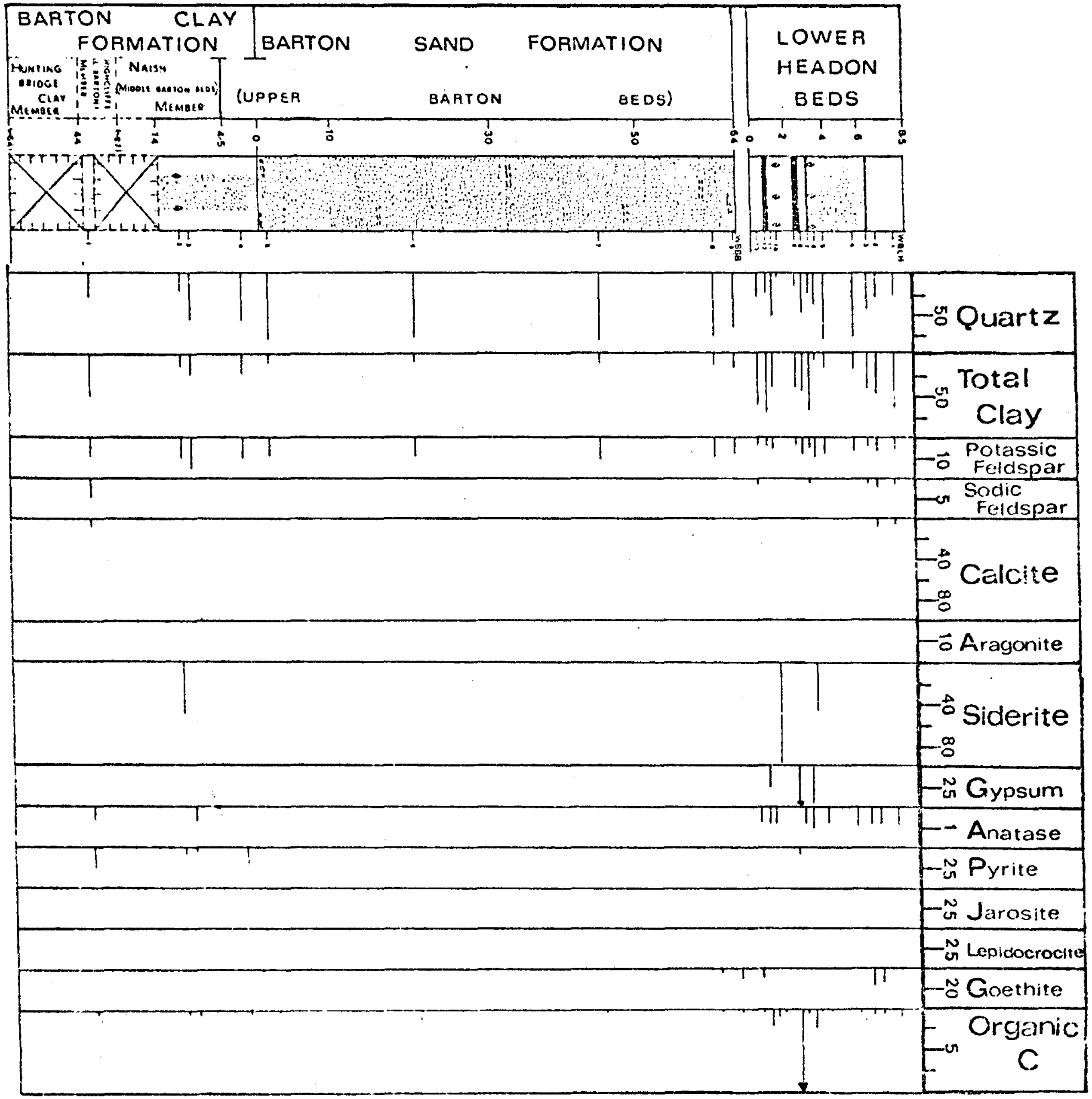


Fig.20c : Stratigraphical Variation of Bulk Sample Mineralogical Composition; Whitecliff Bay, Isle of Wight.

are most common in the succession. A few very sandy clay horizons in the Barton Clay (i.e. ABBB-9) contain a little more, 60-70%, quartz. In general, quartz averages 45 ± 4% in the clayey sediments, which is higher than the 30% quartz reported for average shales (Blatt *et al.*, 1972). Hence these clayey deposits are also quartz-rich.

Optically, quartz is seen to occur mainly as medium sand to silt-sized ($\leq$ 500 μm) grains of monocrystalline rock quartz variety. There are also some grains of polycrystalline and milky-white quartz types. The grains are mostly of rounded, sub-rounded and sub-angular shape (i.e. Plates 26-28,30,31). They have probably undergone several cycles of weathering and erosion, and are not likely to have been derived directly from crystalline rocks. Coarser (> 600 μm) grains occur in substantial quantities in the pebble beds (Plates 40,41). These would have been transported by strong water currents and deposited in a high energy (beach) environment. A few discrete euhedral clay-sized (~ 2μm) quartz crystals (Plate 55b) were also observed in an indurated ferruginous sand (Sample BLH-12) on Hordle Cliff. The crystals are admixed with clays and would either have formed *in situ* or have been derived from a nearby source where they might have neoformed. The indurated sand is one of the horizons regarded as hydromorphic palaeosols in the present study. The well developed podzol palaeosols at the top of the Barton Sand at Alum Bay contain pitted and etched quartz grains (Plates 55a,b). The grains also possess goethite-filled surface cracks. The etchings and cracks are features which suggest chemical weathering. In fact, the quartz grains have been cemented by goethite in the indurated horizons of the podzols (Plates 18,19,49,50,52; Fig. 6b). Similar dissolution features and goethite cementation have also affected the pebbles and quartz grains in the pebble bed, also at Alum Bay. Podzols are acid soils commonly developing in present-day warm and humid climatic regions, and particularly on very porous parent materials such as sands (Hunt, 1972).

Another notable feature is the occurrence of quartz moulds of fossils. In the Barton Sand at Alum Bay and Whitecliff Bay, moulds of plant materials are common and these comprise quartz grains cemented by goethite. Then in a calcareous nodule (ABBB-5) from the Barton Clay at Alum Bay, moulds of foraminifera comprising quartz grains (Plate 66) were observed. These may reflect slow depositional conditions that allowed the moulds to develop prior to deeper burial.

4.3 Feldspars

Feldspars occurring in the studied sediments were identified as potassic feldspars and sodic feldspars. The former are more common, constituting between 2 and 8% (average 6%) of the clays and sand-clays but between 5 and 15% (average 8%) of the sand deposits. Detection of sodic feldspar is infrequent in the succession, and it generally occurs in $<$ 4% where observed. The mineral is least abundant in the Naish Member at Barton and Alum Bay, and most parts of the succession at Whitecliff Bay.

The predominance of potassic feldspar in the sediments would suggest either a potassic feldspar-rich source rock or preferential removal of more weatherable plagioclase feldspars (Goldich, 1938) during the Eocene in southern England. In addition, the 8% average feldspar content of the Upper Eocene sands is in the lower end of the 5-60% range of average feldspar contents of ancient and recent sandstones and sands (cf. Pettijohn et al., 1972). Actually, low feldspar contents are typical of highly matured quartz sands with which the Upper Eocene sands compare closely.

There is a significant variation of the feldspar abundance in the Barton Sand at Alum Bay. The dominant potassic feldspar decreases from about 8% at the base of the sand to about 3% at the top, and is absent in the indurated horizon of the palaeosol profile at Heatherwood Point (Profile A, Fig.6b). This variation is believed to be due to localised contemporaneous pedogenic conditions and flushing of the deposit by acid meteoric waters. Acidic leaching had caused some dissolution of feldspar and 2:1 clay minerals, and the formation of authigenic kaolinite.

Under optical microscopes, the potassic feldspar mainly comprises the microcline variety (i.e. Plate 27); whilst the few sodic feldspars are albite or oligoclase. They occur as sub-rounded and sub-angular, medium sand to coarse silt-sized grains. They would, like the quartz, have been derived from surficially weathered older sediments.

Most of the feldspars within the red-yellow podzol palaeosols at Alum Bay were observed, under the SEM, to be deeply etched and pitted. Some have been broken along cleavage planes into 0·5 - 3 μm by 10-30 μm blocks or plates (Plates 54d-e). These are features that could have resulted from incongruous dissolution (Tchoubar, 1965; Tarzi & Protz, 1978a). Feldspars with similar features are common in soils, and would indicate the prevalence of near-surface conditions with acidic groundwaters (Wilson, 1975).

4.4 Clay Minerals (Total Clay)

Clay minerals occurring in the succession are kaolinite, illite, illite-smectite and traces of chlorite. They are largely detritally-derived, although kaolinite and glauconitic-mica phases in parts of the succession are authigenic. In this section, the 'Total' Clay contents of the sediments are discussed whilst details of the individual phases are given later in separate chapters.

The total clay contents of the clayey sediments vary from 17 to 71%, averaging 45 ± 10%. Amounts $> 55\%$ are possessed by the greyish and brownish clays of the Naish Member of the Barton Clay at Barton, and many of the non-marine green clays and carbonaceous clays of the 'Lower Headon Beds'. Low ($< 25\%$) clay content occurs only in some of the sandy-clay horizons in the Barton Clay at Barton and Alum Bay. Clays in these sediments constitute the matrix materials within which the other mineral constituents are set (i.e. Plates 30,31,33).

The total clay contents of the sand sediments vary from trace amounts to about 17%, averaging 8%. Sands in the 'Lower Headon Beds' and the Barton Sand Formation at Whitecliff Bay generally contain $> 6\%$ clays, whereas lesser ($< 5\%$) amounts of clays characterise sands of the Barton Sand Formation at Alum Bay and Barton. Those at Alum Bay, particularly, contain very small quantities ($\lesssim 2\%$) of clays, although the upper pedounits of the podzol palaeosols capping the Barton Sand contain substantially higher ($\sim 12 - 25\%$) clays. The clays in those soil units are probably translocated or alluviated clays. Clays, however, generally occur in the sand deposits as laminae, lenses and bands. Some of these have thickened into pipe-clays (Plate 17), especially on the Isle of Wight. Also observed in places are disseminated sand- and silt-sized clay clasts and clay coatings of quartz grains.

4.5 Anatase and Heavy Minerals

Anatase commonly occurs in small ($< 1\%$) amounts in the succession. It shows no significant correlation with other mineral phases, possibly because of its small concentration. It could be occurring as finely disseminated material and/or included within clay minerals. In the sand sediments silt-sized needle-like rutile commonly occurs. The heavy mineral assemblage was not systematically studied. Some of the minerals were, however, observed in some of the sediments' thin-sections and grain-mounts. They include zircon, epidote, staurolite, garnet and tourmaline (Plates 26,27,28). Zircon, the most common, is often zoned, and is fine-sand to coarse-sand sized. Some zircons possess shallow surface cracks and etchings, and could have undergone several erosional cycles. The tourmaline is mostly of a purplish variety, while the garnets are mostly colourless. Garnet and epidote often occur as rounded fine sand-sized grains. The heavy minerals have been systematically studied by Walder (1964) and Blondeau & Pomerol (1968). They found granite-derived assemblages typified by tourmaline and zircon, and metamorphic-derived assemblages that include garnet, kyanite, staurolite sphene, brooksite and epidote. In addition, anatase, zoisite and rutile, which are probably authigenic, also occur. The composition of the assemblage varies little up the succession. There are, however, relative variations in the abundances of the minerals that may be attributed to differential sorting and variation in contributions from various sources.

4.6 Pebbles

Pebbles occur mainly in the pebble bed at the base of the Upper Eocene succession at Highcliffe and Alum Bay. The pebbles are dominantly flinty, sand-supported, often rounded or spherical, with long axes measuring up to about 30 cm. Although generally worn smooth, many of the pebbles at Alum Bay possess surface cracks, often filled by goethite (Plate 41). Some pebbles at Highcliffe are also etched, but with no goethite; rather they often contain patches of greyish, powdery chalcedonic quartz. Smaller sized (~ 2 cm) flint pebbles also occur disseminated in the Barton Sand at Alum Bay. These are mostly flattened, and also worn smooth. Chert pebbles are rare; only one, ~ 3 cm-sized, very weathered chert pebble was found in the pebble bed at Highcliffe.

The flint pebbles were excluded from the analysed sediments. They were optically studied only. They were seen to be mainly composed of microcrystalline quartz (Plates 41, 43) which, under the SEM, comprises a mosaic of quartz crystals (Plate 51a). The chalcedonic silica comprises radial, length-fast crystallites (Plates 42a,b). They are a primary constituent of the flint pebbles. Similar chalcedonic silica constitutes the bulk of the chert pebbles (Plates 44,57) from Highcliffe.

A few flint sand-grains were optically identified in the pebble beds and the palaeosols at the top of the Barton Sand at Alum Bay. They are mostly coarse-sand sized, and rounded to sub-rounded or sub-spherical. Some of the flint grains also possess surface etchings and goethite-filled cracks that are similar to those described previously on quartz grains in the same horizon.

An important feature of the pebbles concerns their fossil contents. There are numerous foraminiferid tests, siliceous sponge spicules and some dinoflagellates in the pebbles. The micrographs of some of these are shown in Plates 1-13 in Appendix 4. Unfortunately, the fossils could only be observed in two dimensions in thin sections because the pebbles are not sufficiently weathered to allow separation of the fossils. Identification was thus not possible. The foraminiferal assemblage was thought (Professor C.D. Curry - personal communication, 1982) to resemble the Upper Cretaceous forms not uncommon in the Upper Cretaceous English Chalk. Thus they indicate derivation of detritus from the Chalk during Upper Eocene sedimentation in the Hampshire Basin.

4.7 Discussion

The detrital constituents of the Upper Eocene may be assessed with respect to major lithological and sedimentological factors such as environment of deposition, water depth, prevailing current (wave energy) conditions, composition and hydro-dynamics of the supplied and deposited detritus, and rates of sedimentation. These could then be applied to consideration of their derivation.

4.7.1 Lithological Significance

In the Upper Eocene Hampshire Basin, clastic sedimentation was predominant. The deposits are composed of quartz $\gtrsim$ clays$>\gtrsim$ potassic feldspars $>$ sodic feldspars $\approx$ anatase and heavy minerals, with flint pebbles limited to the pebble beds at the base of the succession at Highcliffe and Alum Bay, and the top of the Barton Sand at Alum Bay.

The sediments are generally more quartz-rich than average sandstones and shales. In fact this exposes the subtlety of the lithological (field) descriptions given to the clastic sediments by earlier workers (i.e. Gardner et al., 1888; Tawney & Keeping, 1883; Burton, 1929), and in the present study. Most of the clay deposits are silty or sandy, whilst some of the sands are clayey in nature. Particle size analysis would best clarify the lithological subtlety, but this could not be performed during the present study. As a substitute for particle-size data, a less satisfactory lithological differentiation was attempted using the quartz, total clay and feldspar contents. The ratios quartz(+ feldspars) over total clay (Q/Cl) and quartz(+ feldspars) over quartz plus feldspars and total clays (or Q/Q.F.C.) were calculated for each sediment sample. The stratigraphical variation of the Q/Cl values are plotted in Figures 21a-c, whilst the histograms of values of the Q/Q.F.C. for sediments in the type sections on mainland Hampshire, and a few representative sediments in the succession on the Isle of Wight, are shown in Figure 22b. These, particularly Figure 22b, show a continuum of the quartz-clay values and underline the difficulty in separating clays from sands in the succession.

Very few of the sediments can be described as clay; i.e. with > 50% clays or Q/Q.F.C. < 0·4 (cf. Pettijohn, 1975; Füchtbauer, 1974; Potter et al., 1980). These comprise the brown clays near the top of the Barton Clay at Barton (i.e. 'Beds E & F', Fig.5) and Alum Bay (Fig.6a); the lignitic clays; and some of the green clays in the 'Lower Headon Beds'. A large number of sediments described as clayey possess Q/Q.F.C. values of 0·4 to 0·6, which not only characterise sandy-clays but clayey-sands as well (cf. Fig.2.1 of Füchtbauer, 1974). These compositions typify the bulk of the Barton Clay Formation and clays in the 'Lower Headon Beds'. Closely similar to these, but relatively more sandy and with ratio values of 0·6 to 0·8 and ~ 10-17% total clay contents, are some very sandy parts of the Barton Clay (i.e. BBB-41, ABBB-9, Figs. 5 and 6a) and clay units in the Barton Sand at Barton (i.e. 'Bed J', Fig.5). The sand sediments constitute a distinct lithological grouping with Q/Q.F.C. > 0·75; the Barton Sand, especially at Alum Bay, being particularly very rich in quartz and having Q/Q.F.C. ratios of over 0·9

4.7.2 Derivation

Mineral grains in the clastic sediments are dominantly medium sand-

Fig.21a : Stratigraphical Variation of some Compositional Parameters; Highcliffe-Milford on Sea, Mainland Hampshire.

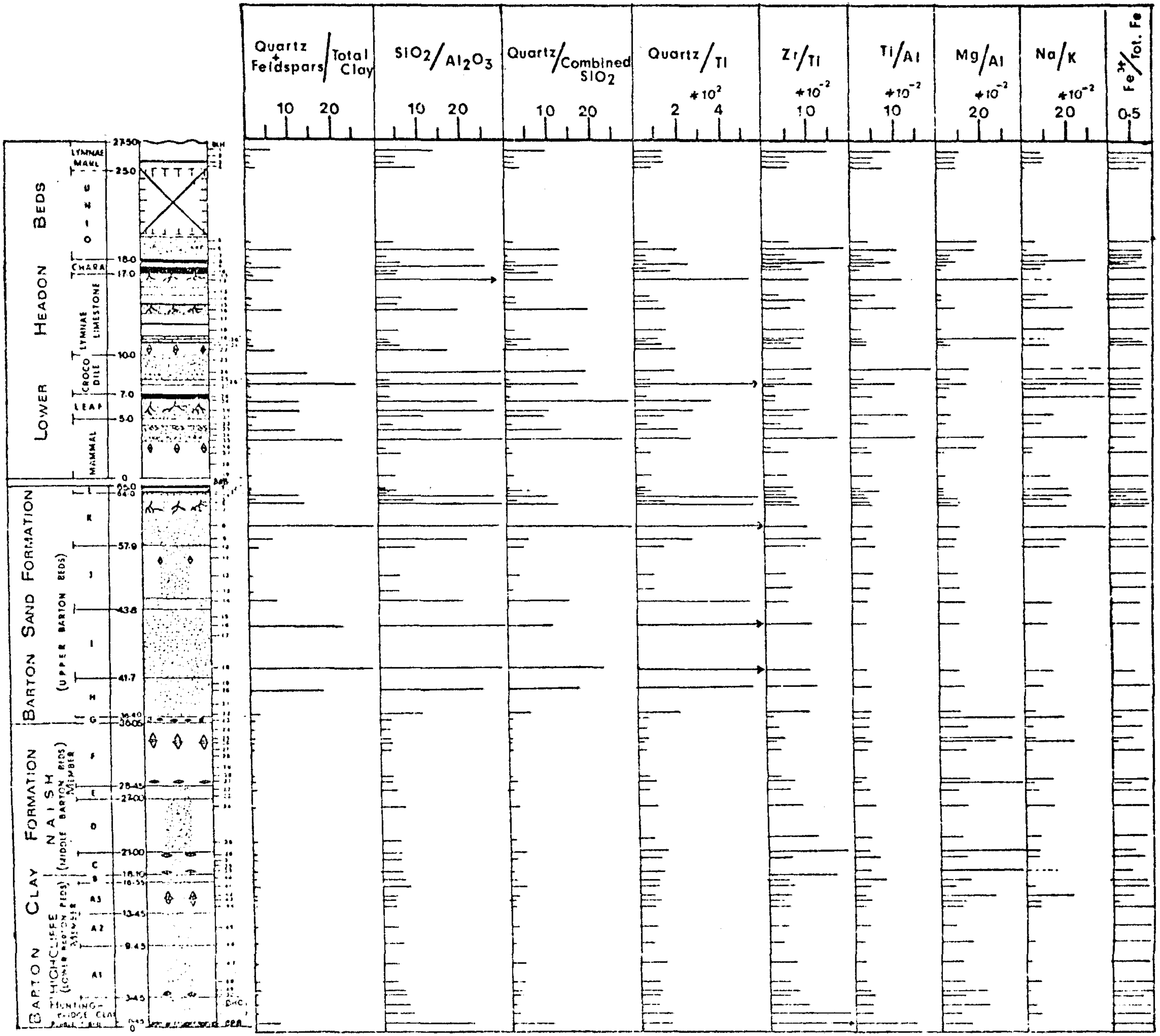


Fig. 21b : Stratigraphical Variation of some Compositional Parameters; Alum Bay-Heatherwood Point, Isle of Wight.

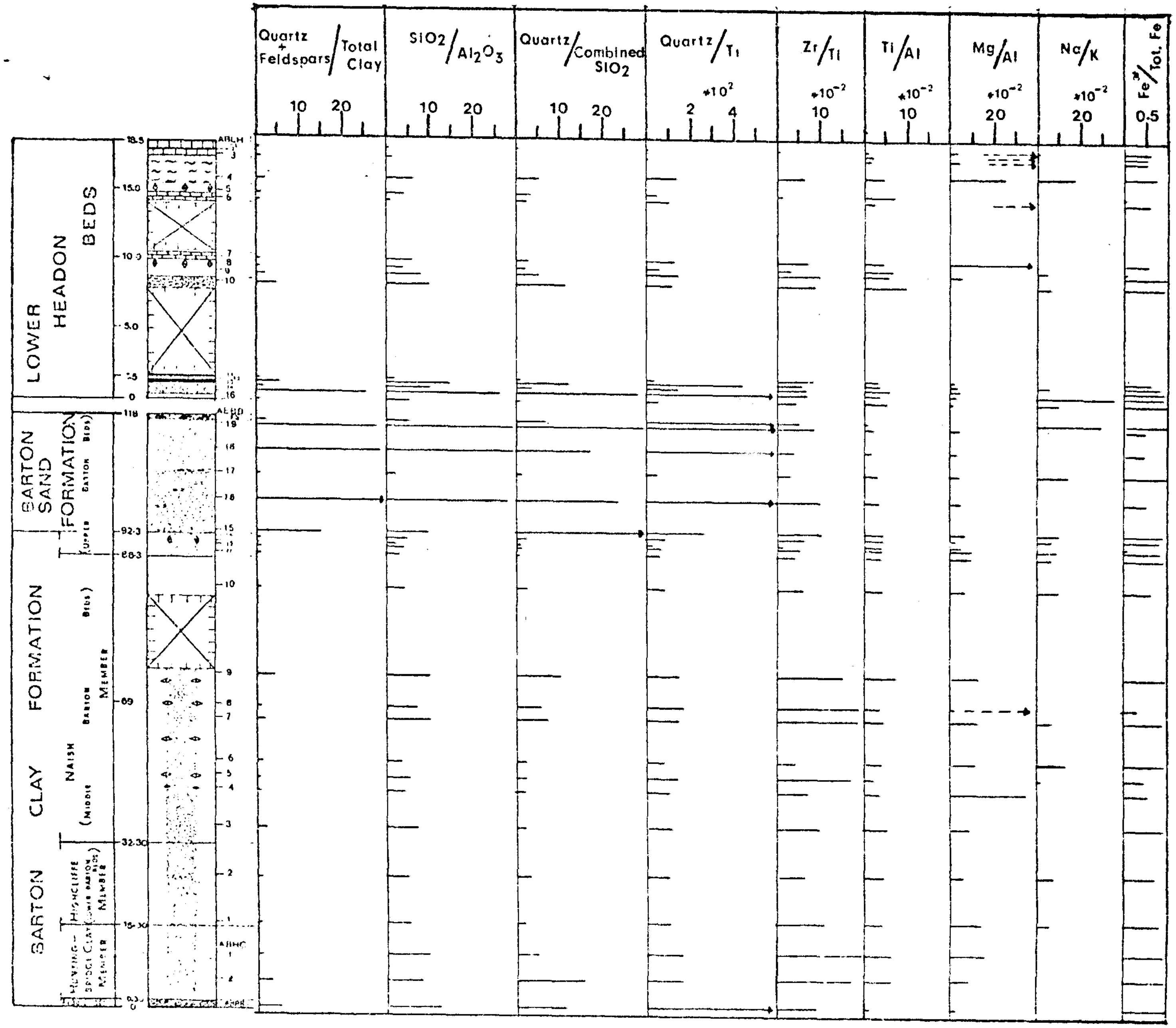


Fig.21c :Stratigraphical Variation of some Compositional Parameters; Whitecliff Bay, Isle of Wight.

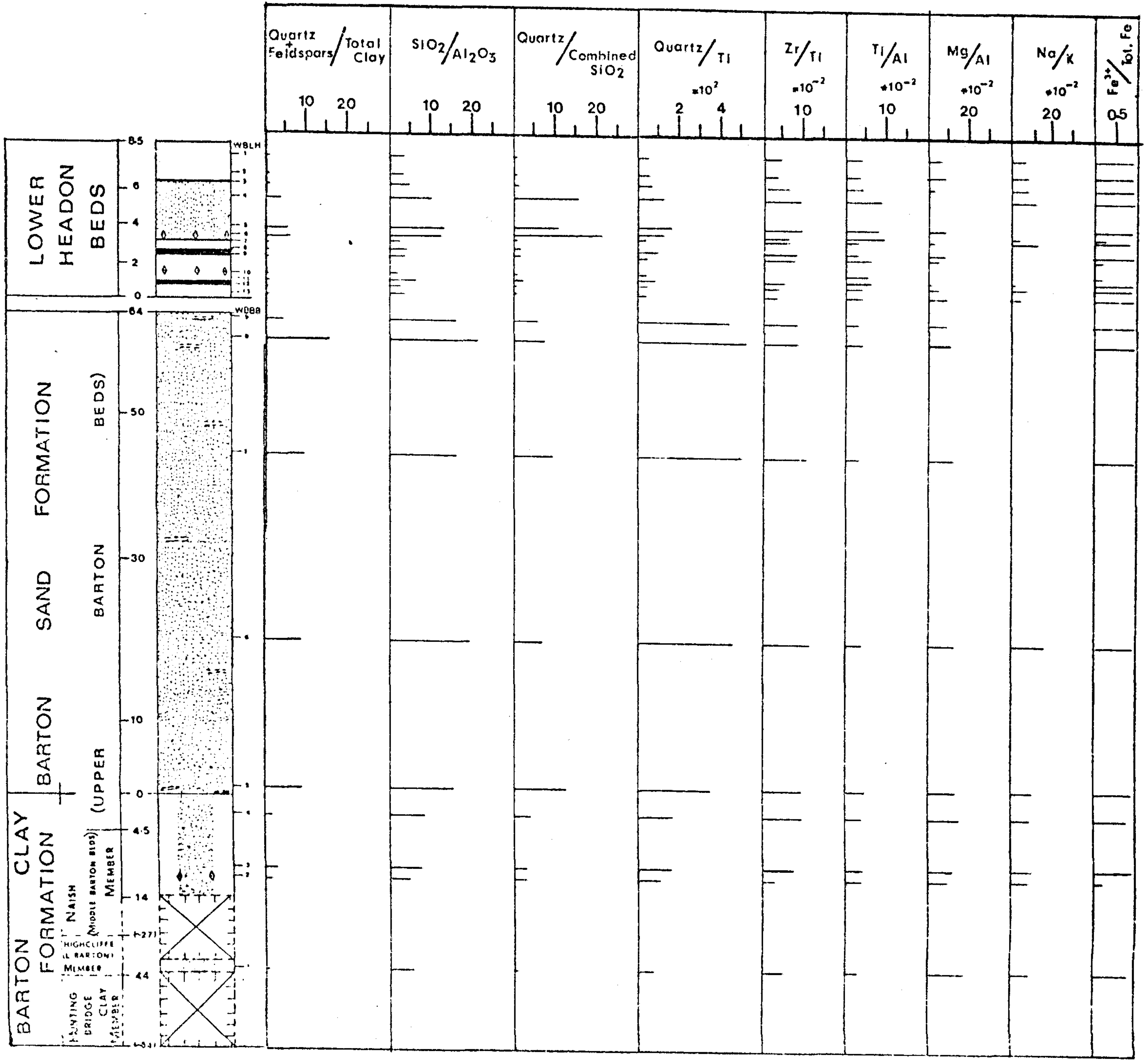


Fig.22a: Histogram Plot of(Quartz+Feldspars)/(Quartz+Feldspars+Clays) Ratios For Clastic Upper Eocene Sediments

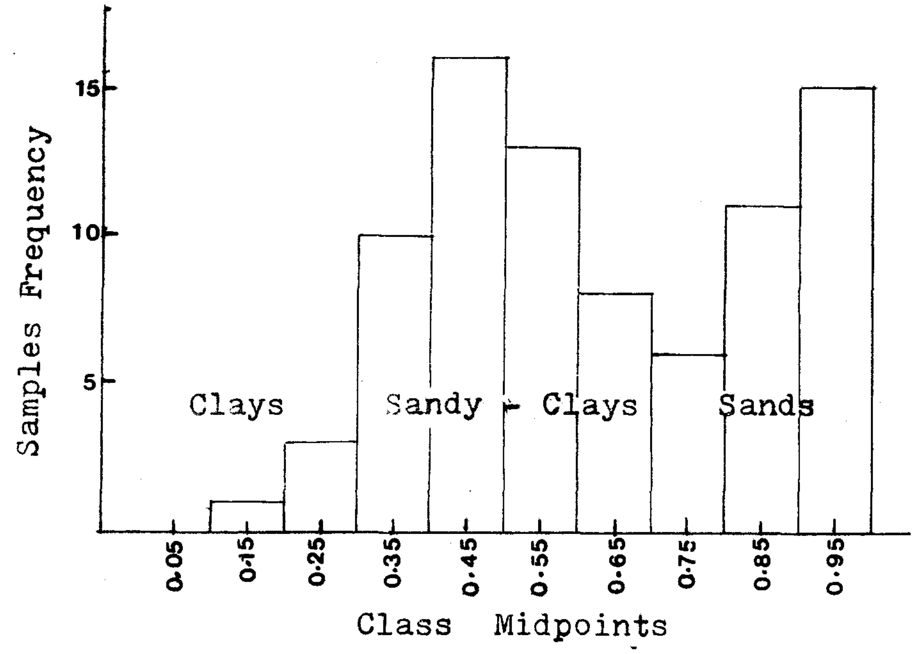
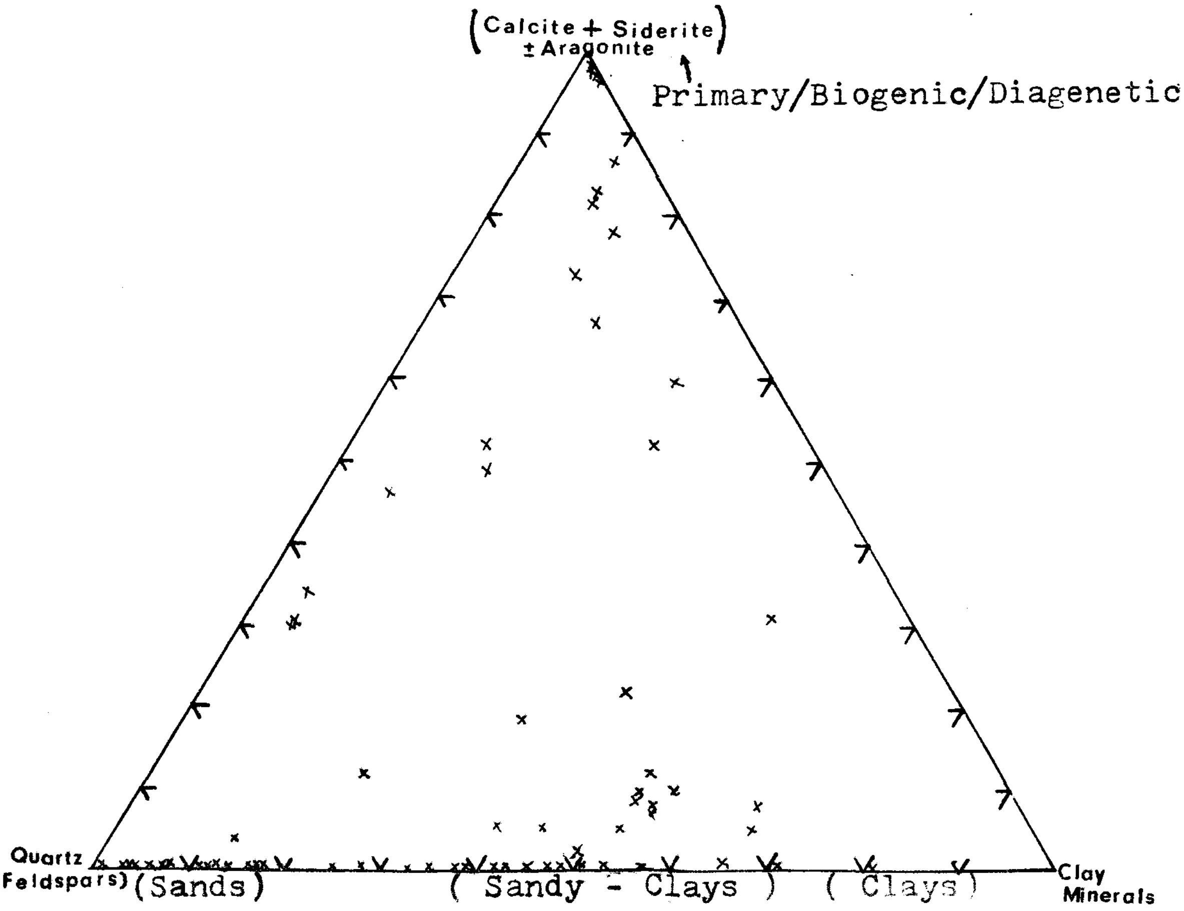


Fig.22b: Triangular Plot of Quartz-Clay-Carbonate Content of Representative Upper Eocene Sediments



to silt-sized, and could have resulted either from long distance transportation or subjection to strong erosion and even several erosional phases. The grains, especially quartz, are generally worn smooth, and sub-rounded to sublspherical in shape. These, also, are attributes of water-borne materials (Krumbein & Sloss, 1951; Pettijohn, 1975) which thus indicate the existence of detrital laden drainages in the Eocene Hampshire Basin, and, hence, humid climatic conditions and active erosions in the source areas.

At the end of the Cretaceous period, England was tilted to the east (Anderton et al., 1978), hence much drainage since Palaeocene times was from west to east. One of the major Eocene drainage channels in southern England was thought to be the 'Solent River' (Jones, 1981; West, 1980). This is believed to have drained exposed complex igneous terrains and pre-Mesozoic meta-sediments and Mesozoic sediments in areas to the south-west and western England and possibly parts of Wales. Other drainage could have occurred over Mesozoic rocks to the north in the English Midlands (Walder, 1964), the Upper Cretaceous Chalk to the north and east (Gilkes, 1966), and the metamorphic complexes to the south in Brittany and France (Blondeau & Pomerol, 1968). Derivation of detritus via the transgressing Barton Sea has also been advocated by Blondeau & Pomerol, especially for some of the garnet, zoisite, epidote contents of the heavy mineral assemblages.

Derivation from nearby sources is very probable and most likely substantial. This would particularly be the case for the pebbles, and perhaps the sands as well. The petrology and fossil contents of the pebbles would suggest a primary Upper Cretaceous Chalk source; whilst the smallness of the pebbles in the Barton Sand at Alum Bay would further suggest probable derivation from re-worked nearby older Tertiary sediments. Plint (1982) has studied pebbles in the underlying Bracklesham Group and has suggested derivation from Chalk forelands located close to the depositional sites and undergoing active erosional phases. Curry (1964) has also suggested Chalk sources for the pebbles in the Boscombe Sands in Dorset. He found a Maestrichtian age foraminifera in one of the pebbles, and suggested derivation from contemporaneously exposed Chalk to the south in the English Channel. Such a source could have been one of the 'inverted Mesozoic basinal deposits' in the area of the English Channel at the end of the Cretaceous (Ziegler, 1982). A probable nearby Tertiary source, suggested by Hooker (1977), could be deposits equivalent to the pebbles described by Huddleston (1902) from underneath the early Upper Eocene (Auversian?) Creechbarrow Limestone Formation (Preece, 1980) in Dorset.

The rarity of chert pebbles in the succession may be due to limited or lack of exposure of older, chert-rich sediments in source areas for the Upper Eocene Hampshire Basin. The dominant chert-rich sediments in southern England are the Cretaceous age 'Greensands'. There is no evidence of these being exposed in Hampshire and Dorset during the Tertiary period. There were, however, some exposures in eastern Devon in south-west England (Isaac, 1981, 1983), and perhaps in the Weald area of south-east England (Jones, 1981). Well-evolved tropical-like palaeosols were reported (Isaac, op.cit.) developed in the exposures in Devon. The pedogenesis, dated as Early Tertiary (pre-Upper Eocene), also affected the Chalk and Cenomanian Limestone deposits. Isaac (1983) further inferred that the re-working of these weathering profiles provided material for contemporaneous fluvial gravels that include the Buller's Hill Gravel and Aller Gravels (Hamblin, 1973; Edwards 1973) in south-west England. Perhaps they were also the source of chert pebbles that Reid (1899) reported present in the early Eocene 'Bagshot Beds' in Dorset. The probable 'Greensands' exposure in the Weald area could have provided the chert pebbles reported in the 'Bagshot Beds' of the London Basin (Dines & Edwards, 1929).

4.7.3 Sedimentological Significance

Generally, sandy sedimentation commonly occurs closer to source areas and drainage outlets, whilst finer-grained deposits are more common in deeper waters and/or low energy regimes. A classical example of seaward-fining shelf deposition is that of the Niger Delta in Nigeria (Oomkens, 1974). In non-marine environments, current turbulence is often high and sandy deposition is greater in river channels; whereas low energy conditions and deposition of finer-grained materials characterise ponds, lakes and sheltered water bodies in the coastal plains. The marine deposits then grade from sands in estuaries and the near-shore shelf to clays in deeper parts of the shelf.

In the presently studied succession, the sandy pebble beds at the base of the succession would be transgressive deposits of high energy regimes, i.e. coastlines with strong longshore currents. Many authors, including Gardner et al. (1888) and Plint (1982) have made similar deductions for the pebble beds. The succeeding Barton Clay deposits represent periods of substantial supplies of mud-laden detritus to the transgressing Barton Sea. The richness in quartz of the clay deposits not only indicates a high quartz supply, but also poor sorting and deposition close to points of detritus discharge. The rate of sedimentation is not likely to have been high because rapid sedimentation would not have facilitated the glauconitisation that was extensive in the Barton Sea. In fact, Odin et al. (1978), from radiometric dating of glauconies in north-west Europe Tertiary sediments, have calculated a more or less uniform sedimentation rate of 2·5 cm/1000 yrs for the Palaeogene Hampshire Basin. This sedimentation rate is within the 2-4 cm/1000 yrs obtained for most recent sediments (Davies et al., 1977). It is, however, a very low rate compared with the several tens and hundreds of centimetres per thousand years that typify some ancient and recent deposits, examples of which are listed in Füchtbauer (1974). These are mostly shoreline-nearshore deposits and include the Lower Freshwater Molasse of southern Germany ($\sim$ 55 cm/1000 yrs) and shallow marine deposits near the Mississippi Delta, U.S.A. ($\sim$ 300 cm/1000 yrs).

Horizons with $>$ 60% quartz content in the Barton Clay would represent deposition when either the detritus became less muddy and/or minor tectonic movements caused the eustatic fall of the sea-level with a consequent increase in current energy. In fact, there is evidence of current turbulence in the Barton Sea. This has caused re-working of fossil shells into drifts and pockets, especially in the succession at Barton.

The change to sand sedimentation in the late phase of the Barton Sea would have been consequential on changes of physical processes at the source areas and depositional sites. The Barton Sand is regarded as shoal-bar or barrier sand deposited in the late shallowing phase of the Barton Sea (Curry, 1965; Murray & Wright, 1974). Like barrier sands in the coastal plain of south-east U.S.A., the Barton Sand is a highly mature quartz-sand type deposit (cf. Pettijohn et al., 1972). That sand type is believed to be formed from largely re-worked older sand deposits, with attendant strong energy conditions effecting good sorting (cf. Leeder, 1982). There are many Jurassic and Cretaceous sandstones in the region bordering the Hampshire Basin, as well as intrabasinal Palaeocene-Middle Eocene sand deposits that could have supplied the quartz-rich detritus for the Barton Sand. But these probable source rocks would also have been part of the sources of detritus for the other clastic sediments in the Upper Eocene succession, including the Barton Clay and the 'Lower Headon Beds'. No significant change of sources can be deduced from the heavy mineral assemblage (Blondeau & Pomerol, 1968) and clay mineralogy (Gilkes, 1966; present study - Chapter 3) of the succession. So other factors must have been involved rather than wholesale changes of detritus source.

The climatic factor, or vegetation in particular, could have been one of such factors. This probably affected the erosion and drainage of the source area. Within any particular climatic region, erosion is often minimal in low-lying, highly vegetated areas (Holeman, 1968). Geomorphological reconstructions of southern England (i.e. Jones, 1981) have shown that much of the area bordering the Hampshire Basin to the west and north was largely lowland with < 400m relief. Abundance of vegetation, at least in areas immediately bordering the depositional sites, has been established from several floral studies, including those of Chandler (1960, 1961), Edwards (1967), Fowler _et al._ (1973) and Collinson _et al._ (1981). The vegetation was predominantly an aquatic and water-loving assemblage typical of low-lying, warm humid climatic regions. There might have been an increase in the vegetation abundance in the latter half of the Upper Eocene. The vegetation bloom was perhaps facilitated by an increase in relative warmness and humidity of the climate, which, in the Eocene southern England has been shown to be deteriorating from tropical-like to sub-tropical climatic types (Daley, 1972, Collinson _et al._, 1981). In fact, Hubbard & Boulter (1983) have found, from palynological data, that the late Upper Eocene in southern England corresponds to a warm episode in the deteriorating Tertiary climate. The increased vegetation could thus have reduced the scale of erosion, and hence the amount of mud transported in run-off, in the source areas to the late Barton Sea.

Other factors that could have influenced the Barton Sand deposition occurred at the depositional sites. As mentioned earlier, strong energy conditions would have prevailed. Indeed evidence of deposition in shallow waters, close to the mean sea level, is provided by numerous clay-like burrows of the crustacean, _Ophiomorpha nodosa_, described by

Edwards (1967) and Daley & Edwards (1973). The strong energy conditions had allowed deposition of small flint pebbles in the Barton Sand at Alum Bay. These pebbles would strongly suggest re-working from older pebble-containing Tertiary sediments with the discharge of the transporting stream being in the vicinity of Alum Bay.

In fact, the peculiarity of depositional conditions at Alum Bay has apparently culminated in the contemporaneous exposure of the Barton Sand and development of the acid red-yellow podzol palaeosols. The pedogenic conditions have significantly caused the dissolution of much of the silicate minerals, particularly the feldspars, and enrichment of kaolinite. These are discussed further in Chapters 5 and 16.

The non-marine sediments succeeding the Barton Sands also comprise sands, clayey sediments and limestones. The sands could have accumulated as bed-load deposits in river channels, whilst the green clays and lignitic clays would have accumulated in lower energy settings away from the channels. Sediment accumulation was greater (∼ 30m) on the mainland than (16-20m) on the Isle of Wight. This could be due to the fact that much detritus came from areas to the west, and that lakes or ponded waters occur more on the Isle of Wight. Palaeo-environmental reconstructions from ostracods (Keen, 1977), molluscs (Edwards, 1967) and plant matter (Chandler, 1961, Fowler et al., 1973) have indicated low-lying coastal plain environments of non-marine deposition during Upper Eocene times. The mini-environments possibly included sluggish rivers, ponds, lakes, swamps and brackish lagoons.

4.8 Summary

The detrital composition of the Upper Eocene sediments of the Hampshire Basin consists of quartz >⩾ clays >⩾ potassic feldspars > sodic feldspars, heavy minerals and flint pebbles.

The clayey sediments are mostly quartz-rich. Their quartz contents are higher than the average composition of clays and shales. They are very silty or sandy. True clay deposits, with > 50% total clay contents, are few, the important one being the upper part of the Naish Member of the Barton Clay (Middle Barton Beds E & F of Burton, 1933) at Barton. This horizon is probably the only true offshore deposit in the Upper Eocene succession. The clayey sediments represent deposition during the supply of muddy detritus. Those in the 'Lower Headon Beds' are more likely deposits of low energy settings in flood-plain environments.

The sand sediments are almost wholly composed of quartz, with feldspars and clay minerals occurring in small ($<$ 20%) quantities. They can be regarded as well-sorted, mature, quartz-sand types. They possibly represent deposition during palaeoclimatic changes with increased vegetational cover of the source areas, but with attendant decrease in erosion and derivation of less muddy detritals. The shallowness of the water bodies, particularly in the late, shallowing phase of the Barton Sea, could also have facilitated current-sorting of the detritus.

The flint pebbles are much more high-energy beach materials; their foraminiferal assemblage (tenuously identified) would suggest Chalk sources, probably exposed intrabasinally. Re-worked nearby older pebble deposits could possibly account for the small, smoothly-worn flint pebbles in the Barton Sand at Alum Bay. A chert pebble was found in the pebble bed at Highcliffe; its source is, however, difficult to establish. It might have been derived from distant localities, as there is little evidence of exposures of chert-containing Mesozoic sediments in areas close to the Hampshire Basin during the Tertiary times. Lack of nearby chert sources may thus account for the rarity of chert pebbles in the studied Upper Eocene succession of the Hampshire Basin.

CHAPTER 5

CLAY MINERALOGY

5.1 Introduction

The clay mineralogy of the Upper Eocene succession in the Hampshire Basin has been studied by Blondeau & Pomerol (1964) and Gilkes (1966). The authors found the clay assemblage to be composed of kaolinite, illite and montmorillonite. In addition, Gilkes observed traces of chlorite in the marine sequence; and, by using electron microscopy, identified halloysite in samples from the non-marine sediments at Whitecliff Bay. In the present study, a more extensive survey of the clay mineralogy of the Upper Eocene sediments was carried out, using X-ray diffraction techniques. For the first time, the mixed-layer content has been estimated, and the relative structural disorder (or crystallinity indices) of the clay minerals deduced. The derivation of the clay mineral assemblage has been assessed in the context of the probable weathering conditions prevailing in the source areas, whilst possible imprints of sedimentological and/or environmental factors on the phases abundance have also been considered.

5.2 Review of Clay Minerals

The term 'clay' in geology has many meanings. It is used physically as a particle size term; and mineralogically for hydrous layered lattice phyllosilicates collectively called clay-minerals (Mackenzie & Mitchell, 1966). In the commonly used Udden-Wentworth size grade scale, clay-sized particles are defined as less than 4 μm and can be present in any rock. The most common clay-sized materials in sediments include anatase, crystalline and amorphous aluminium oxides and hydroxides, iron oxides and hydroxides, silica, organic matter and, of course, the clay minerals. Although clay minerals usually belong to the large family of phyllosilicates, some phases are chain-structure silicates. There are numerous works on clay minerals describing their identifications, properties, genesis, occurrences and uses. The literature on these is very extensive; no brief review of clay minerals, such as that attempted below, can complately and satisfactorily elucidate all aspects of knowledge on them.

i) Structure

Structurally, clay minerals generally consist of tetrahedral sheets with compositions of $T_2O_5(OH)$; octahedral sheets with a composition between $M_2(OH)_6$ and $M_3(OH)_6$, and sometimes with interlayered materials (Bailey,1980).

T, the tetrahedral cations, are mostly Si^{4+} but also Al^{3+} and Fe^{3+}, whereas M, the octahedral cations, can be divalent (Mg^{2+}, Fe^{2+}, Mn^{2+}, etc.) or trivalent (Al^{3+}, Fe^{3+}, Mn^{3+}, etc.). The linking of one tetrahedral and one octahedral sheet would give 1:1 layer-structures; whilst two tetrahedral and one octahedral give 2:1 layered structures. Electrostatic imbalances in the structures resulting from cation substitutions in the sheets are often neutralised by various interlayer cations or molecular groups. In the basic structural unit, there are three octahedral coordination sites. Where all those are filled, the sheet would be trioctahedral; whereas the leaving of one vacant site will result in a dioctahedral sheet. The structure of clay minerals has been dealt with by many authors, including Grim (1968), Grimshaw (1971) and Brown & Brindley(1980).

ii) Nomenclature

The problem of classifying clay minerals is enormous. There have been numerous attempts at classification by the AIPEA Nomenclature Committee or by the IMA Commission on New Minerals and Mineral Names, but none has proved completely satisfactory. The most recent classification, contained in Bailey (1980), is based on layer type (1:1 or 2:1), layer charge (net charge per unit formula) and the octahedral sheet type (trioctahedral or dioctahedral). Eight groups have been defined. These are the Serpentine-Kaolin; Talc-Pyrophyllite; Smectite; Vermiculite; Brittle Mica; Chlorite; Mica; and Sepiolite-Palygorskite. Detailed considerations of the mineral species in the various groups are contained in Brindley & Brown (1980). In the present study, clay minerals of major importance encountered included kaolinite, the smectites, and the micas (illite, glauconite-mica). Others include chlorites, interstratified clay minerals, and perhaps halloysite.

iii) Genesis

Most information on clay mineral genesis is widely scattered through the literature, although reviews are given by Grim (1968), Millot (1970) and Velde (1977). Most clay minerals are formed in nature during chemical weathering of rocks and pedogenesis at surface or near-surface conditions. Considerable amounts are also formed by authigenesis at sediment/water interfaces; diagenetic alteration or transformation during burial; and alteration and authigenesis associated with hydrothermal and/or metasomatic conditions.

The most important environmental factors influencing surficial clay mineral formation are rock-type, climate (temperature, precipitation, evaporation and vegetation), topography, and surface and sub-surface drainage. Also of major importance is the length of time over which the above factors operate. Formational factors in water bodies include pH, Eh, salinities and concentrations of dissolved ions and colloidal material. Sedimentological conditions, particularly rate of sediment accumulation and current energy or turbulency, are also important.

iv) The Distribution of Common Clay Minerals

Illite, montmorillonite, chlorite and kaolinite are the common clay minerals in sedimentary rocks in the earth's crust; the other clay species are more restricted in extent and abundance. Consideration of phases of relevance to the Upper Eocene sediments under study is as follows:

a) Illite: Illite is a 2:1 layered, dioctahedral, potassic and aluminous mica-like mineral. Illite constitutes 26-55% of the total clay minerals in modern oceanic sediments (Blatt et al., 1972); being more abundant in areas adjacent to temperate and semi-arid continental areas. In the weathering zone and shallow surface waters where $SiO_2/Al_2O_3 > 3$ and Mg^{2+} concentration is low but K^+ is abundant, authigenic formation of illites may occur (Millot, 1970). Such illites are believed to be common in the Eocene lacustrine deposits in France (Millot, 1970) and Belgium (Porrenga, 1968). Illites in soils may be degraded by the leaching of their interlayered K^+. Progressive degradation of illite could result in its transformation to vermiculite, interstratified clays and montmorillonites (Fanning & Keramidas, 1977).

b) Montmorillonite: This is the commonest member of the smectite group. Its structural units are liable to substantial cation substitution, particularly those of Mg^{2+} for Al^{3+}, Al^{3+} for Si^{4+}, and Fe^{3+} and Fe^{2+} for Al^{3+} (Grim, 1968; Weaver & Pollard, 1973). These, thus, generally result in net negative charges on their structures; charges that are usually balanced by a small number of interlayered cations, commonly Na^+ or Ca^{2+}, and also Mg^{2+}. Water absorption into positions between structural layers is substantial, usually amounting to between 1 and 3 layers of water molecules (Grim, 1968; MacEwan & Wilson, 1980). This results in basal spacings of between 10 and 21Å, depending on the number of water layers. The replacement of water layers by various intercalating compounds and/or their removal at elevated temperatures (100-200°C) have been widely employed in the characterisation of montmorillonites, and smectites in general (Brown & Brindley, 1980).

Montmorillonite constitutes between 16 and 53% of total clay minerals in modern oceanic sediments (Blatt et al., 1972). It is the dominant mineral in bentonites. The formation of the mineral is favoured in weathering environments where leaching is less intensive, drainage is limited, and where $SiO_2/Al_2O_3 > 2$ and Mg^{2+} is abundant (Millot, 1970; Lukashev, 1972). Such weathering is common in mild, humid sub-tropical and temperate regions (Carroll, 1970). Montmorillonites are major products of aerial weathering or submarine alterations of basic and pyroclastic rocks, and are accompanied by other typical minerals such as allophane and zeolites (Perry, E.A.Jr., 1975; Kastner, 1979). In fact weathering and devitrification of volcanic ash is believed to be the main mode of formation of smectites that predominate in bentonites (Grim & Guven, 1978) and fuller's earths (i.e. Young & Morgan, 1981) In alkaline surface water, with conducive ionic concentrations of Si^{4+}, Al^{3+} and Mg^{2+}, authigenic montmorillonite also forms extensively (Millot, 1970; Velde, 1977); often in association with fibrous clays, sepiolite and attapulgite.

Montmorillonites in soils may be extensively leached, resulting in poor crystallinity or alteration into kaolinite and/or mixed-layered clays (Altschuler et al., 1963). On transportation into oceanic waters, Mg^{2+} may be absorbed into structurally degraded montmorillonite, leading to structural reconstitution or, if absorption is extensive, transformation into mixed-layered phases (Dunoyer de Segonzac, 1970). Transformation of montmorillonite into illite through interstratified illite-smectite phases would also occur in the realms of deep burial diagenesis (Dunoyer de Segonzac, 1970).

c) Kaolinite: Kaolinite is a 1:1 layered clay and is considered as the most stable clay mineral phase at surface conditions. Its structure allows very little substitution; hence its lack of variability. It has, however, been reported as containing traces of Fe, Ti, Mg, Ca, K and Na, mostly as coating impurities, but rarely as structural incorporation (Weaver & Pollard, 1973; Sayin & Jackson, 1975).

Kaolinite predominates in the non-marine flint clay facies (Keller,

(1982) but only constitutes 8-20% of the total clay minerals in modern oceanic sediments (Blatt et al., 1972). It is most common in oceans of tropical regions; and is particularly abundant near-shore because of its differential segregation from the 2:1 layered clays due to its larger size or greater ease of flocculation (Dunoyer de Segonzac, 1970; Potter et al., 1980). Kaolinite is a major product of weathering and pedogenesis in warm, humid tropical, sub-tropical and temperate regions, particularly where drainage is moderate to good, and hence alkalis and alkaline earths are removed, and where the SiO_2/Al_2O_3 ratio is about 2 (Chukrov, 1968; Millot, 1970; Lukashev, 1972; Dixon, 1977). Soil kaolinites are mostly poorly crystalline and structurally disordered; but their transformation only occurs in deep burial diagenesis where, if conditions are alkaline, they transform to micas and chlorites; or, if acidic conditions prevail, to dickite and nacrite (Shutov et al., 1970; Dunoyer de Segonzac, 1970).

Halloysite, which is of the same 1:1 lattice type as kaolinite, is much disordered structurally and contains higher water contents (Honjo et al., 1954; Chukrin & Zvyagin, 1966). The mineral occurs in two forms, the fully hydrated 10Å halloysite, and the less hydrated 7Å halloysite (Churchman & Carr, 1975; Brindley, 1980). The mineral mostly assumes tubular, lath-like or spherulitic morphologies (Bates et al., 1950; Sudo & Takashashi, 1956). Occasionally, tabular forms have also been reported (e.g. Santos, 1966). Because of its rolled-up form and high structural disorder, the diffraction reflections of halloysite are mostly broadened, and the recognition of the mineral in the presence of large amounts of platy kaolinite is very difficult (Brindley et al., 1963). The presence of halloysite is best established by a combination of various procedures, including X-ray diffraction, electron-microscopy and chemical treatments, such as KAc intercalation (Wiewora & Brindley, 1969).

Halloysite can form in similar conditions to kaolinite, and particularly where leaching by acids produced from altered minerals, such as pyrite, occurs (Dixon & McKee, 1974). Halloysite may transform to kaolinite with ageing and during early diagenesis of sediments (Keller, 1977; Calvert et al., 1980).

d) Chlorite: Chlorites have a complex structure of layered tetrahedral, octahedral and brucite $[Mg(OH)_6]$ layers (Bailey, 1980).

Substitution of Al^{3+} for Si^{4+} and Fe^{3+} and Al^{3+} for Mg^{2+} commonly occurs in the structure. Low-temperature authigenic chlorites are often iron-rich. These could form, and be stabilised, in water-logged and poorly aerated surface conditions and soils (Rich, 1968). In marine conditions, chlorite may also form by re-constitution of degraded phyllosilicates (Millot, 1970; Biscaye, 1965). Chlorite comprises 10-18% of clays in modern oceanic sediments; being particularly most common in cool, temperate regions where chemical weathering is restricted (Blatt _et al._, 1972). The phase is also not very stable during erosion and transportation; hence it tends to be abundant in rapidly deposited materials, particularly those derived from moderately weathered iron-rich and/or chlorite-bearing older rocks.

e) Mixed-layered Clays: Mixed-layered or interstratified clay minerals are of various types depending on the nature of the layers and the manner of their alternations (random or regular). The commonest mixed-layered phase is illite-smectite; others include chlorite-smectite, illite-vermiculite, vermiculite-smectite, chlorite-vermiculite and kaolinite-montmorillonite. Details of the structure and properties of the mixed-layered phases are contained in the works of Altschuler _et al._ (1963), Reynolds & Hower (1970), Reynolds (1980) and many others.

Mixed-layered clay minerals may form by partial leaching of K^{+} from illite or mica; or of Mg from smectite and chlorite, during weathering and in soils. In sea environments, they might form as a result of incomplete absorption of K^{+} by highly degraded illites, or of Mg by degraded smectite and vermiculite clay phases. They may also form by transformation of other phases, particularly smectites, during burial diagenesis.

5.3 Clay Minerals in the Upper Eocene Sediments of the Hampshire Basin

The clay mineral constituents of the Upper Eocene succession under study are given in Tables 8a-h, and their variation stratigraphically is shown in Figures 23a-c. Details of each phase are as follows.

5.3.1 Kaolinite

i) Abundance: Over much of the succession, kaolinite occurs in small quantities, usually less than 15% of the clay fraction. This is equivalent to $<$ 5% of the bulk sample composition; abundances that suggest the predominance of kaolinite-poor detritus during much of Upper Eocene

Table 8a : Clay Mineralogy of the 'Lower Headon Beds' , Mainland Hampshire.

	% CLAY PHASES					CRYSTALLINITY INDICES *		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
BLH								
1	9	37	15	39		0.43	0.64	0.15
2	14	39	21	25	0.4	0.57	0.57	0.10
3	12	51	12	24	0.2	0.57	0.71	0.09
4	13	43	14	30		0.71	0.71	0.17
5	14	42	18	25	0.6	0.46	0.50	-0.08
6	12	37	20	30	0.5	0.50	0.64	0.12
7	12	46	18	25	0.4	0.53	0.57	0
8	13	44	18	25		0.50	0.36	0.09
9	13	42	16	29		0.43	0.36	0.16
10	12	49	16	24		0.50	0.36	0.02
11	13	21	10	56		0.64	0.57	0.14
12	12	33	15	40		0.50	0.57	0.02
13	11	43	13	33		0.5	0.64	0.11
14	14	39	13	24		0.61	0.64	0.05
15	22	30	23	25		1.50	1.14	-0.07
16	12	42	19	28		0.50	0.57	0.04
17	11	43	17	24		0.50	0.57	0.02
18	10	57	15	18		0.43	0.57	-0.15
19	13	51	18	19		0.64	0.86	0
20	22	31	21	26		0.93	0.79	-0.1
21	10	64	16	11		0.39	0.64	-0.07
22	10	49	17	23		0.46	0.57	-0.03
23	11	48	17	24		0.50	0.57	0.07
24	14	54	12	19		0.57	0.57	0.03
25	13	53	20	14	0.6	0.50	0.43	-0.28
26	13	43	16	28		0.43	0.57	-0.23
27	14	51	20	16	0.5	0.50	0.50	0
28	18	49	9	23	0.3	0.50	0.39	0.28
29	19	49	9	24		0.50	0.39	0.17
30	19	48	14	19	0.5	0.50	0.36	0
31	20	45	20	16		0.50	0.57	0.11
32	16	51	12	21		0.43	0.39	0.04
33	10	35	17	38		0.50	0.64	0.19
34	12	41	15	33		0.50	0.57	0.12
35	12	31	14	43		0.46	0.46	0.30
36	12	45	15	28		0.57	0.50	0.17
37	7	47	19	27		0.71	0.93	0.07
38	11	49	15	25		0.64	0.79	0.07
39	16	52	12	20		0.53	0.79	0.25

* Indices for Kaolinite is peak width $(2\theta^{\circ})$ at half height of the 7.2Å (001) peak
Indices for Illite is peak width $(2\theta^{\circ})$ at half height of the 10Å (001) peak
Indices for Smectite is the ratio value of 'V/p' of Biscaye (1965).

Table **8b** Clay Mineralogy of the Barton Sand Formation, Barton-on-Sea

	% Clay Phases					Crystallinity Indices		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
BBB								
1	24	27	14	35	0.2	1.10	1.20	0.18
2	10	54	13	23		0.43	0.50	0.39
3	13	34	11	43	0.6	0.50	0.79	0.27
4	10	48	12	31		0.43	0.46	0.20
5	8	71	8	14		0.43	0.71	0.4
6	11	41	13	35		0.43	0.50	0.36
7	16	40	12	33		0.39	0.30	0.34
8	20	42	8	30		0.40	0.43	0.37
9	8	34	10	48		0.32	0.43	0.25
10	10	43	22	26		0.43	0.43	0.33
11	10	38	18	28		0.43	0.47	0.26
12	13	48	17	23		0.43	0.43	0.16
13	11	43	14	31		0.43	0.43	0.21
14	7	37	12	44		0.43	0.45	0.44
15	8	26	15	51		0.43	0.50	0.68
16	10	25	14	52		0.39	0.50	0.60
17	11	25	14	51		0.43	0.43	0.65
18	12	26	11	51		0.39	0.46	0.64
19	8	32	19	41		0.39	0.50	0.59
20	9	31	17	42	0.3	0.43	0.57	0.58
21	5	21	14	60	0.3	0.40	0.43	0.73
22	9	32	18	42		0.39	0.39	0.53
23	12	34	16	38	0.7	0.39	0.57	0.27

Table 8c: Clay Mineralogy of the Barton Clay Formation, Mainland Hampshire.

	% CLAY PHASES					CRYSTALLINITY INDICES		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
BBB								
24	13	35	14	38	0.4	0.39	0.50	0.33
25	13	30	17	41		0.43	0.43	0.26
26	15	42	13	31	0.7	0.39	0.50	0.08
27	13	37	15	36	0.4	0.39	0.46	0.20
28	13	39	18	30		0.43	0.50	0.30
29	10	34	15	42		0.39	0.57	0.42
30	9	28	16	48	0.8	0.36	0.61	0.41
31	8	39	11	42	0.6	0.46	0.71	0.07
32	12	30	16	42	0.5	0.39	0.43	0.30
33	11	32	18	40		0.43	0.57	0.43
34	10	32	16	42	0.3	0.43	0.64	0.40
35	7	34	14	45	0.5	0.43	0.57	0.53
36	5	39	10	46	0.6	0.43	0.57	0.15
37	6	32	14	48	0.5	0.43	0.57	0.32
38	6	34	13	47	0.6	0.39	0.57	0.46
39	5	46	9	42	0.4	0.36	0.71	0.24
40	7	37	10	46	0.3	0.36	0.50	0.49
41	11	43	13	33	0.6	0.45	0.43	0.30
42	15	45	10	30	0.7	0.43	0.43	0.13
43	10	59	8	21	1.4	0.39	0.50	0.15
44	14	53	6	25	0.4	0.39	0.39	0.12
45	15	46	17	22	1.0	0.36	0.36	0.10
46	11	48	11	30	0.5	0.35	0.39	0.13
47	11	38	18	33	0.4	0.36	0.50	0.16
48	9	42	18	32		0.46	0.71	0.20
49	10	42	17	31		0.29	0.64	0.18
50	12	41	16	31	1.1	0.36	0.36	0.19
BHC								
1	7	59	17	18		0.43	0.68	0.16
2	7	53	17	23		0.36	0.71	0.16
BPB								
1	11	45	15	29		0.36	0.50	0.14

Table 8d Clay Mineralogy of the 'Lower Headon Beds', Heatherwood Point, Isle of Wight

	% Clay Phases					Crystallinity Indices		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
ABLH								
1	21	54	17	9	tr	0.39	0.64	0
2	28	42	15	15	tr	0.51	1.07	0
3	11	51	17	22	tr	0.46	0.79	0
4	19	68	-	13	tr	0.50	0.57	0
5	18	13	53	16		0.50	0.43	0
6	11	15	57	31		0.49	0.61	0
7	7	45	12	36		0.39	0.93	0.17
8	9	49	14	28		0.39	1.04	0.14
9	19	50	8	23		0.50	0.79	0.04
10	16	60	9	16		0.50	0.79	0.08
11	36	64				0.43	0.65	
12	37	63				0.39	0.36	
13	20	80				0.43	0.64	
14	19	63	8	10		0.36	0.5	0
16	14	86				0.39	0.61	

Table **8e** Clay Mineralogy of the Barton Sand Formation and Palaeosols, Alum Bay.

	% Clay Phases					Crystallinity Indices		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
ABBB/FS								
1a	39	54	7			0.36	0.40	
2a	33	58	9			0.43	0.43	
3a	100	-	-			0.25		
4a	100	-	-			0.25		
1b	35	57	7			0.36	0.50	
2b	34	59	7			0.36	0.39	
3b	35	54	12			0.36	0.39	
4b	33	57	10			0.36	0.39	
5b	37	53	10			0.36	0.50	
6b	37	63				0.39	0.43	
7b	35	55	10			0.39	0.43	
8b	41	48	11			0.39	0.43	
ABBB								
19	99	1				0.3		
18	81	19				0.43	0.5	
17	35	49	15			0.39	0.54	
16	50	44	6			0.46	0.57	
15	29	46	9	16		0.36	0.43	0.13

Table **8f** Clay Mineralogy of the Barton Clay Formation, Alum Bay

	% Clay Phases					Crystallinity Indices		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
ABBB								
14	18	47	10	23	3	0.43	0.50	0.08
13	14	49	13	23	3	0.43	0.79	0.14
12	14	46	10	30		0.43	0.86	0.13
11	10	41	10	37	2	0.43	0.64	0.23
10	10	31	9	51		0.50	0.93	0.35
9	10	41	8	41		0.46	0.46	0.52
8	7	43	7	43		0.39	0.50	0.31
7	6	35	5	53		0.39	0.50	0.55
6	8	29	5	58		0.36	0.50	0.60
5	6	42	10	32	2	0.39	0.36	0.14
4	8	47	12	34		0.43	0.64	0.26
3	15	42	10	32	2	0.39	0.50	0.14
2	10	37	9	44	1	0.50	0.50	0.37
1	5	31	6	59		0.36	0.64	0.64
ABHC								
1	9	46	10	35		0.36	0.50	0.52
2	22	65	8	5		0.36	0.64	-0.30
ABPB								
1	50	50				0.32	0.29	

Table 8g Clay Mineralogy of the 'Lower Headon Beds', Whitecliff Bay

	% Clay Phases					Crystallinity Indices		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
WBLH								
1	5	48	14	34		0.36	0.75	0.23
2	10	53	12	25		0.36	0.93	0.10
3	8	32	8	52		0.43	0.64	0.50
4	10	39	13	39		0.43	0.39	0.36
5	12	45	15	29		0.43	0.50	0.40
6	18	57	7	17		0.36	0.36	0.23
7	5	46	15	34		0.46	0.57	0.29
8	8	35	10	48		0.41	0.50	0.43
9	8	45	14	33		0.61	1.21	0
10	7	50	10	33		0.46	1.36	0.12
11	5	32	11	52		0.36	0.64	0.56
12	6	44	13	38		0.41	0.75	0.48
13	2	70	8	19		0.43	1.04	0.15

Table 8h Clay Mineralogy of the Barton Sand and Barton Clay Formations, Whitecliff Bay.

	% Clay Phases					Crystallinity Indices		
Samples	Kaolinite	Illite	Illite-Smectite	Smectite	Chlorite	Kaolinite	Illite	Smectite
WBBB								
9	-	62	-	38		-	1.64	0.48
8	4	38	10	48		0.36	0.79	0.60
7	2	34	7	57		0.36	0.71	0.60
6	3	28	8	60		0.27	0.54	0.67
5	4	34	10	52		0.29	0.86	0.64
4	5	40	10	45		0.36	0.93	0.53
3	7	32	10	52		0.32	0.46	0.54
2	9	42	11	39		0.36	0.46	0.23
1	1	18	8	74		0.29	0.43	0.75

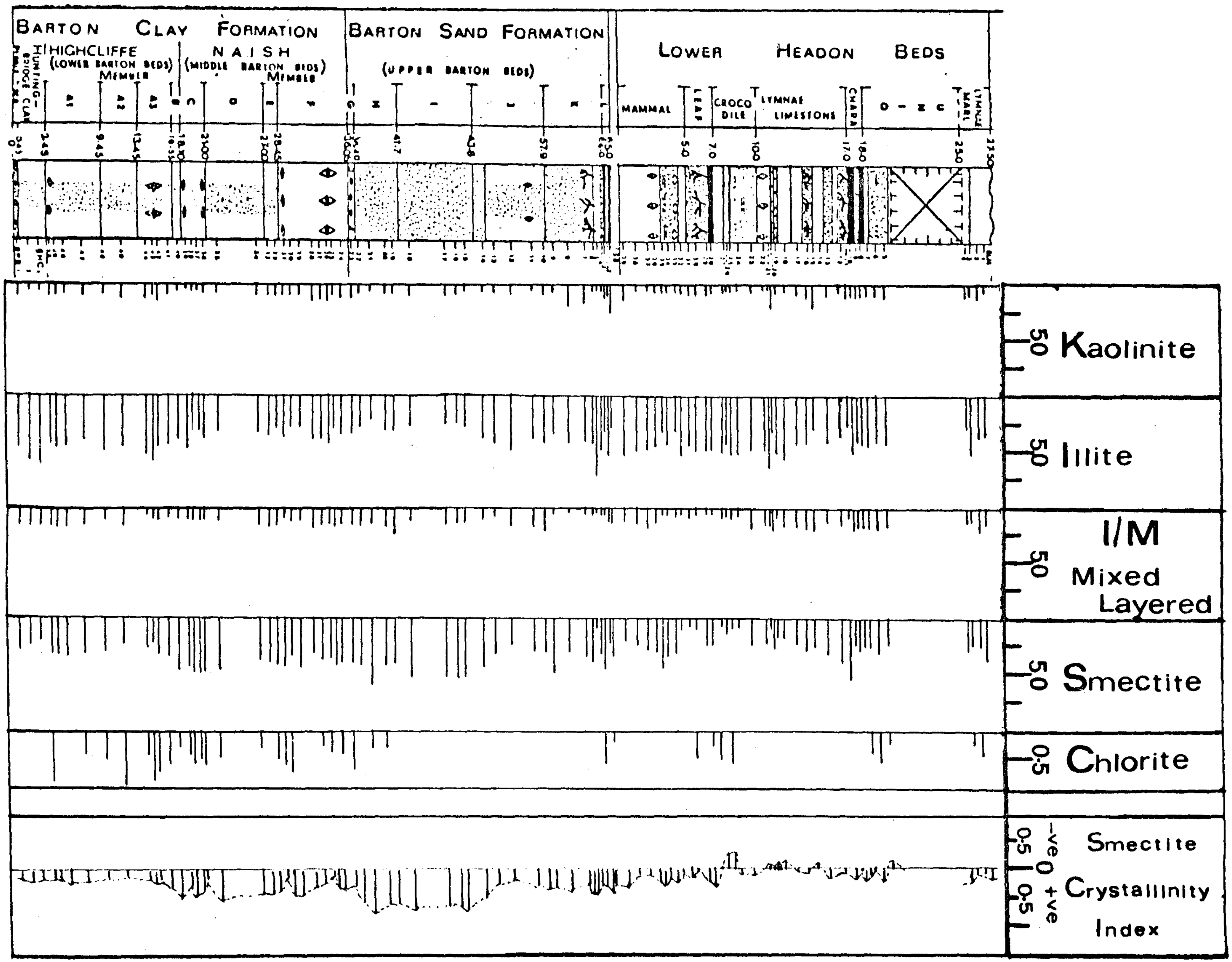


Fig.23a :Stratigraphical Variation of the Upper Eocene Clay Mineralogy; Highcliffe-Milford on Sea, Mainland Hampshire.

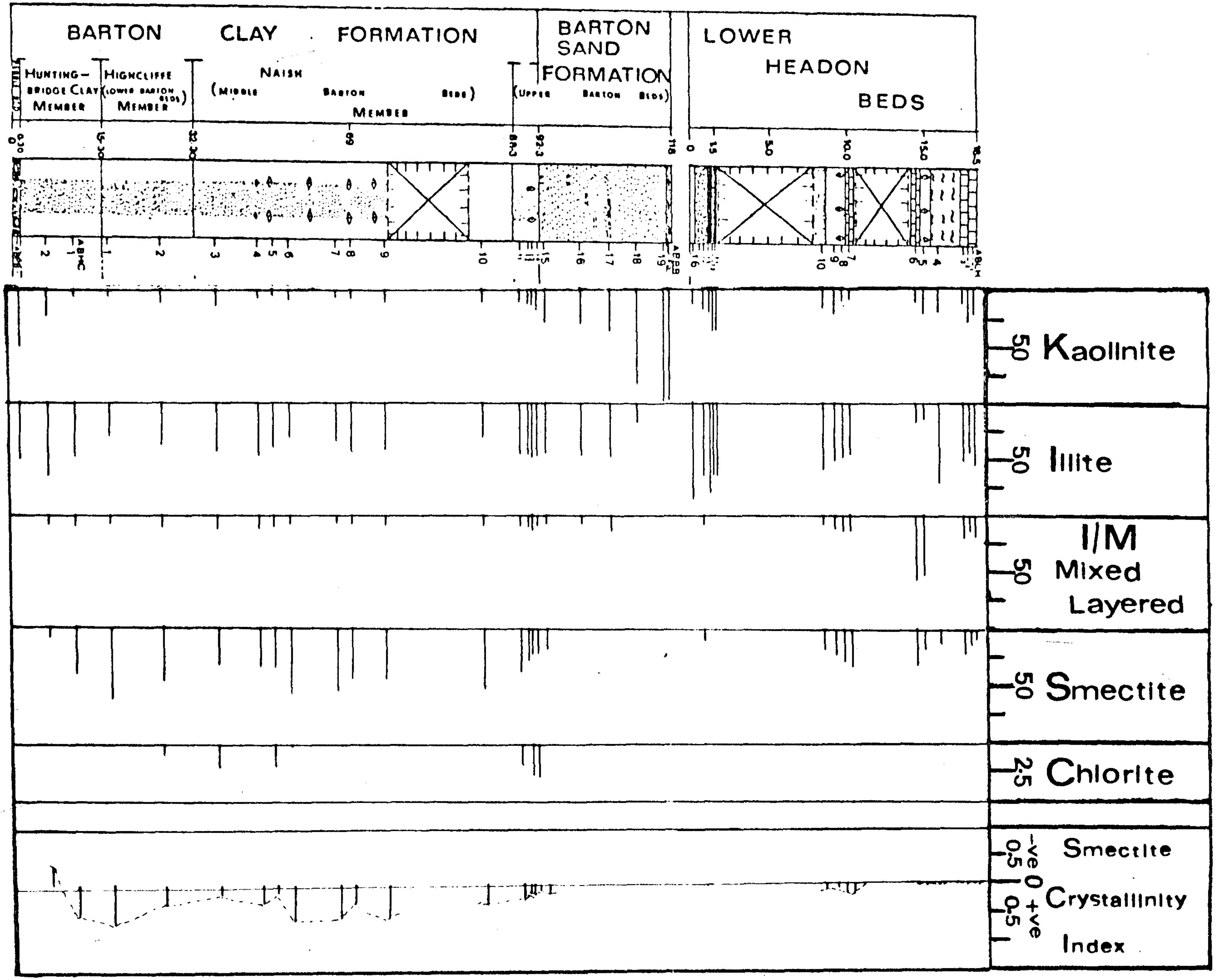


Fig.23b :Stratigraphical Variation of the Upper Eocene Clay Mineralogy; Alum Bay-Heatherwood Point, Isle of Wight.

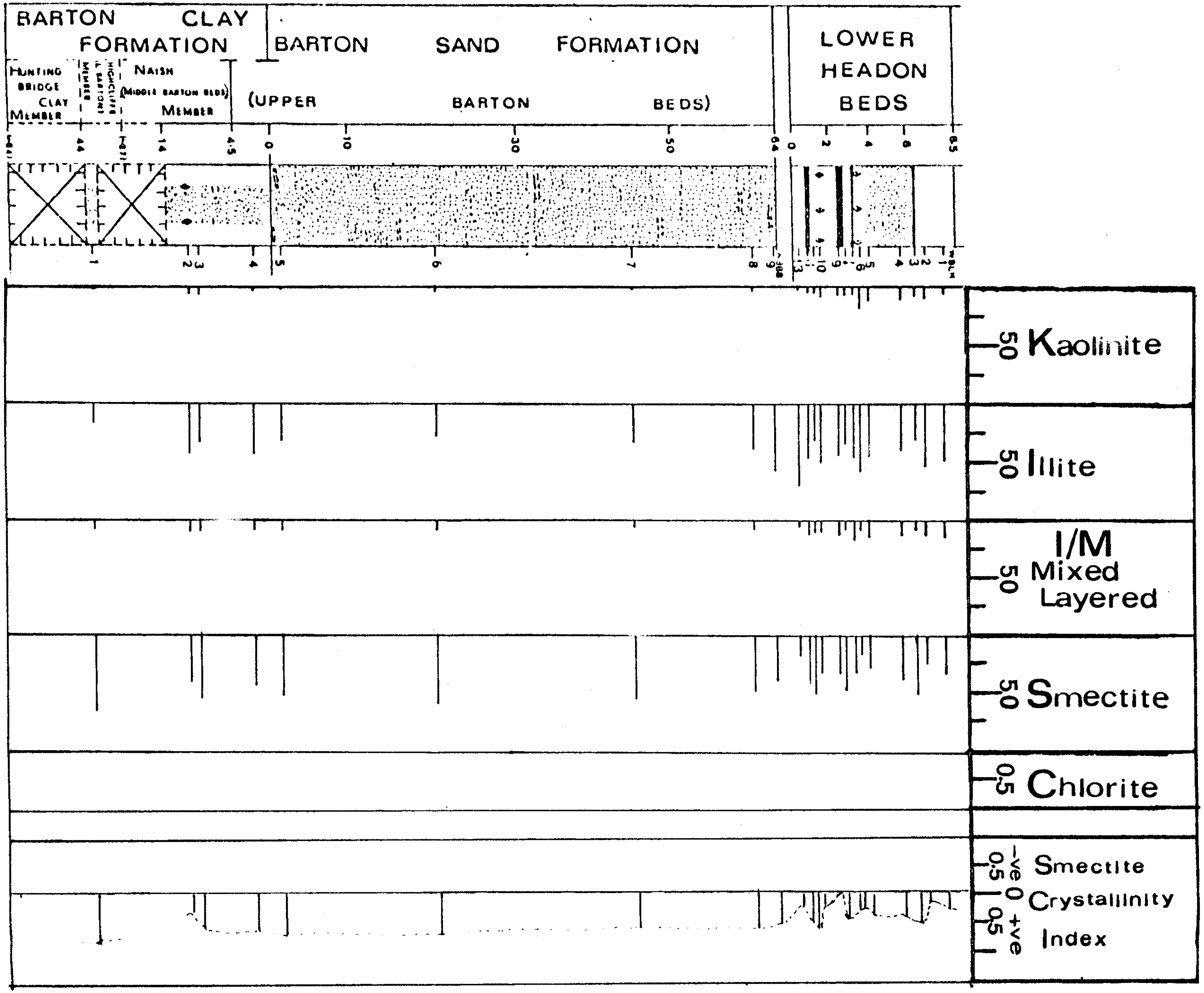


Fig.23c :Stratigraphical Variation of the Upper Eocene Clay Mineralogy; Whitecliff Bay, Isle of Wight.

times. Deviations from this generality, with probable regional sedimentological significance, occur in the succession at Whitecliff Bay, whilst deviations resulting from localised environmental factors occur in the Barton Sand at Alum Bay, and some lignitic horizons at Alum Bay and the mainland.

At Whitecliff Bay, kaolinite occurs in uniformly low, $< 10\%$, amounts. It is in fact absent in the ferruginous clayey-sand at the top of the Barton Sand (see Fig.10a). A westerly located source of the kaolinite coupled with the general tendency of kaolinite to flocculate and settle near-shore (Parham, 1966) could be the cause of the lower abundance of the mineral in the marine succession at Whitecliff Bay compared to the succession at Alum Bay and Barton.

In the lignitic clays, relatively high (20-37%) amounts of kaolinite occur in the clay fractions. This is thought to be reflecting the addition of authigenic kaolinite following penecontemporaneous acidic leaching of silicate phases in the swamp environments in which the lignites accumulated. This is discussed further later.

Substantially high kaolinite enrichment occurs in the pebble bed and the Barton Sand at Alum Bay as a result of acidic surficial and pedogenous processes on contemporaneously exposed parts of the sediments and/or in nearby land areas. Kaolinite constitutes 50% of the clay minerals constituent of the pebble bed, with illite accounting for the remaining 50%. In the Barton Sand, kaolinite increases from 29% at the clayey base through 35% in the pipe-clays to 100% in the palaeosol profile at the top. Actually, two palaeosol (red-yellow podzols/gleysols - Fitzpatrick, 1971) profiles were recognised at the top of the Barton Sand (Fig.6b). These possess different kaolinite abundances. The lower pedounit of Profile A is richer in kaolinite and, in fact, contains specks and a few lenses of kaolinite in its indurated $B2_{ir\&m}$ horizons (Plate 18c,d). The kaolinite contents of the upper unit of Profile A and much of Profile B are uniformly lower, being about 35%. Only towards the base of Profile B is there an increase to about 50% kaolinite.

ii) Crystallinity: The kaolinite peaks are usually slightly asymmetrical and broad at base. The recorded crystallinity indices mostly ranged from 0·3 to $0{\cdot}5^{\circ}2\theta$ Applying the relationships between peak width and structural state given by Wiewora & Brindley (1969), the kaolinite would be regarded as being very poorly crystalline and structurally disordered. This probably suggests that the kaolinite was predominantly derived from moderately weathered sources; similarly disordered kaolinite is commonly found developing in poorly weathered saprolites (Gallez et al., 1975) and in young soil profiles (Calvert et al., 1980; Hughes & Brown, 1979; Eswaran & Bin, 1980).

Higher crystallinity indices of 0·6 to 1·5°2θ are possessed by kaolinites in some lignitic sediments of the sections on the mainland and at Whitecliff Bay (Samples BBB-1, BLH-15 and 12, and WBLH-9). These kaolinites are more disordered than the above and can be regarded as 'highly-disordered' using the nomenclature of Wiewora & Brindley (1969). This could also be one of the manifestations of contemporaneous acidic leaching in the horizons. It is, however, uncertain whether the very broad 7·2Å reflection in some of the lignitic clays (i.e. Fig.10b from BLH-15) is due to halloysite. Gilkes (1966) detected halloysites in sediments of the 'Lower Headon Beds'. But in the present study, investigation by potassium-acetate intercalation (Miller & Keller, 1963) gave no conclusive result for the presence of halloysite. It is, however, possible that the mineral is present but in such small amounts that it cannot be satisfactorily detected by X-ray diffraction in the presence of substantial amounts of platy kaolinite (cf. Brindley et al., 1963).

5.3.2 Illite

i) Abundance: Prior to the consideration of illite abundance in the succession, it should be noted that estimates of illite within glauconitic sediments of the Barton Clay Formation include glauconitic-mica which is structurally similar to illite and cannot be differentiated on the (001) 10Å reflection employed for estimation.

The illite content of the clay assemblage varies widely from about 20% to 80%, with sediments of the Huntingbridge Clay and the 'Lower Headon Beds' mainly possessing the > 50% illite amounts. Considering the clayey sediments alone, the estimated mean values of illite vary from about 56% in the Huntingbridge Clay to 40% in the Highcliffe and Naish Members of the Barton Clay Formation, and 49% in the 'Lower Headon Beds'. These were found to be equivalent to absolute illite contents of about 22% in the 'Lower Headon Beds' and the Huntingbridge Clay; but a lower amount of 17% in the rest of the Barton Clay. A particularly high, 60-86% illite occurrence in the clay fraction of sediments in the lower half of the Lower Headon section on the Isle of Wight is possibly due to the imprint of localised environmental factors on the prevailing regional sedimentological conditions. This is discussed further later.

The illite contents of clays in the sand sediments also vary widely from trace to about 50%. In the sands of the 'Lower Headon Beds' and the Barton Sand at Barton and Whitecliff Bay, the clay assemblage contains substantial amounts ($>$ 30%) of illite. These values are similar to the illite contents of adjacent clayey sediments. However, these illite contents mostly amount to less than 5% of the bulk sands composition. The mineral significantly occurs in trace amounts in the uppermost parts of the Barton Sand at Alum Bay, and particularly in the podzol palaeosol profiles at Heatherwood Point where authigenic kaolinite abounds. Much of the Barton Sand at Alum Bay, however, uniformly contains about 38% illite.

ii) Crystallinity: The crystallinity indices of illite in most of the sediments vary narrowly between $0{\cdot}4^{o}$ and $0{\cdot}6^{o}2\theta$. These, as for kaolinite, indicate very poor crystallinity and the degraded nature of the illite. Even more poorly crystalline illites with indices of $0{\cdot}7^{o}$ to $1{\cdot}6^{o}2\theta$ occur, with highly disordered kaolinite, in the lignitic clays and in most of the sediments with high illite contents. Those in the lignites could have resulted from acidic leaching, as argued for the kaolinite, but those of the latter sediments could be inherited.

5.3.3 Smectite

i) Abundance: The group name 'smectite' has been employed for the expanding $14{\cdot}5\mathring{A}$ expanding phase. Gilkes (1966), using electron diffraction studies, suggested that smectites in the Palaeogene sediments of the Hampshire Basin are montmorillonite. However, in the absence of full chemical analysis, uncertainty remains as to the exact smectite types present.

Clay fractions of the Upper Eocene sediments contain between 20% and 72% smectite, although the mean value is estimated to be around 30%.

There are substantial vertical and lateral variations in the mineral abundance in the succession, possibly as manifestation of differential, sedimentological and environmental conditions. In the mainland sections, the smectite concentration increases from about 20% in the Huntingbridge Clay to about 40% in the rest of the Barton Clay Formation, and 50% in the 'Chama Bed' and 'Bed I' in the lower part of the Barton Sand Formation. The smectite values drop to about 30% in most parts of the succeeding upper parts of the Barton Sand and the 'Lower Headon Beds'. The vertical variations at Alum Bay are more pronounced. With the exception of the Highcliffe and Naish Members of the Barton Clay, which contain substantial amounts (25-58%) of smectites, the mineral occurs in significantly low amounts (trace - 30%) in many parts of the succession compared with the mainland. The mineral was not recorded in the pebble bed at the base of the succession, nor in the greater parts of the Barton Sand and the basal parts of the 'Lower Headon Beds'. This, as discussed later, possibly resulted from acid soil pedogenesis. The smectite contents of the sediments in the succession at Whitecliff Bay are generally higher. Apart from the exceptional 72% smectite recorded for WBBB-1 from lower down the Barton Clay, the clay assemblage in most parts of the marine sediments contains about 50% smectite. However, lower amounts of smectite, 25-45%, occur within the 'Lower Headon Beds'. These amounts are similar to those in equivalent sections on the mainland.

Finally, using the mean smectite values in the clay fractions. the equivalent content of smectite in the bulk sediment composition is about 8% in the Huntingbridge Clay, 16% in the rest of the Barton Clay, and 11% in the clayey sediments of the Lower Headon. Excepting the Barton Sand at Alum Bay with no smectite content, the equivalent amounts of smectite in the bulk compositions is between 2 and 10% of the sand sediments at Barton and Whitecliff Bay, and trace amounts for the limestones at Heatherwood Point. These are functions of the low amounts of clay in those sediments.

ii) Crystallinity: The crystallinity indices of smectite in the succession vary widely from -0·3 to +0·75. These indicate crystallinity variation from very poor or highly degraded to relatively good. But a cautious use of this data and any deductions from it is necessary because there is a strong positive correlation ($r > 0{\cdot}7$) between the crystallinity index obtained and absolute amount of smectite present. The crystallinity index is therefore to some extent a function of abundance and should be regarded as relative. Nevertheless, the somewhat wide spread of the samples in Figure 24 still suggests some sedimentological significance in the stratigraphical variation of the crystallinity indices shown in Figures 23a-c.

There are three relative crystallinity groupings of the smectites observed. The first comprises highly degraded smectites with negative and low positive ($< 0{\cdot}2$) indices. These occur mainly in the sediments of the 'Lower Headon Beds', especially in the sections on the mainland and at Heatherwood Point. The second group comprises smectites possessing relatively better crystallinity, with indices varying between 0·1 and 0·4. These occur in most parts of the Barton Clay and Barton Sand at Barton and Alum Bay. The last group includes smectites with the highest crystallinity indices (0·4 to 0·75); occurring in the succession at Whitecliff Bay, and the basal parts ('Beds H and I') of the Barton Sand at Barton. The reason for these variations in crystallinity may be in the difference or changes in the nature or source of the detritus deposited and/or imprint of environmental factors such as leaching (degradation) in the non-marine environments, and halmyrolysis in the Barton Sea. These are discussed further later.

5.3.4 Chlorite

The occurrence of chlorite is relatively limited. It is usually found in amounts of $< 1\%$. Chlorite is present in most parts of the Barton Clay at Barton and Alum Bay. It is also frequent in the lignitic clays. The How Ledge Limestone at Heatherwood Point also contains trace amounts of the phase. These small abundances show that detritus sources and composition were largely non-chloritic.

5.3.5 Illite-Smectite

Illite-smectite is the dominant mixed-layered phase in the Upper Eocene sediments. X-ray diffraction indicates that the phase is inhomogeneous, randomly stratified and comprises a range of illite-smectite ratios with a centred reflection occurring at around 12Å on glycolation. Its abundance up the succession varies only narrowly between 8 and 20%, averaging 13% of the clay fraction. As for kaolinite, this is equivalent to $< 10\%$ of the bulk sediment composition. As with smectite, the illite-smectite also occurs in depleted amounts in the Pebble Bed and

Fig.24 :Plot of Crystallinity Index vs. Abundance for Smectite

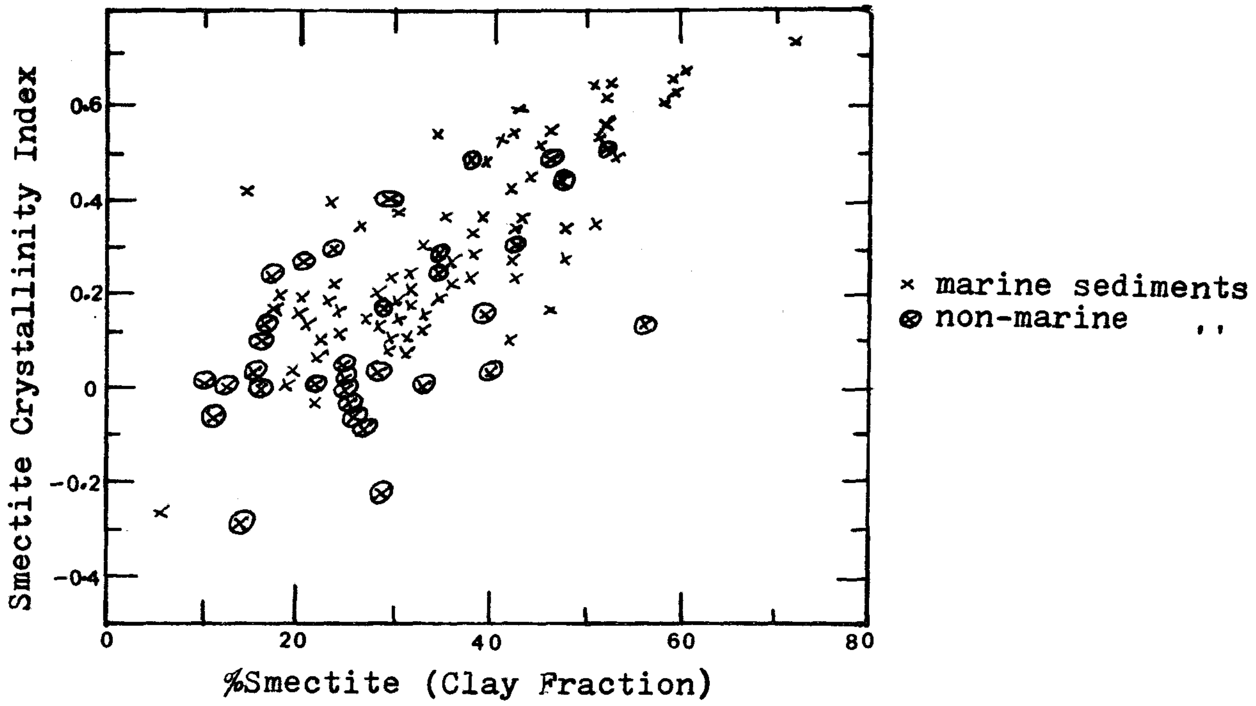
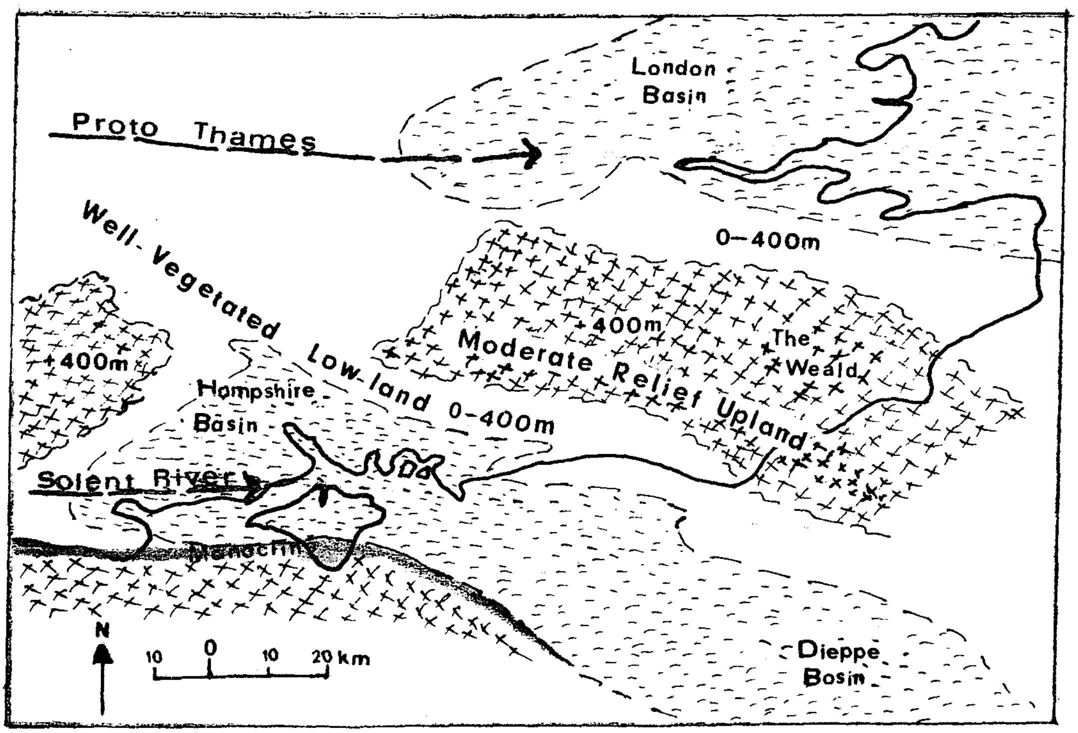


Fig.25 :Palaeogeography of the Palaeogene Hampshire Basin and Adjoining Areas (After Jones,1981).



the Barton Sand at Alum Bay; whilst with kaolinite, it is absent in the ferruginous top of the Barton Sand at Whitecliff Bay. However, a particularly high (~55%) illite-smectite content was recorded in the limestone ABLH-6, and its associated ironstone ABLH-5, in the Lower Headon section at Heatherwood Point. This occurrence is difficult to explain.

5.3.6 Smectite with 'Chlorite-like Hydroxy-Aluminium Interlayer'

Some smectites did not collapse fully on heating to 350°C (i.e. Fig.10c). It has been suggested that this type of behaviour is due to the presence of a small amount of hydroxy-aluminium or chlorite-like layers (Rich, 1968; Brown, 1980). This phase mainly occurs in some of the lignitic clays, including samples BBB-1, BLH-28 on the mainland, and WBLH-9 at Whitecliff Bay. It was also recorded in two carbonaceous limestone horizons (samples ABLH-2 and ABLH-7) at Heatherwood Point. The phase could not be differentiated from the smectite for estimation.

5.3.7 Summary of the Clay Minerals Abundance

The clay mineralogy of the Upper Eocene succession of the Hampshire Basin essentially comprises illite $\gtrsim$ smectite $>$ kaolinite $\simeq$ illite-smectite $\ggg$ chlorite. This assemblage is similar to that observed by Gilkes (1966); the major difference concerns the mixed-layered phases, now identified and estimated.

Dioctahedral smectite and illite dominate. Together, these two phases generally account for about 70% of the clay fractions. Illite occurs in higher amounts than smectite in the non-marine 'Lower Headon Beds', whilst approximately equal amounts of illite and smectite occur in the marine Barton Clay and Barton Sand Formations. Some horizons, however, possess considerable higher smectite contents. These notably include the marine sequence at Whitecliff Bay and the lower parts of the Barton Sand at Barton. Kaolinite and illite-smectite occur in lesser amounts of around 8-20%. Chlorite occurs only as a minor constituent in a limited number of the marine sediments, and the lignitic clays. In addition, some smectites with chlorite interlayers occur in some of the lignitic clays and limestones, with abundant carbonaceous matter.

Deviations from the above occur in the succession at Alum Bay. At this locality the smectite, illite-smectite and chlorite are absent or occur in very low amounts in the clay fractions of the pebble bed and the Barton Sand. The depletions are of high significance in the palaeosol at the top of the Barton Sand and the succeeding lower parts of the 'Lower Headon Beds' at Heatherwood Point. The depletion of these phases is accompanied by a substantial increase in the amounts of kaolinite and/or illite. This peculiar clay mineralogy at Alum Bay is thought to be due to localised differential derivation of detritus and/or the imprint of surficial (acid soil pedogenesis) processes. These are assessed further later.

5.4 Discussion

The discussion of the clay mineralogy of the Upper Eocene sediments is centred on three factors that generally dictate the assemblage and relative abundance of clay minerals in sedimentary rocks. These are the nature of the source; contemporaneous neoformations and/or alterations; and sedimentological factors such as 'differential settling'. Diagenetic transformations (Shutov et al., 1970a) are not considered important because of the shallow burial ($\lesssim$ 200m depth) history of the Upper Eocene succession under study. The clay assemblage of the sediments and those of other Palaeogene sediments in southern England were then employed for deducing the palaeo-environmental conditions and presenting a new view of the derivation of the clay assemblage.

5.4.1 Derivation of the Clay Assemblage

i) Constancy of Source

The general constancy of the illite-smectite-kaolinite-illite/smectite assemblage in the Upper Eocene sediments suggests constancy of sources of detritus. A similar deduction of constancy of source was made by Blondeau & Pomerol (1968) from a study of heavy mineral assemblages in the sediments.

With illite and smectite dominating in the clay fractions, the clays belong to the 'eastern province' assemblage of Gilkes (1966, 1967). This, Gilkes believed, was derived mainly from rocks exposed to the north and east of the Hampshire Basin. This hypothesis is broadly acceptable. However, recent advances in the geology of southern England necessitate re-assessing and updating views on the clay derivation.

ii) Source Rocks

Derived clays in sediments usually comprise phases inherited directly from the source rocks and/or phases resulting from hydrolytic decomposition of weatherable alumino-silicates in the source rocks and their soil mantles. The source rocks to the Upper Eocene Hampshire Basin will thus be considered with respect to what types of weathering they underwent. This is particularly essential in view of the reported occurrences of Tertiary deep weathering (lateritic) profiles and immature soil profiles in eastern Devon (Isaac, 1981, 1983) and Cornwall (Freshney et al., 1982); the lateritic weatherings believed to be widespread in the regions surrounding the Eocene Paris Basin (Chatteauneuff, 1980); and the various hydromorphic and red-yellow podzolic palaeosols in the Hampshire Basin (Buurman, 1980; present study).

The probable source rocks for the Upper Eocene sediments have been considered earlier (Chapters 1 and 4). These include the complex crystalline and Palaeozoic meta-sediments in south-west England (the Cornubian Massif) and northern France (Amorican Massif); the Jurassic to Lower Cretaceous sedimentary rocks in western England, Wales (?) and the English Midlands; the Upper Cretaceous Chalk deposits in southern England and the English Channel; intrabasinally exposed Palaeogene sediments; and submarine transported materials from the North Sea areas.

A broad outline of the clay mineralogy of these rocks has been given by Gilkes (1966), Perrin (1971), Cosgrove (1972) and Selwood & Sladen (1982). Important amongst rocks in south-western England are the hydrothermally and/or superficially kaolinised Dartmoor Granites (Exley, 1959; Sheppard, 1977; Bristow, 1977). The Lower Cretaceous and the older meta-sediments and sedimentary rocks mostly possess illitic-mica dominated clay contents with subordinate amounts of kaolinite and/or chlorite. Many occurrences of these rocks are, however, rich in expanding clay phases, including smectites. The clay mineralogy of the Upper Cretaceous Chalk is dominated by smectite (montmorillonite) with lesser amounts of illite, kaolinite and chlorite (Weir & Catt, 1965; Jeans, 1968). Gilkes (1966) has shown that the clay assemblages in the Palaeogene sediments in the Hampshire Basin essentially comprise illite, smectite and kaolinite. These, however, show an environment-related geographical distribution from illite and kaolinite dominated assemblage in the non-marine sediments in the 'western province' of the basin, to smectite and illite dominated assemblage in marine sediments in the 'eastern province'. Of the probable North Sea material, it is difficult to ascertain which sediments were involved. Perhaps they included the Palaeocene - Early Eocene clastic sediments, with interbedded ash layers that are widespread in the North Sea (Jacques & Thouvenin, 1975; Knox & Harland, 1979).

iii) Weathering of the Source Rocks

Chemical weathering was prevalent in southern England during the Palaeogene period. Residual palaeosols occurring in south-western England (Isaac, 1983) and in the Hampshire Basin (present study) are testimony of the chemical weathering. Other evidence includes various dissolution features on Pre- and Intra-Eocene erosional surfaces on the Chalk (Jones, 1981).

The types of weathering that rocks undergo depend on many factors, especially climate (temperature and precipitation) and topography.

Britain lay at about latitude 40°N during the Eocene (Smith & Bridden, 1977), and floral studies in southern England (i.e. Chandler, 1926, 1961; Daley, 1972; Collinson et al., 1981; Hubbard & Boulter, 1983) have indicated the prevalence of a warm, humid tropical-like climate in the Eocene, deteriorating into a frost-free sub-tropical climate during the Oligocene. The physiography of the Hampshire Basin and adjoining areas has been elucidated from several geomorphological studies of the sub-Palaeogene erosional surfaces in southern England. These are reviewed in great detail by Small (1980) and Jones (1980, 1981); a summary of the reconstructed relief given by Jones (1981) is shown in Figure 25. This indicates the existence of 10-20 km long low-lying (0 - 300m) areas to the north and west of the basin. This low relief was much more extensive in the north-west of the basin, towards the English Midlands. Beyond the low-lands are moderate relief (400-700m) peneplains in areas to the west in Devon, in the Weald to the north and north-east, and in a belt spanning Purbeck - the southern half of the Isle of Wight and parts of the English Channel. These probably continued southwards into the Amorican Massif in northern France.

In present day areas similar to those described above, chemical weathering is paramount (Ollier, 1969). Depending on the nature of local drainage, relative relief and physical attributes of the rocks, leaching and decomposition of unstable alumino-silicates would vary from poor to moderate and very intensive, the processes being generally more pronounced in the tropics compared to the sub-tropics. Literature on clay mineral formation and stability in surface conditions and in present-day weathering zones is extensive, and includes contributions by Grim (1968), Lukashev (1972) and Eswaran & Bin (1980).

With the earlier mentioned source rocks in mind, the types of weathering would be as follows. In moderately weathered areas, particularly the low-lying areas, there would be a wide range of inherited and neoformed phases including kaolinite, illite, mixed-layered phases, smectites and hydrated iron-oxides. Some incompletely weathered phases such as feldspars and micas could also be present. This mineral spectrum often predominates where intense weathering in tropical conditions has not progressed sufficiently (i.e. $\lesssim 10^6$ years) and immature or senile soils (USDA, 1967) have developed (Kronberg et al., 1979). The minerals are, however, encountered more often in sub-tropical climatic regions where precipitation, and hence leaching, are generally not as high or intense as the tropics (Millot, 1970). Where precipitation is very high and local conditions favour very intense leaching, advanced weathering (Kronberg & Nesbitt, 1981) will result in time ($\gtrsim 10^7$ years), with neoformed well-ordered kaolinite occurring in very high amounts (Koppi & Skjemstad, 1981). These processes mainly occur in the tropics (Kronberg et al., 1979) where, if the weathering continues to the extreme, gibbsite can also be neoformed, whilst the accumulation of iron-oxides and/or silica may be substantial, often causing induration of soil horizons. These constitute lateritic weathering (Mohr & Van Baren, 1954; Carroll, 1970).

Assuming that weathering, erosion and sedimentation were in-phase or contemporaneous in the Eocene southern England, the clay assemblage in the sediments can be interpreted with respect to the weathering types and products enumerated above. The illite $\gtrsim$ smectite $>$ kaolinite $\simeq$ illite-smectite assemblage in the Upper Eocene sediments can be regarded as material derived from poor to moderate weathering of, or immature soils on, illitic and/or smectitic rocks in tropical to sub-tropical conditions.

The illite contents of the clay assemblage would possibly be largely inherited, although some could have resulted from degraded micas and mixed-layered phases in the source areas. The general degraded nature of the phase is a feature that often characterises 1Md illites inherited from chemically weathered rocks (Weaver, 1958), but which may also result during erosion and sedimentation (Dunoyer de Segonzac, 1970). As for illite, the smectite in the clay assemblage will also largely be inherited. The conservation of smectite significantly suggests poor drainage or even water-logged conditions. The ground-water could also have contained substantial amounts of dissolved alkali and alkaline-earth elements. These situations would have been possible to achieve in low-lying carbonate-rich source rocks. The most notable of such rocks is the Chalk, whose calcium carbonate content is generally very high (up to 99·5%) and with non-carbonate contents very rich in smectite (Young, 1965; Jeans, 1968). It is envisaged that, during sub-aerial dissolution of the Chalk or any other carbonate-rich rocks (e.g. the very fossiliferous 'Upper Greensand'), susceptible silicate minerals would not be intensely attacked until all the carbonate phases have virtually been taken into solution. So, if dynamic conditions prevail and erosion kept pace with weathering, the silicates would not have suffered much leaching and alteration before being eroded.

The constantly low abundance of kaolinite has a wide implication. First it precludes the consideration of intense or advanced weathering conditions in the regions bordering the Hampshire Basin in Upper Eocene times. Secondly, it probably indicates insignificant contribution of kaolinite-rich detritus from the kaolinitised Dartmoor Granites (Bristow, 1977) and lateritic residual weathering profiles and gravelly deposits in Devon (Isaac, 1983). Gilkes (1966), in his clay mineralogy studies of the Hampshire Basin, tried to explain variations in the kaolinite contents of the Palaeogene sediments in terms of changes in the degree of dilution of Dartmoor detritus by illitic Mesozoic sediments such as the 'Upper Greensand'. This is not discounted here, but probable palaeoclimatic influences on the derived assemblages were not fully considered by Gilkes.

The disordered nature of the kaolinite in the clay assemblage is of even greater importance. If the Dartmoor Granite was the main source of the kaolinite, then the well-ordered kaolinite characterising the altered granite must have degraded during erosion. This is not improbable because Shutov et al. (1970a) have documented degradation of well-ordered triclinic kaolinite to disordered pseudo-triclinic kaolinite during erosion and early diagenesis. Nevertheless, a poorly developed weathering profile origin is more likely because disordered kaolinite is widely observed characterising the lower parts of weathering profiles (Eswaran & Bin, 1980), especially where alkali ions and weatherable mineral phases are present (Millot, 1970; Hughes & Brown, 1979). A similar situation was also observed by Isaac (1981, 1983) in the residual soils in Devon, and it is envisaged to be widespread in the Tertiary of southern England. This is because low crystallinity typifies the whole Palaeogene succession in the region (Gilkes, 1966; Bristow, 1968; Freshney et al., 1982). It is even the form found in the present study to have authigenically developed in the red-yellow podzols at Alum Bay. The kaolinite partings in the 'Bracklesham Bed V' of Fisher (1862) at Whitecliff Bay were, however, reported by Gilkes (1966) to be well ordered. This kaolinite probably developed by 'diagenisation and dialysation' (Keller, 1981) of primarily derived clays in the host coal (primarily swamp) deposit.

The closely similar abundance of kaolinite and illite-smectite mixed layer phases would suggest that they both resulted from similarly immature weathering profiles. They could have formed from degraded smectites, altered micas and chlorite in the source rocks.

In summary, the illite $\gtrsim$ smectite > kaolinite $\simeq$ illite-smectite clay assemblage in the Upper Eocene succession is typical of the assemblage found in less intensely weathered rocks in warm and humid subtropical and tropical conditions. This inference is later (in Section 5.4.) employed for interpreting the regional Palaeogene palaeo-environment and reviewing the derivation of the clay assemblages in the Palaeogene sediments.

5.4.2 Explanation of the Phases' Abundance and Crystallinities

The general constancy of clay assemblages in the Upper Eocene succession is broadly taken as indicating a relative constancy of source. There are, however, significant variations in the distribution of the phases, particularly with respect to the very poor crystallinities of illite and kaolinite in the lignitic clays, and the relative abundance and crystallinity indices of smectite across the succession. These are thought to be due to the imprint of localised sedimentological and/or environmental factors which include: i) degradation/aggradation processes; ii) differential settling; and (iii) changes in detritus composition and/or source.

The occurrence of very poorly crystalline kaolinite, illite and smectite is thought to be due to continuous degradation in the non-marine environments in which the 'Lower Headon Beds' were deposited, in particular, the near-surface conditions in which the lignitic clays accumulated. In fact, in the present study, the lignites and associated sediments in the succession are regarded as having primarily constituted swamp (hydromorphic) soils. In present-day swamp and marsh soils, such as the 'cat-clays' (Fitzpatrick, 1971), alternate wetting and drying often occurs, leading to the production of acidic solutions from oxidised and hydrated sulphide phases (usually pyrite) (Dones & Lynn, 1977). Acidic leachings that follow cause alteration and degradation of existing clay minerals, as well as producing disordered kaolinite (Dixon, 1977). This would not only explain the very poor crystallinities of the clay phases, but also account for the relatively higher kaolinite contents of the lignitic clays compared to their immediate non-lignitic sediments.

Although degradation of the clay phases was most likely to be contemporaneous, probable contributions from Recent surficial alteration cannot be completely discounted. The serious problem of differentiating contemporaneous alteration from that of Recent times also concerns altered pyrites, goethite, lepidocrocite, gypsum and jarosite. These are discussed in later sections of this chapter. In the case of the highly degraded phases, a Recent age seems unlikely because if this were so, the phases would have been surficial only and would also have developed on other carbonaceous and pyritic sediments in the exposed succession.

Contemporaneous degradation is a process that mainly attends clay minerals' instability in non-marine conditions, such as the brackish and freshwater environments in which the 'Lower Headon Beds' accumulated. In marine environments, it is the re-constitution or aggradation of 2:1 layered structure phases that often occurs (Dunoyer de Segonzac,1970). Several works, including those of Nicholls & Loring (1960), Millot (1970) and Grim (1968), have shown that alkaline conditions, such as in estuarine and marine environments, are favourable to the conservation of 2:1 phases and possibly neoformation of smectites. In these environments, degraded smectites can reconstitute or aggrade by absorption of ions (e.g. Mg^{2+}) removed during weathering. These processes would be expected in the marine conditions of deposition of the Barton Clay and Barton Sand. It is difficult, however, to ascertain whether this occurred on a significant scale. If substantial smectite re-constitution has taken place, closely similar high crystallinity should be observed all through the marine section. But this is not so. The crystallinities are only consistently good in the section at Whitecliff Bay (Fig.23c). Although the extent of aggradation could depend on rates of deposition, and hence length of sediment exposure on the sea floor, it is not thought that these varied significantly during the deposition of either the Barton Clay or Barton Sand within the area of the present study. Their sedimentation proceeded at grossly low rates (i.e. 2·5 cm/1000 years - Odin et al.,1978); with glauconitisation in the shelf Barton Sea being the only significant sub-aqueous process. Also, the chemical analyses of a few clay-fraction samples across the succession at Barton (Table 9) were found to be very similar, showing no differences that may be attributed to aggradational variations.

Differential settling (Whitehouse et al., 1960; Parham, 1966) is one of the major sedimentological factors influencing clay mineral distribution in sedimentary basins. The process causes basinward increases in abundance of clay phases in the order kaolinite - illite - smectite. Numerous cases have been documented by several workers including Parham (1966), Porrenga (1966), Krumm(1969) and Dunoyer de Segonzac (1970). Burnett & Fookes (1974) have also attributed the variations of kaolinite and smectite in the Lower Eocene London Clay Formation, in the London and Hampshire Basins, to differential settling. A similar process is apparent in the marine sediments of the Upper Eocene succession presently being studied. Earlier, it has been advanced to account for the very low ($<$ 5% clay fraction) kaolinite abundance at Whitecliff Bay compared to the 8-15% kaolinite contents at Alum Bay and Barton. Antipathetically, the smectite content of the Barton Clay and Barton Sand decreases from $\gtrsim$ 55% at Whitecliff Bay to $\lesssim$45% at Barton and in the Barton Clay succession at Alum Bay.

The explanation described above is inadequate to explain some exceptional situations in the succession. First of all, no discernible

Table 9: Clay (<2μm) Fraction Compositions, Upper Eocene Sediments, Mainland Hampshire.

Samples	Lower Headon Beds		Barton Sand Fm			Barton Clay Fm					Pebble Bed
	BLH	BLH	BBB	BBB	BBB	BBB	BBB	BBB	BBB	BHC	BPB
Composition	15	34	18	20	23	25	26	27	40	1	1
Bulk Mineralogy (%)											
Quartz	3·6	16.6	9.8	6.3	6.7	5.9	7.3	10.3	8.3	9.7	10.3
Total Clay	96.4	67.1	80.8	92.4	95.3	94.1	92.7	83.4	91.6	86.6	87.5
Calcite	-	8.9	-	-	1.0	-	-	5.7	-	-	-
Aragonite	-	4.2									
Pyrite	-	3.2									
Anatase	0.8	0.8	0.8	0.8	0.7	0.9	0.8	0.9	0.7	0.8	0.7
Jarosite				1.3						3.7	2.3
Clay Mineralogy (%)											
Kaolinite	22	12	12	9	12	13	15	13	7	7	11
Illite	30	31	26	31	34	30	42	37	37	59	45
I/Sm	23	14	11	17	16	17	13	15	10	17	15
Smectite	25	43	51	42	38	41	31	36	46	18	29
Chlorite	-	-	-	0.3	0.7	-	0.7	0.4	0.3	0.01	-
Crystallinity Indices											
Kao. XI	1.50	0.46	0.39	0.43	0.39	0.43	0.39	0.39	0.36	0.43	0.36
Ill. XI	1.14	0.46	0.46	0.57	0.57	0.43	0.5	0.46	0.5	0.68	0.5
Sm. XI	-0.07	0.3	0.64	0.58	0.27	0.26	0.08	0.20	0.49	0.16	0.14
Partial Bulk Chemical Compositions (%)											
SiO_2	50.92	51.57	50.88	53.70	52.47	53.21	52.6	50.91	56.05	52.81	55.36
TiO_2	0.23	0.77	0.57	0.71	0.76	0.94	0.89	0.83	0.74	0.73	0.87
Al_2O_3	26.57	23.30	22.06	20.79	21.05	21.25	22.28	21.66	20.08	20.10	20.73
Fe_2O_3	4.76	6.10	7.80	10.44	8.15	8.39	7.73	6.7	8.04	9.23	7.45
MgO	0.38	1.06	1.20	1.46	1.96	1.89	2.03	2.34	2.17	1.40	0.88
CaO	0.94	3.72	0.54	0.12	2.27	0.20	0.6	4.00	1.19	0.09	0.17
Na_2O	0.29	0.10	0.17	0.28	0.19	0.37	0.20	0.06	0.23	0.10	0.26
K_2O	1.79	2.84	2.43	3.03	3.06	3.35	3.33	3.21	3.84	4.06	3.61
P_2O_5	0.02	0.09	0.12	0.15	0.06	0.04	0.15	0.08	0.05	0.09	0.06

or convincing differential settling effect is observed in the general clay contents up the succession. At each locality there is no significant vertical variation of the kaolinite abundance. Although there are relatively higher illite than smectite contents in the non-marine upper parts of the succession, this is thought to be due to minor changes in detritus composition. Secondly, differential settling cannot account for the relative high smectite abundance at the base of the Barton Sand ('Beds H and I') at Barton. The Barton Sand is believed (Murray & Wright, 1974) to have accumulated during the late shallowing phase of the Barton Sea. Had differential settling been strongly operative at the time, kaolinite and illite rather than smectite would have accumulated more. Indeed, the fact that the clay assemblage of 'Beds H and I' at Barton is closely similar to that in the marine succession at Whitecliff Bay suggests derivation from similarly composed detritus and/or sources.

The source(s) of smectite concerned would have been located to the east of the basin in order to have had its greatest influence at Whitecliff Bay. The source(s) would have been rich in smectite which, if aerial, could be moderately weathered Chalk deposits, and/or if submarine, could be re-worked smectite-rich, ash-bearing early Tertiary sediments from the North Sea. In the absence of volcanic material in the sediments, the submarine derivation is difficult to ascertain. There are, however, ash layers in the Palaeocene and Lower Eocene sediments of the North Sea and the adjacent London Basin (Elliot, 1971; Knox & Ellison, 1979). Also clinoptinolite, which could have resulted from submarine alteration of volcanic material, was reported present in the Bracklesham Group succession at Whitecliff Bay (Gilkes, 1966). Then the fact that high smectite abundances occur in the transgressive facies of the Hampshire Basin (i.e. the London Clay Formation, the Bracklesham Group in the east of the basin, and the Barton Clay and Barton Sand) are indications of probable submarine derivation of smectite. This will be additional to smectite from exposed and sub-aerially weathered Chalk sources. Submarine derivation would not be limited to the smectite, and indeed Blondeau & Pomerol (1968), in a study of heavy mineral assemblages in the Hampshire Basin, deduced that garnet, zoicite, epidote and hornblende in the sediments were possibly derived from northern sources via the North Sea. Similar heavy mineral assemblages were found by Morton (1982) in Late Palaeocene and Early Eocene sediments from northern parts of the London Basin. Morton (op.cit) argued that the assemblages were possibly derived from the Scottish Highlands to the north, with the transportation being by longshore drift.

Finally, it is probable that, by the nature of their derivation, the submarine-derived smectites would be better crystalline than the sub-aerially derived smectites. Hence, it could be said that the relatively higher smectite abundance and better crystallinities recorded at Whitecliff Bay, the most easterly and offshore locality, were due to a greater contribution of submarine materials via the westwardly transgressing Barton Sea. The submarine contribution decreases in significance westwards towards Alum Bay and mainland Hampshire because of the increasing influx of river-discharged sub-aerially derived materials. However, with changes in the nature of the Barton Sea to a shallow, clear water body receiving much less muddy detritus, the contributions of the submarine material to the base of the Barton Sand at Barton became substantial and discernible.

5.4.3 The Kaolinitic and Illitic Clay Assemblages at Alum Bay

The lithostratigraphy of the Upper Eocene succession shows that changes in the nature of the Barton Sea, from an early, relatively deep water body to a late shallowing phase, were accompanied by region-wide changes from clayey sedimentation to the deposition of sands. The composition of sediments in the succession at Barton and Whitecliff Bay further shows that the decrease in mud deposition was not accompanied by changes in the clay assemblage. This is taken to indicate no significant region-wide changes in the detritus sources. But at Alum Bay, a locality that is roughly mid-way between Barton and Whitecliff Bay (Fig.1), there is a change from the general clay assemblage discussed above. The limited aerial extent of the change indicates very localised factors being responsible. These are thought to be:

i) penecontemporaneous in situ alterations of the earlier-considered general clay assemblage and/or ii) derivation from very close-by sources cut off from the other localities, but very rich in primary or neoformed kaolinite or illite.

i) In situ kaolinite authigenesis

After deposition, the Barton Sand at Alum Bay emerged and its uppermost part, brought into ground-water zones, pedogenically developed into 'red-yellow podzol' and 'terra rossa'. The morphology, composition and development of these palaeosols are given in Chapter 16. The pedological features include rootlets in the growth position, strong coloration and substantial iron (goethite)accumulation. In addition, petrographic studies show feldspars in the soils to have suffered layer-weathering (see Feldspar in Chapter 4). Also very important in parts of the soil profiles are lenses and specks of kaolinite. SEM studies showed them to consist of platy kaolinite crystals and vermiforms in an open-textured aggregation. These are features that Keller (1982) documented as characterising in situ weathered profiles. Further details of the kaolinite lenses are given in Chapter 7.

The significance of the kaolinite lenses is that they mainly developed within the 'arenosol' unit as the lower pedounit of the palaeosol profile (Profile A) at Heatherwood Point (Fig.6b). The clay mineralogy of this unit is almost exclusively comprised of kaolinite; traces of illite being the additional phase recorded. The illite would be a relict of the primary clay content. The 'red-earths' comprise the other pedounits of Profile A and Profile B (Fig.6b). These possess a consistently similar 38% kaolinite - 55% illite - 6% illite-smectite assemblage, and apparently represent the product of less intense leaching or weathering when compared to the 'arenosol'. It appears that the primary clay content, prior to pedogenic developments, was similar to the general illite - smectite - kaolinite - illite/smectite assemblage in the rest of the Upper Eocene succession. This being so, the development of the palaeosols could then be said to have mainly involved moderate leaching with complete loss of the smectites and, in places, intense leaching with further loss of the illitic phases. These still typify moderate to advanced weathering in warm, humid tropical - sub-tropical climatic conditions with relatively good drainage - and low relief (Carroll, 1970; Fitzpatrick, 1971).

The palaeosols were developed within the topmost 1m of the sand body, the lower soil unit being represented by the gleysons (11Cg) (Fig.6b). These gleyey horizons also mark the lowest ground-water level. But as the sand body is unlithified, acidic meteoric water would also have flushed through the deposit. Hence, below the lowest ground-water level, or in the phraetic zone, a somewhat gradual decrease of leaching - and hence increase in amounts of the susceptible phases - would be expected. This is indeed the case and is clearly shown in the stratigraphical plot of the clay mineralogy (Fig.23b). Downwards from the soil profile, kaolinite decreases, whilst illite and then illite/smectite increases. Smectite only occurs in the clayey base of the sand.

ii) Localised derivation

Acidic meteoric water alteration of the whole sand body is seriously questioned by the clay assemblage in the pipe clays. These contain kaolinite - illite - illite/smectite assemblage, with the relative proportion of each phase being similar to those of the less developed 'red-earths' palaeosols. The pipe clays cannot be regarded as alluviated material; rather, they possibly settled out of low energy, ponded shallow waters, with floating macerated plant matter. The pipe clay would not have been permeable to flushing acidic solutions. If there had been any alteration at all in the deposit, the extent of such alteration on the primary materials had been slight and difficult to ascertain. Hence the clay assemblage and phases abundance in the pipe clays may be regarded as the 'equilibrium derived material'. The sources concerned would be depleted in smectite in favour of kaolinite, and likely to be undergoing warm, humid weathering. The sources would not only have supplied clay minerals for the pipe-clays, but also for the whole or much of the Barton Sand at Alum Bay. If so, then the earlier suggested primary sand detritus needs to be revised to that virtually containing no smectite. Then the 'red-earths' could be regarded as representing the 'equilibrium weatherings'. Any subsequent suggested alterations in the 'arenosol' would then have mainly involved the illitic phases.

The above inferences are probably closely related to the suggestion put forward in Chapter 4 for nearby intra-basinally exposed older (Tertiary) sediments. The suggestion was based on the presence of disseminated small-sized well-worn flint pebbles in the Barton Sand at Alum Bay. One of the most probable sediments would be the late Lower Eocene 'Bagshot Sands' and its equivalents. The 'Bagshot Beds', apart from containing pebble bed horizons, was also found (Gilkes, 1966) to possess a clay mineralogy dominated by kaolinite and illite, although high smectite abundances also occur in places.

The above sets of arguments will also apply to the indurated pebble bed at the base of the Upper Eocene succession at Alum Bay.

There, the absence of smectite, illite-smectite and feldspars is attended by high kaolinite content. Ferruginous and kaolinite-rich sands underlie the pebble beds (Gilkes, 1966). The sands and the pebble bed could have constituted a soil profile in which the groundwater table fluctuated considerably, and high iron (goethite) accumulation occurred.

iii) High illite abundance

Occurrences of high amounts ($\gtrsim$ 60%) of illite are more limited and not as systematic as the kaolinite. They are, however, worthy of consideration because these concern the basal parts of the 'Lower Headon Beds' at Alum Bay and Whitecliff Bay, which stratigraphically represent the onset of non-marine sedimentation. The high illite contents may be due to two possibilities: either they are an in situ alteration phenomenon, or they indicate a greater contribution of illite-rich detritus.

The enriched illite shows very poor crystallinity and occurs with similarly crystalline kaolinite. This suggests formation by in situ alteration. It might have involved progressive fixation of potassium into a degraded smectitic structure. Such processes have been suggested for illites in soils of arid climatic regions such as Iran (Majhoory, 1975) and south-western U.S.A. (Nettleton et al., 1973). Fanning & Keramidas (1977) also argued that the process is probable in other regions where potassium from plants or leached from coarser (silt)-sized micas is abundant and made available during dry seasons for interaction with beidellitic smectites. These processes would, however, almost certainly involve an intermediate vermiculitic phase. But no such phase is present in the presently studied sediments, so the possibility of K-fixation by smectite seems unlikely.

The alternative possibility is derivation of highly illitic detritus from nearby or distant sources in drainage discharging closer to the Isle of Wight, particularly Alum Bay. Gilkes (1978), in reassessing his earlier clay mineralogy work in the Hampshire Basin, argued that the high illite contents in the clay fractions of the 'Lower Headon Beds' and the succeeding Oligocene sediments were not due to derivation from distant illitic sources, but rather from very nearby sources where illites were largely neoformed. This hypothesis is not very convincing. Firstly, illite neoformation is most likely in hot and dry regions, particularly in water bodies with low magnesium concentration, abundant potassium and a SiO_2/Al_2O_3 ratio greater than 3 (Millot, 1970; Lukashev, 1972). It is unlikely that such conditions strictly existed in the late Eocene-Oligocene Hampshire Basin. Gilkes (1978) tried to extent, to the Hampshire Basin, aspects of the proven prevailing hot and very dry conditions that alternated with humid periods in the Paris Basin (i.e. Chatteauneuff, 1980). The author envisaged the existence of arid seasons with intense evaporation and low precipitation. But several floral studies in the region mainly show plant assemblages typifying warm and humid conditions. Very warm periods possibly existed only briefly during that period. These are the 'Palynological Zones e and v_2' of Hubbard & Boulter (1983), which correspond respectively to the time of deposition of the latest Upper Eocene 'Lower Headon Beds' and Oligocene 'Bembridge Beds'.

As an alternative to neoformed illite sources, derivation of high illite content might have been from illite-rich source rocks. If, because of the limited areal extent of the illitic-rich horizons, nearby sources are envisaged, then Mesozoic sediments upthrown on Palaeogene-age fold axes in the region (Phillips, 1964; Anderton et al., 1980) and intra-basinally exposed older Tertiary sediments would be the most likely major source materials. In addition, there could have been differential loss of smectite during mild weathering prior to erosion or re-working

5.4.4 Chlorites

The trace amounts in which chlorite occurs do not facilitate the assessment of its derivation or diagenetic formation. If detritally derived, then it could have been inherited from any of the sedimentary and meta-sediment source rocks discussed earlier. Some of those rocks contain chlorite in substantial amounts, and some could have survived where weathering was poor and leaching was minimal. If diagenetically formed, this could have been during shallow burial diagenesis and/or in sediments subjected to penecontemporaneous water-logged environments. The reducing conditions would be favourable to chlorite stability and formation (Borchardt, 1977). This may also account for chlorite being limited to the marine Barton Clay and some of the lignitic and limestone horizons.

The observed occurrences of hydroxy-chlorite phases in the lignitic clays may, however, have been due to surficial factors. The phase is possibly another manifestation of the penecontemporaneous leaching to which the very poorly crystalline kaolinite and illite in the lignitic horizon have been attributed.

5.4.5 The Palaeo-environmental Significance of the Clay Assemblage

In many earlier studies, the interpretation of clay mineral assemblages in the Tertiary sediments of southern England has mostly been with respect to the clay compositions of the probable source rocks, with little consideration given to the attendant influence of palaeo-environmental factors. Some of the few works with palaeo-environmental interpretations are those of Buurman (1980a) and Freshney et al. (1982). It is realised in the present study that, because of their shallow burial history and apparent absence of diagenetic transformations, the clay mineral contents of the sediments should be a good palaeo-climatic indicator (cf. Singer, 1980). The mineral assemblages should, at least, provide information complementary to that from floral studies, which indicate changes in the Tertiary climate from humid tropical-like in early Eocene times to warm, humid sub-tropical in Oligocene times (Daley, 1972; Hubbard & Boulter, 1983). Also important is the recent discovery of mature lateritic residual soils of pre-Upper Eocene (possibly Palaeocene) age and immature soil profiles of Eocene age in eastern Devon (Isaac, 1983) and Cornwall (Freshney et al., 1982). These, along with the occurrences of residual kaolinite-rich palaeosols in the Hampshire Basin (Buurman, 1980b; present study) necessitate a reconsideration of the derivation of Tertiary clay assemblages in southern England.

i) Absence of residual profiles in source areas of south-eastern England

Unlike south-western England, there are no known reported occurrences of preserved sub-aerial weathering profiles on the Upper Cretaceous Chalk deposits and other older rocks exposed in the rest of southern England. Neither have early Tertiary residual deposits convincingly been proved as occurring in the regions outside Devon; the two oldest residual deposits in the regions are the 'Clays with Flint' and Plateau Gravels (Melville & Freshney, 1982). They have, on geomorphological, stratigraphical and compositional bases, arguably been shown to be largely Neogene in age (Jones, 1981). However, there are erosional surfaces on the Chalk and the older rocks. These range in age from Palaeocene to Quaternary (Small, 1980; Jones, 1980, 1981), and may be taken as an indication of dynamic environmental conditions in which erosional loss of weathered mantles took place, possibly before they had developed for the long period of time ($\gtrsim 10^6$ years) needed for matured weathering.

ii) Climatic interpretations of the Palaeogene clay assemblage

A broad consideration of the relationship between climate and weathering types and products has been presented earlier in Sections 5.2.4iii and iv. This was employed in interpreting the poorly-crystalline illite $\gtrsim$ smectite > kaolinite $\simeq$ illite/smectite clay assemblage in the Upper Eocene succession as a manifestation of poor to moderate pedochemical weathering in sub-tropical conditions or weathering over short periods ($\lesssim 10^6$ years) in tropical conditions. Very localised moderate to intense weathering was, however, believed to account for the kaolinite-rich Barton Sand and the palaeosol horizons at Alum Bay. On a similar climatic basis, and assuming that weathering was in phase with erosion and sedimentation, the clay assemblage of the other Palaeogene sediments in south-east England has been interpreted as shown in Table 10 and discussed below.

The clay assemblages can be differentiated into two groups: Assemblage 1, comprising illite and/or smectite dominated clays; and Assemblage 2, with dominant abundance of kaolinite or kaolinite and illite.

The dominance of Assemblage 1 in the late Palaeocene Thanet and Woolwich Formations, the oldest Tertiary deposits, does not indicate the existence of widespread advanced Palaeocene weathering such as that suggested by Isaac (1983a) for Devon. This indicates that either the kaolinitised Dartmoor Granites and the suggested kaolinitic lateritic soils in south-west England were not contributing detritus to the newly created London Basin, or their contributions were heavily diluted by material from less advanced weathering that would have been more widespread in the region. Changes to Assemblage 2 during the deposition of the Reading Clay later in late Palaeocene times, when the Hampshire Basin came into existence, indicate climatic changes to warmer periods and derivation of sediment from deeply weathered, kaolinitic sources. The existence of conducive conditions for kaolinitisation during this period is reflected in the kaolinite enrichment of some horizons of hydromorphic (Pelosols) palaeosols that Buurman (1980a) described from the Reading Clay succession

Table 10 : Palaeogene Clay Assemblages and Palaeoclimates in Southern England

Series	Succession	Clay Mineralogy	Environmental Interpretations*		Comparison with Palynological (Climatic)Zones of H & B, 1983
			Weathering Types	Climates	
Oligocene	Hamstead Fm. Bembridge Marl Fm. Bembridge Limestone Fm. Solent Fm. (minus 'Lower Headon' Member)	$I \gg Sm \gg K$ $\pm$ ML $\pm$ Chl (G)	Non-intensive weathering	Humid sub-tropics	Cool climate 'Zone f' with warm episode 'Zone v2'
Upper Eocene	'Lower Headon Beds' Barton Sand Fm. Barton Clay Fm.	$I \gtrsim Sm \gg K \simeq ML$ $\pm$ Chl Locally at Alum Bay $K \gg\gtrsim I \gg ML$	Poor to moderately intensive	Warm, humid sub-tropics	Warm climate 'Zone d' with high thermal sub-stage 'Zone e'
Middle * Eocene	Bracklesham Group	(1)$K \simeq I \gg Sm$ (plus limited (2) $Sm > I > K \pm Chl$)	Possibly widespread advanced weathering (plus contribution of submarine material)	Humid tropics-warm sub-tropics	Warm climate 'Zone c'
Lower * Eocene	Dorset Ball Clay/ 'Bagshot Beds'	$K \gtrsim I$ (G) (in places, $Sm > K \simeq I$)	Advanced weatherings (plus localised poor weathering)	"	Prolonged high thermal stage, 'Zone b'
	London Clay Fm.	$Sm \gtrsim I > K \pm Chl$ (B), (G)	As in the Upper Eocene		'Zone a' Unequable humid tropics to warm sub-tropics
Late Palaeocene	Reading Clay Fm.	$K \simeq I$ plus local $Sm \gg I \simeq K$ $\pm$ Chl. (G), (P)	As for the Bagshot Beds		
	Woolwich Fm. Thanet Fm.	$Sm \gg I \simeq K$ (P)	Non-intensive weathering	Cool sub-tropics	

Key: I = Illite; Sm = Smectites; K = Kaolinite; Chl = Chlorites;
ML = Mixed-layer clay phases.
(G) = Gilkes (1966); (B) = Burnett & Fookes (1974); (P) = Perrin (1970)
H & B = Hubbard & Boulter, 1983.
* Approximate equivalents.

exposed at Alum Bay. Weathering in some areas was, however, still poorly advanced, allowing smectite-rich material to be deposited such as observed at Otterbourne in Hampshire (Gilkes, 1966) and Clapham in Sussex (Weit & Catt, 1969). This less intensive weathering continued during much of Lower Eocene times, when the London Clay was deposited. It would be tempting to infer a cool climatic condition for that period, as it would coincide with the proposed cool 'northern sea' of the London Clay (Curry, 1965; Murray & Wright, 1974). But this would not be in agreement with floral data (Reid & Chandler, 1926) which, although showing the presence of some (~ 12%) sub-tropical plant species, is basically dominated by tropical rain-forest plant remains. Daley (1972) reviewed the floral data and suggested that the climate was tropical-like, but with lower temperatures than for present-day tropics. In general, the clay assemblage variations of the Late Palaeocene to Early Eocene indicate climatic fluctuations that would agree with warm but unsteady climatic conditions deduced as 'Palynological Zone a' by Hubbard & Boulter (1983). The succeeding 'Palynological Zone b', in part, coincided with the widespread derivation of Assemblage 2 minerals for the late Lower Eocene 'Bagshot Beds' and its western equivalents that include the Dorset Ball Clays studied by Gilkes (1966).

The succeeding Bracklesham Group possesses clay contents which, to the east of the basin, consist of Assemblage 1, but shows Assemblage 2 to the west from Alum Bay (Gilkes, 1966). Differential settling cannot satisfactorily account for the large compositional variations over the short distance (~ 10 km) between the 'west and east regions'. Satisfactory explanations would mainly be based on derivation from differential sources. The 'eastern province' received less weathered smectite-rich detritals. At Whitecliff Bay, the presence of clinoptilolite associated with glauconitic marine sediments suggests strongly that there were submarine derived smectites. This would be in addition to contributions from moderately-weathered Chalk. In the light of this, a cool climatic inference seems rather inappropriate. It appears, however, that the 'western province' received materials from deeply weathered sources. Such sources need not necessarily be the kaolinitised Dartmoor Granites, as suggested by Gilkes (1966); rather they might possibly be from nearby localities or even be due to in situ acidic penecontemporaneous sub-aerial weathering. Indications of local emergence and pedogenous processes are provided by occurrences of rootlet-bearing (in the growth position) horizons and/or very ferruginous (goethitic) horizons in the deposits at many localities. Similar sub-aerial conditions also typify the 'Bagshot Beds' considered earlier. The kaolinite partings in the 'Bracklesham Bed V' of Fisher (1862) at Whitecliff Bay may, however, have formed by 'diagenisation and dialysation' (Keller, 1981) of primarily deposited smectite that dominates in the lignite-seam matrix. Kaolinite formation by these processes has been advocated for some swamp-related flint clays in the U.S.A. by Keller (1981). Although Gilkes (1966) found the kaolinite partings to contain vermiforms , their detailed textural features are not known; a further investigation of this kaolinite could throw more light on sedimentological conditions at Whitecliff Bay.

The inferences of warm aerial conditions bordering on tropical-like climates prevailing during much of the Middle Eocene times seem to be likely. The period also witnessed the transgression of the warm Bracklesham Sea (Curry, 1965; Murray & Wright, 1974). However, the floral data of Collinson et al. (1981) and Hubbard & Boulter (1983) showed cooling of the climate compared to the Lower Eocene. Much of the Bracklesham Group is equivalent to the 'Palynology Zones c-d' that Hubbard & Boulter (1983) consider to be characterised by changes from relatively unstable but equable conditions to less equable conditions.

During the Upper Eocene times, derivations of material, as stated earlier, occurred mainly from poorly to moderately weathered sources. The period is equivalent to much of the 'Palynological Zone d' of Hubbard & Boulter (op.cit.). The warm (high thermal maximal) episode of 'Zone e' is probably first manifested as the kaolinite and illite clay mineralogy of the Barton Sand at Alum Bay and, more importantly, the kaolinitic palaeosols developed at the emerged top part of the sand body. The warm episode appears to prevail during deposition of the 'Lower Headon Beds' where penecontemporaneous leachings in the lignitic horizons (primarily regarded as hydromorphic swamp soils) caused greater degradation of the clay phases and some increase in the kaolinite contents. The warm conditions may also have facilitated the accumulation of the freshwater limestones, especially at Alum Bay. The limestones are apparently part of an extensive limestone deposit that continues into the English Channel (Curry & Smith, 1975) and the Paris Basin, where drier and hotter conditions possibly prevailed (Pomerol, 1973).

The succeeding Oligocene sediments studied by Gilkes (1966) are also mainly characterised by the clay Assemblage 1. This would agree with the warm sub-tropical climatic conditions suggested by Daley (1972) from the review of floral assemblages reported by other workers. This is also the cool climate characterising 'Zone f' of Hubbard & Boulter (1983). With the maximum summer temperature shown to be about 10°C by Hubbard & Boulter (1983), it is very improbable that the hot, arid season which Gilkes (1978) advanced for illite neoformation, prevailed in the Oligocene Hampshire Basin. As argued earlier (p.157), the high illite contents of the Oligocene sediments are probably due to the greater contribution of detritus from less intensely weathered sources where illite is abundant and/or the smectite was differentially removed. A warm episode 'Zone v_2' was observed by Hubbard & Boulter (1983) and equated to the time of 'Bembridge Beds' sedimentation. This episode, however, is not reflected in the clay mineralogy of the deposit studied by Gilkes (1966).

5.5 Summary

The clay mineralogy of the Upper Eocene succession in the Hampshire Basin dominantly comprises illite $\gtrsim$ smectite $>$ kaolinite $\simeq$ illite/smectite $\pm$ chlorite. This assemblage is detritally derived and the phases are mostly poorly crystalline. In addition, authigenic kaolinite was formed during penecontemporaneous emergence and pedogenous development of parts of the succession - namely at the top of the Barton Sand and in the pebble bed at Alum Bay.

The probable sources of the clay minerals would include distantly located illite-rich Upper Palaeozoic meta-sediments and Mesozoic sediments, and smectite-rich Upper Cretaceous Chalk deposits. Other possibilities are submarine derived smectites via the North Sea; and re-worked intra-basinally-exposed older (Tertiary) sediments. It is doubtful if the kaolinitised Dartmoor Granites made a significant contribution to much of the succession.

The clay assemblages, as a consequence of their shallow burial history, allow the deduction of warm, humid sub-tropical palaeo-climatic conditions with poor to mild weathering to be made. Localised advanced weathering, allowing kaolinite authigenesis within red-yellow podzol to develop, may have been due to brief very warm climatic conditions coupled with locally good drainage. The very warm period may be equivalent to the warm 'Palynological Zone e' of Hubbard & Boulter, 1983.

CHAPTER 6

GLAUCONIES

6.1 Introduction

Glauconitic sediments constitute a significant proportion of the Barton Clay Formation, particularly in the Highcliffe member and the lower parts of the Naish member. These are the youngest glauconitic sediments exposed in southern England. Older glauconitic sediments of Lower Cretaceous to Palaeogene age are also common in southern England. Glauconies from some of the Cretaceous sediments have been studied mineralogically and chemically by McRae & Lambert (1968), Zumpe (1971) and Buckley et al. (1980). Buckley et al. (1980) included two samples from the Bracklesham Group in their studies. But no such studies, except for K-Ar radiometric dating (Odin et al., 1978), have been made of glauconites in most of the Palaeogene sediments in the Hampshire Basin. In the present study, granular glauconies from glauconitic sediments of the Barton Clay have been separated and studied. The glauconitic phase constituents have been characterised, and their sedimentological significance discussed.

6.2 Review of Glauconies and Glauconite

6.2.1 Terminology

The term 'glauconite' commonly has a dual connotation in geology. It has been used both as a mineral species term and also as a morphological description of green pellets occurring in sediments (Murray, 1891; Schneider, 1927; Correns, 1937). Warshaw (1957) and Burst (1958a,b), using X-ray diffraction, showed that some green pellets, in fact, contained none of the glauconite mineral species, whilst many others contained heterogeneous mixtures of glauconite and other clay mineral species. This double meaning of glauconite has created much confusion, and has led some authors (Millot, 1964; Odin & Matter, 1981) to propose the use of the term glaucony (pl. glauconies) to represent the glauconitic facies (grains, films, etc.) and glauconite or glauconitic-mica to represent the mineral species. These terms are adopted in the present study. In many glauconies the mineral constituents often contain substantial amounts of interstratified expandable layer lattice. Odin & Matter (1981) use the term glauconitic-smectite to represent such expandable lattice phase.

6.2.2 Morphology

Glauconies occur in variable forms. The most common are granular glauconies with sizes ranging from coarse sand to fine silt. Also common, but less obvious, are clay-sized discrete particles and films of finely-disseminated glaucony. Fine glaucony often occurs as coatings on coarser-grained minerals, pebbles and rock-clast. Glauconies showing only partial replacement of the substrate are also frequently observed, and are believed to represent intermediate states between films and pellets (Odin & Matter, 1981).

The external morphologies of granular glauconies are diverse and include ovoidal, tabular, discoidal, mammillary, lobate, spherical, composite pellets, vermicular grains and casts and moulds of microfossils (Triplehorn, 1966). In contrast, the internal morphologies are less variable. In thin section, glauconies are often weakly pleochroic and possess light-green, deep green or yellowish-green colour in plane-polarised light. Glauconies are composed of cryptocrystalline ($< 2\mu m$) material (Triplehorn, 1966) that, sometimes, aggregate into radially-oriented layers on the outside rim (or corona) of the grains (Odom, 1976; Zumpe, 1971; Loveland, 1980), but often are randomly oriented or aggregated throughout the grains. Under the electron microscope, glaucony crystallites vary in size from $< 0{\cdot}5\ \mu m$ to 2 or 3 μm; and are either lath, wafer-like flakes (Borst & Keller, 1969) or flattened blade (Kohler & Koster, 1973). The flakes are thought to typify glauconitic-mica while the blades represent glauconitic-smectite (Odin & Matter, 1981).

6.2.3 Structure and Composition

Gruner (1935) first established glauconite to be an iron-rich 2:1 dioctahedral clay mineral. Later X-ray diffraction studies (Warshaw, 1957; Burst, 1958; Hower, 1961) showed that most glauconites are interstratified with layers of expanding-lattice montmorillonite (smectite) and non-expanding illite. Chemical analyses (Hendrick & Ross, 1941; Weaver & Pollard, 1973; Köhler, 1980, etc.) have also shown the

Table 11 Classification of Glauconitic Materials According to Various Authors

BURST (1958a, b)	HOWER (1961)	BENTOR & KASTNER (1965)
Well Ordered : non-swelling, high potassium lattice showing sharp symmetrical peaks characteristics of micaceous 10Å lattice at 10, 5, 3.3Å. This constitutes the mineral glauconite sensu stricto.	10% Expandable layers (-Montmorillonite)	Class 1 : mineral glauconite, sensu stricto (a) well-ordered 1M with symmetric and sharp diffraction at 10.1, 4.53, 3.3 Å. Reflections (112) and $(\bar{1}12)$ are always present.
Disordered : non-swelling, low potassium lattice, micaceous and monomineralic but with subdued peaks displaying broad bases and assymetric sides.	10-20% Expandable layers (-Montmorillonite)	(b) Disordered 1Md with assymetric basal diffractions broadened at base. Reflections (112) and $(\bar{1}12)$ are absent.
Interlayered Clay Mineral - extremely disordered, expandable, low potassium montmorillonite type lattice	20% Expandable layers (Montmorillonite)	Class 2 : interlayered glauconite, d(001) 10.15Å
Mixed Mineral - mixtures of two or more clay minerals as normal constituents - the most frequent combinations being of illite with montmorillonite, and illite with chlorite		Class 3 : mixed mineral (a) two or more clay minerals (b) mixture of clay with non-clay minerals
(There is no separate classification for pellets containing minerals which could be classed as impurities)		Class 4 : green pellets containing no glauconite.

BORCHERT & BRAUN (1963)	FORSTER (1969)	SHUTOV et al (1972)	BIRCH et al (1976)	ODIN & MATTER (1981)
Type I : Iron glauconite - extremely high Fe content, low Al content.	Type II : Interlayer charge 0.8 (low charge glauconite)	Type IV : $K_2O \geqslant 8\%$	4th Stage of maturity $\sim 9.01\% K_2O$	Highly-evolved glauconitic mica 10Å (001), 8% K_2O
		Type III : $7\% < K_2O > 8\%$	3rd Stage of maturity $\sim 7.96\% K_2O$	Evolved glauconitic mica 10Å (001), 6% K_2O
Type II : Ordinary glauconite - average content of Fe and Al.		Type II : $6\% < K_2O > 7\%$	2nd Stage of maturity $\sim 6.73\% K_2O$	Little-evolved glauconitic mica 10Å (001), 4% K_2O
Type III : Alumina glauconite - low in Fe but high Al content.	Type I : Interlayer charge 0.88 (High charge glauconite)	Type I : $K_2O \leqslant 6\%$	1st Stage of maturity $\sim 5.22\% K_2O$	Nascent glauconitic smectite 14Å (001), 4% K_2O

variability of the glauconies composition and structural formula. Much of the chemical variation is due to differing amounts of interstratified layers.

Variations in composition is believed (Burst, 1958; Birch et al., 1976; Odin & Matter, 1981) to be related to, and reflect, the extent of evolution (or stage of development) of glauconies. The well-evolved glauconies predominantly consist of glauconitic-mica, whereas glauconitic-smectite is more abundant in the little-evolved or immature glauconies. The relationship between composition and extent of glaucony evolution, according to some authors, is given in Table 11. The evolution of grains within a given horizon may be homogeneous or heterogeneous. Actually, the highly-evolved glauconies are not common; they have been recorded in a few rocks, including the Ordovician of Estonia (Odin & Matter, 1981) and the Cambrian Lower Franconia Formation in Wisconsin, U.S.A. (Burst, 1958b).

6.2.4 Genesis

Extensive reviews of literature on the formation of glauconies have been undertaken by McRae (1972), Weaver & Pollard (1973), Velde & Odin (1975), Birch et al. (1976), and many others. A very recent review by Odin & Matter (1981) contained a far-reaching and radical reappraisal of the modes and controlling factors of glaucony formation. These include the nature of the parent-materials (or substrate) and the environmental conditions present.

i) Parent materials: Glauconies can form from many types and sizes of substrate. These include internal moulds of microfossils, especially foraminiferal tests (Ehlmann et al., 1963); faecal pellets (Takashashi & Yagi, 1929; Tooms et al., 1970; Pryor, 1975); biogenic carbonate debris (Lambroy, 1974); mineral grains and rock fragments, including silicates, quartz, calcite, dolomite, phosphate and volcanic and plutonic rocks (Weaver & Pollard, 1973; McRae, 1972).

As will be described later, glauconies form by progressive replacement of substrate material. The rate of growth and evolution of the glaucony depends on the diffusion of ions between semi-confined micro-environments within the substrate material and the open sea-water and/or interstitial waters (Odin & Matter, 1981). Thus one might expect that the size, degree of fracturing and relative solubility of the substrate would be important factors.

ii) Environmental conditions:

a) Water depths of 50-500m within the continental shelf and upper continental slopes are conducive for glauconitisation. In waters of less than 50m depth, current turbulency may affect the very sensitive range of glauconite stability by bringing the grains into the oxidising zone and subjecting them to re-working (Odin & Matter, 1981).

b) Moderately alkaline (pH 7-8) and normal sea-water salinity (~ 33‰) would be needed for stabilisation of neoformed 2:1 clays.

c) Mildly-reducing (Eh ~) conditions at the sediment/water interface and near-surface low level micro-biological activities would also be required.

d) Very low, or even negative sedimentation rates are essential for the growth of glauconies. Since the diffusion of ions is involved, the most evolved grains will be those whose substrates have been exposed the longest to the diffusion processes. Using Recent glauconies, Odin & Matter (1981) have shown that formation occurs mainly in open seas away from river mouths or deltas; and that grains exposed for 10^5 - 10^6 years are better evolved than those exposed for lesser (10^3 - 10^4 years) periods.

e) Takashashi & Yagi (1929) and Porrenga (1967) suggested that water temperatures of 15-20°C were most conducive for glaucony formation. However, the distribution of Recent glauconies extend from the tropics to cool-temperate oceans. Cloud (1955) and Fairbridge (1967) suggest that suitable water temperatures would be attained at depths as shallow as 30m in the temperate regions, but mainly at depths greater than 250m in the tropics. Extensive glauconitisation is common in zones of warm and cold current convergence because of associated high organic productivity.

6.2.5 Modes of Formation

There are two main current theories of glaucony formation. The earlier, 'Layer Lattice' theory, was first propounded by Burst (1958a,b).

This envisaged parent materials of degraded 2:1 layered lattice structures altering to glaucony. It was thought that the degraded structures possessed low lattice charge and were subjected to a gradual adsorption and substitution of Fe^{3+} in octahedral layers. An increase in the octahedral charge would then be balanced by potassium adsorption into inter-layer positions. This would result in the progressive contraction of expandable layers into a 10Å non-expandable type. Odin & Matter (1981) suggest that this theory is defective in that the most common parent material is kaolinitic (1:1 layered-lattice). Only in rare instances are 2:1 lattices (smectite) involved (i.e. Velde & Odin, 1975). The layered-lattice theory also does not account for glauconies associated with non-clay materials. The theory also lacks geochemical support. with no correlation between iron and potassium (Weaver & Pollard, 1973; Birch et al., 1976). There is even evidence for the presence of high amounts of iron at the onset of glaucony formation (Ehlmann et al., 1963; Seed, 1965; Forster, 1969). These led to the proposal of an alternative theory by two groups of workers. These are referred to as the 'Epigenetic Substitution' theory (Edhlmann et al., 1963) and the 'Verdissement of Glauconies' theory (Odin & Matter, 1981). These envisaged the diffusion of iron into the potential substrate, very early in the diagenetic process of glauconitisation. The iron emplacement was independent of the potassium fixation. Growth was maintained by the continuous diffusion of ions (K, Al, Si, Mg, etc.) from sea-water and/or interstitial water into a semi-open micro-environment within the substrate. Velde & Odin (1975) and Odin & Matter (1981) further argued that the growth involved an early phase of in situ crystallization of smectite-type clay with composition intermediate between montmorillonite and nontronite. The latter phase involved recrystallization of earlier formed smectite - into illitic types. Growth would be inwardly from the surface, possibly perpendicular to grain walls, and also enhanced along cracks, fissures and other porosity-enhancing features. Concurrent with growth would be loss of primary texture and/or deformations resulting from displacive and differential growth of the glauconitic crystallites in the substrate material.

6.3 Glauconies from the Barton Clay Formation

6.3.1 External and Internal Morphologies

The coarse glauconitic grains are mainly moulds of foraminiferal tests in spheroidal, oval and, less commonly, discoidal and subangular forms (Plates 59; 61a, b). The finer grains are mostly subangular or sub-rounded (Plates 60, 61a). They all possess smooth surfaces, a feature which, along with the general roundness of the grains, Odin & Matter (1981) thought would mainly result from long-time exposure of evolving glauconies to sea-water. Alternatively, the surface smoothness and subangular grains could have resulted from the current re-working and winnowing of earlier formed coarser grains.

Very common on the grains are shallow surface fissures that appear to contain greyish brown material. The fissures appear to be relicts of sutures or ornamentation of the foraminifera tests. Triplehorn (1966) considered similar features observed on mammilated and lobate grains to be shrinkage or aggregation cracks depicting the grain formation via semi-solid or colloidal aggregates. Galliher (1935) thought them to be expansion cracks of proto-glauconitic colloidal aggregates. Odin & Matter (1981), however, suggest that the fissures might be deformation features during the late growth phase. They will be related to relatively rapid differential, displacive growth of crystallites at the centres of the evolving grains.

In addition to the relatively large granular glauconies described above, spots, coatings and clay-sized glauconies were observed. Patchy film-coatings of glauconies were observed on detrital quartz grains, although these were not common. The clay-sized glaucony constitutes a substantial, but difficult to estimate, part of the $< 2\mu m$ clay fraction of the glauconitic sediments in the Upper Eocene succession under study.

In thin section, the glaucony grains are composed of pleochroic green or yellowish-green, randomly oriented masses of interwoven micro-crystals. The grains mostly possess a thin ($< 10\ \mu m$), ragged or diffused outer rim, but no corona-rim wall. This differentiates the Eocene glauconies from the corona-rim possessing Cretaceous-age grains studied by Zumpe (1971) and Loveland (1980).

Under the SEM, the glauconies were seen to be composed of variously oriented aggregated materials. In the thin ($< 5\ \mu m$) outer walls, the aggregates were flattened and aligned parallel to the wall

(Plate 61b,c). The flattening could have been due to the growth pressure of the crystallites against the enclosing inner wall of the substrate, the foraminiferal tests. Away from the walls, the grains consist wholly of 2-5 µm-sized platy crystallites. These are often aggregated into 6-20 µm-sized sheaf-like bunches (Plates 61e - j) and, sometimes, mound-like bulbous and interwoven aggregates (Plates 61h - j). These are thought to be illitic materials. They are similar to the 'delicate wafer-like flakes and book-like crystallites' that Borst & Keller (1969) described from some glauconies, and believed to be inherited illitic parent material. According to Odin & Matter (1981), the flakes are probably glauconitic-mica crystallized from earlier formed glauconitic-smectite, i.e. the flakes are late-phase crystallites typifying highly-evolved glauconies.

It is significant that bladed crystallites, believed to typify glauconitic-smectites (Köhler & Köster, 1976), were not observed in the Barton Clay glauconies.

6.3.2 Structure and Compositions

The similarity of the fine and coarse glaucony grains petrologically also extend to the X-ray characteristics and chemical composition.

The observed diffraction peaks (Figs. 26a, b) are wholly attributable to glauconite; so the glauconies contain no detectable amounts of mineral impurities. The 10·04Å (001), 4·54Å (020) and 3·33Å (003) reflections are slightly asymmetrical with fairly broad bases. The 3·64Å $(1\bar{1}\bar{2})$ and 3·09Å $(11\bar{2})$ reflections are present as small, very broad peaks. These suggest some degree of structural disorder. Glycolation of oriented smears of the glauconies produces no shift in the peak positions of the basal reflection. This indicates the absence, or suggests the presence of insignificant amounts, of expandable lattice phase. The Barton Clay glauconies can be described as 'monomineralogical glauconitic-mica of the disordered, non-swelling 1 Md mica-polymorph'. The dioctahedral nature of the glauconite-mica is confirmed by the 1·54 - 1·516Å(060) reflections. This differentiates the glauconies from the common dioctahedral illites with 1·50Å(060) (Zen, 1955; Grim, 1968) and the greenish celadonite with 1·509Å(060) (Grim, 1968; Buckley et al., 1980). The absence of 7.2Å reflection also shows that the grains are not barthierine (Odin & Matter, 1981).

The chemical composition of the grains (Table 12) falls well within the range of average compositions reported for glauconies (Weaver & Pollard, 1973; Köhler, 1980). The mean structural formula of the Barton Clay glauconies is:

$$(Si^{4+}_{3.69}Al^{3+}_{0.31})(Al^{3+}_{0.25}Fe^{2+}_{0.18}Fe^{3+}_{1.28}Mg^{2+}_{0.33})Ca^{2+}_{0.06}K^{+}_{0.65}O_{10}(OH)_2.$$

There is very little Al^{3+} substitution for tetrahedral Si^{4+}. The values of the octahedral cations (2.04 ± 0.03) are very close to the ideal 2.00 values for dioctahedral 2:1 phyllosilicates. This indicates that there is little excess octahedral occupancy, and also little or no interlayer hydroxyl complexes of iron, magnesium and aluminium, such as was the case for some glauconies analysed by Thompson & Hower (1975). The Fe_2O_3 contents of over 20% account for the high R^{3+}_{Oct} value of 1.51 and the Fe^{3+}/Fe^{2+} ratio of about 7. These high ferric ion contents support the observations of Shutov et al. (1970b) that glauconies in Tertiary (and Cretaceous rocks contain relatively high Fe^{3+}_{Oct} compared to those of other ages. High (5) Fe^{3+}/Fe^{2+} ratios are also thought (Warshaw, 1957; Weaver & Pollard, 1973) to have some relationship to the greenish colour of granular glauconies and the high proportion of contracted 10Å layers in the glaucony structure. These also show the glauconitic grains to be different from the less iron-rich ferric-illites of continental sediments (see Kossovskaya & Drits, 1970; cf. Velde & Odin, 1975).

Using the relationship between potassium content, percentage expandable layers and cation exchange capacities (c.e.c.) in glauconite and aluminous illite-smectite (Figs. 3 & 4 of Manghnani & Hower, 1964; Figs. 4 & 5 of McRae & Lambert, 1968), the Barton Clay glauconies, with their K^+ int. layer value of 0.65 ± 0.04, should contain between 85% and 95% illitic layers or 5-15% smectite layers, and possess c.e.c. values of about 10-20 megv/100g. The deduced 5-15% expandable lattice phase content is far in excess of the nil or insignificant amounts of expandable phase indicated by X-ray diffraction. It is also at variance with the micro-texture in which no bladed crystallites of glauconitic smectite were observed. These variances, albeit minor, could mean that the use of compositions to differentiate variously evolved glauconies (cf. Table 11) should be regarded as subjective or subtle; at least for evolved and highly-evolved glauconies of Odin & Matter (1981), or the

TABLE 12: Chemical Composition and Structural Formula of Glauconitic Grains from the Upper Eocene Barton Clay Formation, Hampshire Basin.

Sample	BBB-38		BBB-47		BHC-1		ABBB-1		WBBB-1		Mean %	Standard Deviation ±
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse		
%												
SiO_2	48·84	49·91	49·38	52·43	50·58	49·47	49·90	50·13	50·04	49·87	50·06	0·96
TiO_2	0·13	0·14	0·14	0·11	0·35	0·07	0·18	0·11	0·16	0·12	0·15	0·08
Al_2O_3	6·09	5·53	7·15	6·76	6·36	5·85	6·26	6·24	6·81	6·20	6·33	0·48
FeO	3·20	3·39	3·23	3·03	2·64	3·03	3·10	2·89	nd	2·21	2·97	0·36
Fe_2O_3	23·27	21·92	22·17	22·66	23·64	24·79	20·12	22·70	25·11	23·35	22·97	1·44
MgO	2·67	2·59	2·79	2·49	2·73	2·69	4·10	2·98	3·35	3·41	2·98	0·50
CaO	0·53	0·09	0·38	0·73	-	0·50	0·48	0·62	0·10	0·15	0·36	0·25
Na_2O	-	0·05	0·02	0·20	-	-	-	-	-	-	0·03	0·06
K_2O	6·96	6·97	6·78	7·14	6·54	7·20	7·58	6·83	6·54	6·42	6·90	0·35
P_2O_5	0·08	0·07	0·05	0·10	0·05	0·07	0·06	0·03	0·04	0·04	0·06	0·02
L.O.I.	8·60	9·85	8·20	nd	6·95	7·70	8·15	7·45	8·15	7·95	8·11	0·81
Total	100·37	100·51	100·36	95·65	99·84	101·37	99·93	99·98	100·30	99·72		
STRUCTURAL FORMULA BASED ON 11 OXYGENS (ANHYD.)												
Tetrahedral												
Si^{4+}	3·67	3·77	3·67	3·74	3·72	3·65	3·72	3·70	3·67	3·70	3·69	0·04
Al^{3+}	0·33	0·23	0·33	0·26	0·28	0·35	0·28	0·30	0·33	0·30	0·31	0·04
Octahedral												
Al^{3+}	0·21	0·26	0·30	0·31	0·27	0·16	0·27	0·24	0·26	0·24	0·25	0·04
Fe^{2+}	0·20	0·21	0·20	0·18	0·16	0·19	0·19	0·18	nd	0·14	0·18	0·02
Fe^{3+}	1·31	1·25	1·24	1·22	1·31	1·38	1·13	1·26	1·39	1·30	1·28	0·08
Mg^{2+}	0·30	0·29	0·31	0·27	0·30	0·30	0·46	0·33	0·37	0·38	0·33	0·06
Octahed.	2·03	2·01	2·05	1·98	2·03	2·03	2·04	2·02	2·01	2·07	2·03	0·03
Interlayer												
$Ca^{2+}/2$	0·08	-	0·06	0·10	-	0·06	0·06	0·10	-	0·04	0·06	0·03
Na^+	-	0·01	-	0·03	-	-	-	-	-	-	-	-
K^+	0·67	0·67	0·63	0·65	0·61	0·68	0·72	0·64	0·61	0·61	0·65	0·04
Inter-layer	0 75	0·68	0·69	0·78	0·61	0·74	0·78	0·74	0·61	0·65	0·70	0·06

well-ordered and disordered non-swelling phase-containing glauconies of Burst (1958b).

Finally, the chemical compositions obtained in the present studies are very similar to that obtained by Livering (in Fisher, 1862) for glauconies from the basal parts of the Highcliffe member at Highcliffe. It is a credit to the skill of the nineteenth century analyst.

6.3.3 Genesis and Sedimentological Conditions

Glauconies in the Barton Clay Formation are predominantly composed of glauconitic-mica and could be regarded as equivalent to the evolved/highly-evolved glauconies of Odin & Matter (1981). The presence of glauconies in the Barton Clay raises the question of origin, i.e. detritally derived or authigenic; and aspects of the prevailing sedimentological conditions. These are considered below.

Probable glauconitic source rocks include the Cretaceous 'Lower Greensands' and Lower Chalk in regions flanking the Hampshire Basin (Melville & Freshney, 1982), and intrabasinal earlier Palaeogene sediments. But glauconies are very susceptible to alteration in surface conditions (Abudelgawad et al., 1975), and any grain that survives weathering and transportation would be expected to show alteration features - in particular, iron oxide coatings. No such features or coatings were seen in the glauconies studied, so they are not likely to be land-derived detritus.

Derivation by submarine re-working is unlikely. One could think of glauconies forming in deeper waters further out in the Barton Sea and, by bottom current re-working, becoming incorporated in the accumulating land-derived detritus of the Barton Clay. Possible break-up and winnowing of grains during the re-working could have produced the sub-angular finer-sized glauconitic grains. Since re-working could only have been within wave-base levels, the water would possibly have been well aerated and the glauconies would have suffered some alteration. The lack of alteration features, and the suggestion that break-up of large glaucony grains could occur during a long period of evolution (Odin & Matter, 1981), makes the idea of derivation by submarine re-working rather tenuous. Another flaw in the idea is that there are no patchy or inhomogeneous accumulations or distribution of the glauconies in the glauconitic sediments as might be expected for current-concentrated material such as the shell drifts in the succession at Barton. Re-working from places further out to sea and mixing with incoming river-transported detritus would not have produced the continuous homogeneous mixing for the long period required to deposit > 25m of glauconitic sediments over a lateral distance of more than 15 Km.

The glauconies had probably formed by the 'verdissement mode' of Odin & Matter (1981), with foraminiferal tests acting as the substrate materials. Walls of foraminiferal tests have acted as a good semi-permeable interface for ionic diffusion, whilst spaces created by decay of protoplasm within the test have provided semi-confined micro-environments and reducing conditions conducive for glauconitisation. The possibility of the glauconies being formed by the 'layer lattice mode' of Burst (1958b) or from any parent material, for that matter, cannot be advanced because of the absence of 'impurities' that could, otherwise, be regarded as 'relicts' of parent material. But if there had been parent materials, perhaps they have been completely altered to glauconies during the long (10^4 - 10^6 years - Odin & Matter, 1981) period that glauconitic-mica takes to evolve.

The probable nature of the Barton Sea and rate of sediment accumulation are two aspects of the early Upper Eocene sedimentation that may be assessed from the presence of the glauconies.

The distribution of Recent glauconies, although extending over wide latitudes (50^{o}S - 65^{o}N:**Odin&Matter,op.cit.**),suggests that glaucony predominantly forms in shelf environments often removed from outlets of detrital-laden drainages, and in water depths of > 30m, bottom temperature of 16-20°C and a very low rate of sediment accumulation or non-deposition (Fairbridge, 1967). It is questionable if all these conditions strictly prevailed in the Barton Sea. Cool water (16-18°C) shelf regimes with water depths of about 50m possibly existed for most of the period of deposition of the Barton Clay. Evidence for this is provided by foraminiferal assemblage in the sediments (Murray & Wright, 1974). But then the presence of abundant plant matter and some stray estuarine mollusc fossil shells (Burton, 1929), indicate nearness of land areas and drainage outlets close to Highcliffe. Nearness of stream outlets would not be expected to facilitate glauconitisation. But as glaucony formation did occur, then other sedimentological factors would have been operative. Apart from the conducive water temperature mentioned earlier, the more significant factors would be the rate at which detritus for the Barton Clay accumulated, and the abundance of deposited detrital iron-oxide.

A relatively uniform sedimentation rate of about 2·5 cm/1000 years has been deduced for the Palaeogene Hampshire Basin by Odin et al. (1978), following a work on K/Ar radiometric age of glauconitic grains in the Tertiary sediments of north-west Europe. Although that rate is within the average 2-4 cm/1000 sedimentation rate for Recent sediments (Davies et al., 1977), it is nevertheless a low rate when compared to rapid depositional rates of several tens and hundreds of centimetres per thousand years, such as that of shallow marine deposits off the Mississippi delta (~ 400 cm/1000 years, Füchtbauer, 1974), and the Cariaco Trench in the Caribbean Sea (~ 46 cm/1000 years, Toth & Lerman, 1977).

A manifestation of slow depositions in the Barton Sea is the penecontemporaneous exposure of calcareous concretions, formed in shallow-burial diagenetic conditions (see Chapter 14) over a considerable length of time allowing encrustation by mollusc shells. Other evidences include the preserved trace fossil impressions and burrows in the sideritised 'Shell Bed' at Barton; and the pebble bed at Alum Bay that had emerged and allowed to develop as part of a goethitic red-yellow podzol palaeosol (see Chapter 16).

It is therefore probable that the supply and accumulation of clastic detritus to the Barton Sea were respectively low and slow. The low detritus supply might, as previously suggested in Chapter 4, be due to extensive vegetation cover and inland ponds in the extensive low-lying flood plans believed (Jones, 1981; Plint, 1983) to border the Hampshire Basin. The slow sedimentation would thus allow longer residence period of evolving glauconies at or close to the sediment/water interface.

Influx of iron-oxide becomes important for consideration when it is appreciated that the glauconitic-mica grains could not have taken the very long, 10^4-10^6 years, period advocated by Odin & Matter (1981) as essential. This is because, assuming the 2.5 cm/1000 years sedimentation rate obtained for the Palaeogene Hampshire Basin by Odin et al. (1978), the 20-30m-thick glauconitic sediments of the Barton Clay would, together, have accumulated over a period of $\sim 10^6$ years. Each of the several beds concerned would certainly have, thus, accumulated in a much shorter time. Sedimentological factors are, hence, inadequate to account for the glauconies.

Glauconitisation is generally believed to involve utilisation of dissolved-iron contents of sea-water. But this is mainly in trace ($<$ 1 ppm) concentrations (see Garrell & Mackenzie, 1971). Iron derivation from such sources would have to be over very long periods for well-evolved glauconies. Hence, other iron sources would most certainly have contributed to the glauconies under study. The most probable would be detrital iron-oxides. In oxic conditions at sediment/water interface, the detrital iron will largely be in a colloidal state and can be easily mobilised for the glauconitisation. Influx of detrital iron was very extensive in the Hampshire Basin; indications of this are given by the disseminated goethites, goethitic palaeosols and the early diagenetic ferroan calcites and siderites in the succession under study. These are discussed elsewhere. The correlation of iron-rich glauconies with periods of high iron influx was also realised by Shutov et al. (1970a) from works on glauconies of various ages in the U.S.S.R.

6.4 Summary

Widespread authigenic formation of glauconies occurred in the shelf Barton Sea most likely as a result of high influx of detrital-iron oxides and the slow accumulation of clastic detritus. The investigated glauconitic grains are wholly composed of platy crystallites in sheaf-like or wafer-like aggregations. They are of a high-Fe, moderate-K, glauconitic-mica variety formed, predominantly, within foraminiferal test substrates.

Fig.26: Sketch of Diffraction Traces of a) Smeared mounts and b) Powdered Glaucony Grains From The Barton Clay Formation (Sample BBB-47)

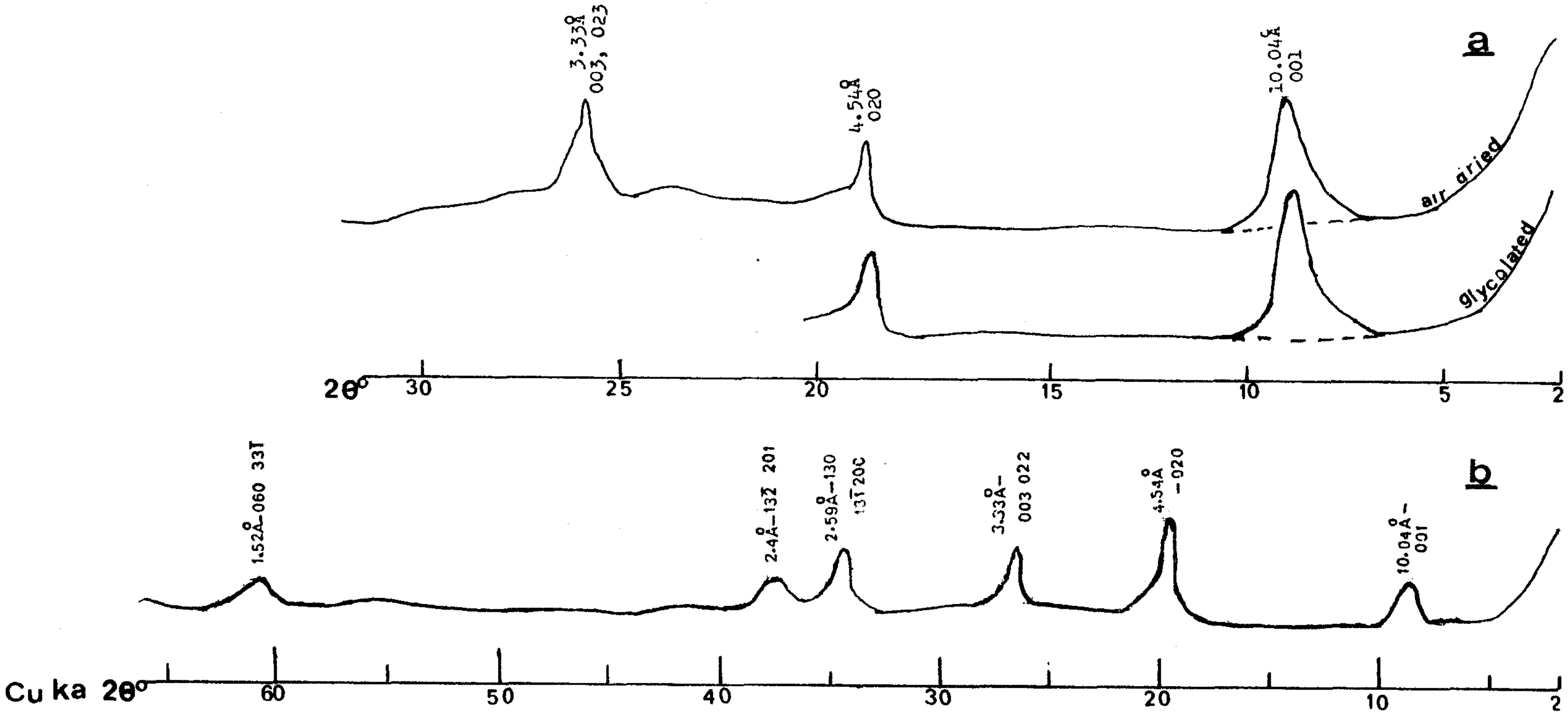
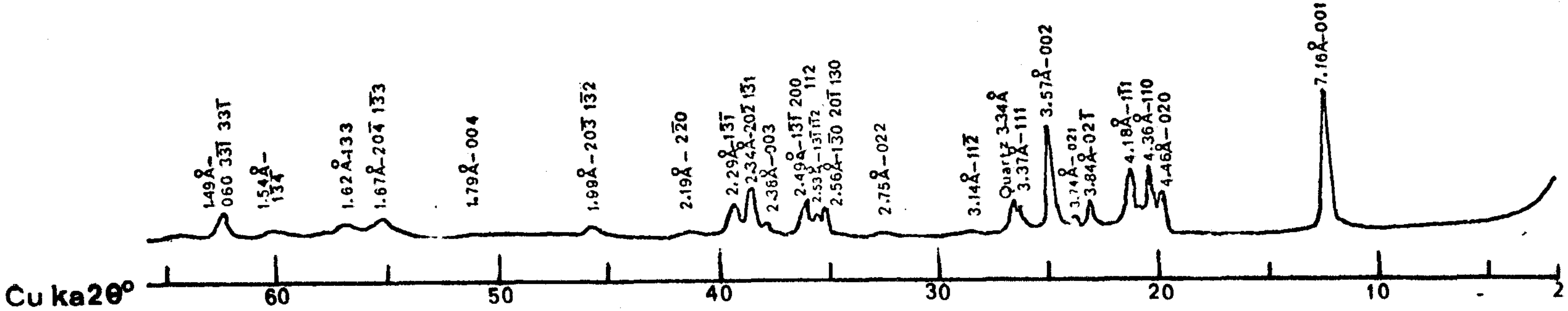


Fig.27: Sketch of Diffraction Trace of Authigenic Kaolinite From The Red Yellow Podzol Palaeosol, Barton Sand Fm.; Alum Bay



CHAPTER 7

AUTHIGENIC KAOLINITE

7.1 Introduction

Lenses and specks of kaolinite occur in the indurated horizon, veson (IIBr ir & m) of the red-yellow podzol palaeosol, Profile A (Plates 18a, b; Fig.6b) at the top of the Barton Sand Formation exposure at Heatherwood Point. In order to establish the mode of formation of the mineral, and hence obtain some insight into the development of the palaeosol, it has been studied in some detail. Petrological investigations of its morphology were made with a scanning electron microscope. Using powdered (hand-ground) material prepared from a fairly large ($\sim$ 1½ cm by 1 cm) lens, the chemical composition and aspects of its crystallographic characteristics were also determined. A sketch of the diffraction trace obtained is given in Figure 27, whilst the chemical composition and the structural formula are given in Table 13.

7.2 Macromorphology

Kaolinite, in the red-yellow palaeosol at the top of the Barton Sand at Heatherwood Point, occurs as greyish-white specks and $<$ 1 cm-sized lenses in association with voidal and grain-coating goethite. The specks and lenses (henceforth referred to a kaolinite-masses to distinguish them from kaolinite clay-phase) are mostly irregularly disseminated and oriented in the indurated soil horizon, only a few being concentrated within or aligned parallel to bedding planes (planar voids) (Plate 18c,d). The kaolinite masses are texturally fine-grained, non-slacking, compact and break with conchoidal fracture. Their properties typify 'flint-clays' (Keller, 1968) and apparently distinguish the kaolinite masses from the 'free-slacking kaolinites' that characterise residual deposits in many parts of the world (Keller, 1982). The 'flint-clay type' kaolinite masses, by their mode of occurrence (i.e. constituent of an in situ sandy podzol) also differ from flint-clay kaolin deposits that have a sedimentation or hydrothermal primary origin (Keller, 1968, 1978, 1982), or flint clays and tonstein of volcanic and volcanoclastic origin (Bohor & Pillmore, 1976; Keller, 1977b).

7.3 Micromorphology

The micromorphology and textural features of kaolinite from diverse sources and origins have been extensively studied by Keller in a series of publications between 1938 and 1982. The author showed that although kaolinite commonly occurs in the form of books and vermiforms of platy crystals and variably-sized platelets, there are marked differences in textural aggregations in relation to modes of occurrence and origin. In primary (first cycle) weathering profiles (i.e. Missouri Granite - Keller, 1977) and free-slacking kaolin, the kaolinite forms are mostly randomly oriented and loosely aggregated into an open, porous texture. In flint clays, where kaolinites are possibly secondary precipitations, the 'dialyzation' and 'diagenization' of earlier deposited clay minerals (Keller, 1981), the crystals are relatively better crystallized and much more intergrown, interlocked and tightly or densely packed.

In the present study, the microtextures of the kaolinite masses observed under the SEM appear to be intermediate between the loose and tight crystal-packing textures. The gross textural feature observed at magnifications of < 5000X is that of dense aggregations of randomly oriented fine-sized kaolinite crystals (Plates 56a,b). This resembles the dense packing feature of a 'sandy' flint clay in Missouri, U.S.A. (Fig. 18 of Keller, 1982), and of some tonstein in Australia (Figs.1-3, 7 and 20 of Keller, 1977).

At higher magnifications (> 5000X), the gross dense texture becomes less obvious, although the three kaolinite crystal forms that can now be distinguished are intimately mixed and/or interwoven. The kaolinite forms, in decreasing order of abundance are:

i) Small (0·3 - 0·5 μm sized) subhedral platy crystals (Plates 56c,h,j) usually in stacks and small aggregations. They are the dominant crystal form, and mostly stack face to face, or have edge to edge contact. The crystals are also commonly observed coating the other much larger crystal forms.

ii) Wedge and elongated S-shaped vermiforms and books of tightly-packed subhedral platy crystals (Plates 56e - j).
The crystals are individually less than 0·1 μm thick but have 2-10 μm wide basal (001) faces. They are mostly closely stacked face to face, but in places splitting or delamination

has occurred, with some crystals showing a tendency to roll up (Plates 56i,j).

iii) Less common are disseminated, relatively large (5-10 µm sized) platy, pseudohexagonal crystals with serrated or slightly curved edges, and with thickness up to 1 µm (Plate 56h). They usually occur singly, but occasional loose stackings of a few individuals can also be seen.

Although the crystal forms described above are intimately mixed or intergrown, they significantly differ from the 'tightly interlocking, compact packets and sheaves of kaolinite with mutual boundary contacts' that typify flint clays (cf. Figs.15-17 of Keller, 1982) and, as well, the well crystallized kaolinites of hydrothermal origin (cf. Figs. 21-23 of Keller, 1982). Rather, the crystal forms and texture of kaolinite in the presently-studied kaolinite masses closely resemble the crystal morphologies and open texture of kaolinites in some primary weathering profiles and a free-slacking kaolin studied by Keller (cf. Figs.1, 4-6, 9 and 13 of Keller, 1982). A major difference from many of the weathering profile examples is the absence or non-observation of elongate or tubular crystal morphologies (mainly halloysite presumably), nor was growth contact of kaolinite from altered feldspar grains observed.

7.4 X-ray Characteristics (Crystallinity and Structural Disorder)

Having employed SEM to show that the kaolinite masses essentially comprise platy crystals of kaolinite, X-ray diffraction was further used to deduce the degree of crystallinity and structural disorder (if any) in the a-b plane. Different authors have employed various X-ray methods involving both basal and non-basal reflections from oriented smear-mounts and/or ramdomly oriented powdered materials. Details of the principles involved and methods are contained in many publications, including those of Hinckley (1963), Wiewora & Brindley (1969), Placcon & Tchouber (1977), and Brindley (1980). In the present study, powdered material was used, and the variously obtained characteristics are:

a) Using the relationship between width at half peak height of the 7·2Å (001) reflection and crystallinity grade of Wiewora & Brindley (1969), the $0{\cdot}3^{\circ}2\theta$ width measurement made suggests poor crystallinity. Lower width values ($0{\cdot}1 - 0{\cdot}2^{\circ}2\theta$) would have meant a sharp, relatively symmetrical reflection of well-crystallized and well-ordered crystals, whilst higher width values ($> 0{\cdot}35^{\circ}2\theta$) would be for very poorly crystallized and highly disordered kaolinite.

b) Using the heights of the $1\bar{1}0$ and $11\bar{1}$ peaks above a line drawn from the trough between the 020 - $1\bar{1}0$ peaks to the background just beyond the $11\bar{1}$ peak (Hinkley, 1963), a Hinckley Crystallinity Index value of 0·65 was obtained. This value may be within the 0·3 - 0·8 values possessed by disordered kaolinites in some Cretaceous-Eocene flint clays in Japan (Sudo & Shimoda, 1980) and Georgia, U.S.A. (Hinckley, 1963). In comparison, lower crystallinity index values (0·1 - 0·6) typify well crystallized kaolinite; examples of which are kaolinites in some Pliocene deposits in Japan (Shimizu, 1972 - quoted in Sudo & Shimoda, 1980).

c) The relationship between crystallinity and the splitting or resolution of the doublet reflection - 4·13A($1\bar{1}\bar{1}$) and 4·18A($1\bar{1}1$) (Brindley, 1980) - was also considered. The material under study only shows a small 'shallow shoulder' partial resolution of the ($1\bar{1}\bar{1}$) reflection. This is regarded as characteristic of disordered kaolinite (Keller, 1978b; Sudo & Shimoda, 1980). Had the doublet been well split, a well-ordered kaolinite would have been inferred.

d) The nature of grouping of the (13ℓ), (20ℓ) and (003) reflections occurring in the region of 35 to $40^{\circ}2\theta$ were also considered in relation to crystallinity. These occur as two groups with three reflections each, a characteristic thought to be typical of slightly disordered kaolinites (Brindley, 1980). Had the kaolinite been highly disordered, the reflections would have resolved into two doublets or, for halloysite, fuse into a continuous band.

From the measurements and observations made above, the kaolinite masses in the podzol palaeosol can be regarded as poorly crystallized and slightly disordered structurally. They thus resemble the b-axis disordered kaolinites that occur in the other horizons of the red-yellow podzol palaeosols. They also very closely resemble the detritally-derived disordered kaolinites in most parts of the Upper Eocene succession under study.

7.4.1 Non-kaolinite Contents

Quartz is the only extraneous material detected in the kaolinite masses. It, however, occurs in trace amounts and is not quantified. The quartz would be incorporated skeletal grains, some of which were observed under the SEM (Plates 56a, b). The absence or non-detection of goethite is significant; it suggests segregation of the clay and iron-oxide phases during precipitation.

7.5 Chemical Composition

Kaolinite is a 1:1 layered-lattice phase with very little ionic substitutions in the structure, and hence little surface charge density and very small adsorption capacity (Brindley, 1980). The chemical composition of kaolinite is thus essentially that of silica, alumina and structural water (Weaver & Pollard, 1973). However, the compositions of natural kaolinites often deviate from the 'ideal' composition. Perhaps, as a result of different modes of formation or derivation and the nature of associated materials, kaolinite may contain trace to small amounts (often $< 2\%$) of titania iron-oxides, alkali and/or alkaline-earths (Weaver & Pollard, 1973).

The chemical composition of the kaolinite masses, by β-probe spectrometer, is given in Table 13. The calculated structural formula is

$$Si^{4+}_{2\cdot03}\ Al^{3+}_{1\cdot91}\ Fe^{3+}_{0\cdot05}\ O_5(OH)_4.$$

The excess silica indicated by the structural formula is possibly due to the presence of free silica (quartz), which, by its trace-amount abundance, was not corrected for in the chemical data. Much of the recorded 1·56% Fe_2O_3 could be due to finely disseminated goethite, although this was largely undetected by X-ray diffraction. Iron incorporated in kaolinite is believed to be generally small, possibly not more than 0·3% Fe_2O_3 (Malden & Meads, 1967). However, high amounts of iron are not uncommonly found present in kaolinites, especially those from tropical soils. Herbillon (1976) reported 2% Fe_2O_3 in such kaolinites. The very low 0·03% TiO_2 content suggests probable derivation of the kaolinite from low titanium-containing materials. It also differentiates the kaolinite from transported, sedimentary kaolin, which may contain as much as 2% TiO_2 (Weaver & Pollard, 1973). Although the titanium may be structurally

Table 13: Composition of Authigenic Kaolinite from the Red-Yellow Podzol Palaeosol (Profile A), Barton Sand Formation, Heatherwood Point, Isle of Wight

Chemical Composition

SiO_2	45·60
TiO_2	0·03
Al_2O_3	36·34
Fe_2O_3	1·56
FeO	n.d.
MgO	-
CaO	0·06
Na_2O	-
K_2O	-
L.O.I.	15·70
TOTAL	99·30

Structural Formula based on 7 Oxygen

Si^{4+}	2·03	
Al^{3+}	1·91	1·96
Fe^{3+}	0·05	

held, it is not improbable that it occurs as adsorbed anatase or even iron-substituted anatase $(Fe,Ti)O_2$ such as those Sayin & Jackson (1975) observed in some soil kaolinites. The 0·06% CaO recorded is also very small and close to the lower detection limits of the element on the β-probe spectrometer. If really present, it could be a relict of the altered parent material.

7.6 Genesis

The kaolinite masses, by their mode of occurrence as lenses and specks and being restricted to the indurated palaeosol horizon only, can be regarded as a product of in situ weathering. It is, in fact, a constituent of a residual red-yellow podzol palaeosol that developed on a quartz-sand deposit - the Barton Sand Formation, at Alum Bay - Heatherwood Point on the Isle of Wight. That mode of occurrence conveniently helps to distinguish it from the flint clay facies (Keller, 1968, 1978), hydrothermal kaolin (Keller, 1982) and, in addition, eliminates any thought of regarding it as a translocated material. The question, however, remains as to whether it is wholly a primary weathering product or has formed (at least partially) by other kaolinisation processes such as secondary crystallization from 'dialysed and diagenised' earlier clay minerals (Keller, 1978) and re-silification of gibbsitic material (Curtis & Spear, 1971). These are considered below, using the crystal morphologies and textural features of the kaolinite masses described above, and the mineralogy and petrology of the whole podzol palaeosols described elsewhere in the present study (Chapter 16).

Kaolinisation is a common feature of present-day weathering zones in humid, tropical to warm temperate climatic areas (Mohr & van Baren, 1954; Chukrov, 1966; Kittrick, 1969; Hunt, 1972). Variously-dissolved soil acids (Grim, 1968; Keller, 1957) would hydrolyse feldspars, micas and other weatherable silicates. Loss of bases and some of the silica through drainage and/or plants' intake would lead to vadose water with alumina:silica concentration ratios of 2:1 conducive for the precipitation of the 1:1 layered-silicate kaolinite (Lukashev, 1970; Velde,1977).

Kaolinite produced during primary weathering (first-cycle or direct weathering) of silicates have been shown to possess open-textural features (Keller, 1982). A similar relatively open texture also characterises the kaolinite masses in the palaeosol, albeit distinct only at high magnification of > 5000X. They are possibly a primary weathering product. Further evidence is given by the crystal morphologies, which mainly comprise loose aggregations of platelets, books and vermiforms. Apparently, the crystals have had sufficient space to grow - a condition that is easier to achieve in surface weathering zones. But if there had really been sufficient space for growth, why then the large variation in crystal sizes of the platelets compared to the books? Perhaps other factors were operative. These could include the number of nucleating sites and ionic concentrations. It is envisaged that, at the onset of precipitation, ionic concentration is high and numerous nucleation sites were available, so the resulting crystals were small. Later, and probably as concentration decreased, crystallization became limited to a few sites - where the books and vermiforms occur. What is certain is the absence of evidence of one crystal form recrystallizing to another form.

The above comment suggests that the kaolinite was precipitated from a solution phase. Supportive inference is given by the void-filling nature of the kaolinite,and the absence of kaolinite coatings on corroded and incongruously dissolved feldspar in the palaeosol that would have suggested direct replacement of feldspars. Further, the non-observation of tubular crystals (kaolinite/halloysite) suggests that the kaolinisation did not involve the formation of such crystals; or, if they had been the early product(s), that they had subsequently transformed into platy kaolinites. Kittrick (1969) has argued that halloysite is thermodynamically unstable with respect to crystalline kaolinite; whilst field evidence obtained by several authors, including Parham (1969), Sudo & Shimoda (1980), Hughes (1980), has also shown that any fast-forming precursors, including halloysite, would with time transform to kaolinite.

The possibility of forming the kaolinite masses by diagenisation of earlier clay material lacks convincing morphological or textural support. Keller (1981) advocated this mode of formation mainly for the densely packed and tightly interlocked packets and stacks of crystallographically well-ordered kaolinite crystals that typify flint-clay facies. The parent material could be illitic, smectitic, or even kaolinitic, and might have gone through one or more previous cycles of weathering or sedimentation. These, within non-marine, low-lying coastal swamps, marshes and stream channels with low energy currents (i.e. paludal and fluviatile environments), and in warm, humid, tropical-like climate, would have undergone depotassification, desilification by way of dissolution, hydrolysis and dialysis during very early diagenesis (i.e. syndepositional). The resulting tightly interlocked crystals further suggest in situ crystallization from a congruent solution or colloid within a limiting confined space. A closely similar dense aggregation observed in the kaolinite masses at low magnifications ($<$ 5000X) is mainly due to the fine-grained nature. But this was less apparent at higher magnifications, which show that the crystals are less interlocked, nor do they possess mutual boundary or reciprocal indentation; they have not grown in confined spaces.

Resilification of gibbsitic clays (Curtis & Spear, 1971) is one other mode of forming kaolinite. Gibbsite and related phases generally result from extreme weathering conditions in tropical regions (Chesworth, 1975). But there is no mineralogical or field evidence that the Barton Sands underwent such weathering phases. However, a similarly extreme weathering has been proved in parts of Britain. From Devon, south-west England, Isaac (1981) has described some lateritic palaeosol and silcrete developed on the Lower Chalk and uppermost parts of the 'Upper Greensands' or on the overlying Tertiary clastic sediments. Similar lateritic soils of Danian age also occur as an interbasaltic formation in Northern Ireland (Wright 1924; Montford, 1970). In the work of Isaac (1981), well-ordered kaolinites constitute the core of goethite granules of ferruginous concretions within mottled zones and red-earth horizons. The contrast of these to the presently-considered material is quite substantial. The Barton Sand had only undergone a weathering similar to that termed by Chesworth (1975) as 'kaolinitic stage of goethite facies of weathering' or equivalent to the 'intermediate and advanced weathering stages' of Kronberg & Nesbitt (1981) that is common in warm and humid, tropical and sub-tropical climatic conditions.

7.7 Summary

The lenses and specks of kaolinite in the indurated horizons of the red-yellow podzol palaeosol at the top of the Barton Sand, at Alum Bay - Heatherwood Point on the Isle of Wight, are possibly primary weathering products. The kaolinite comprises poorly-crystalline, slightly disordered platy crystals in small platelets, vermicules and book forms. They would suggest intermediate to advanced weatherings in a humid, warm climatic condition prevailing during the Upper Eocene times. Petrological features of the palaeosols and variations in mineralogy across the Barton Sand at Alum Bay suggest feldspars to be the mainly altered parent material; however, some illite and smectite could also have been involved.

CHAPTER 8

PYRITE

8.1 Introduction

Pyrite is the only sulphide phase found in the Upper Eocene sediments studied. Its occurrence has been studied, and its genesis inferred.

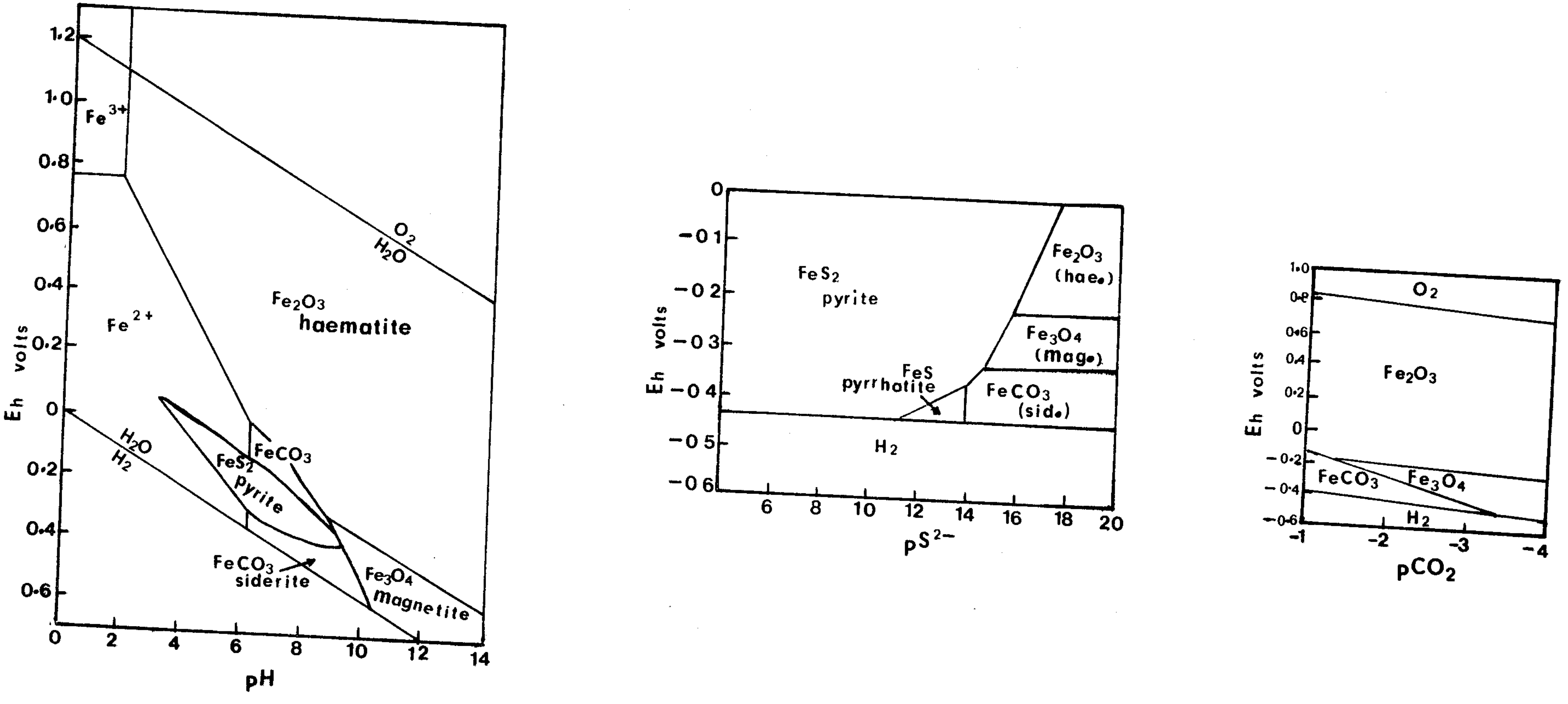
Pyrite is a common constituent of sedimentary rocks and often occurs in association with plant and animal remains, and as disseminated or cementing material. Works on synthetic and natural pyrites have been undertaken by many authors, including Kaplan et al. (1963), Love & Murray (1963), Goldhaber & Kaplan (1974) and Hudson (1980). A bibliography of works on pyrites has been compiled by Love & Amstutz (1966), whilst reviews of much of the literature have been undertaken by Goldhaber & Kaplan (1974),Hudson (1980) and many others.

Factors deduced as conducive to the formation of pyrite include: availability of organic matter for microbial metabolism; presence of reducible sulphate ions (low pS^{2-}); and high abundance of active iron (Fe^{2+}). The rate of sulphate reduction is also important (Goldhaber & Kaplan, 1974).

Pyrite essentially results from processes occurring in the sulphate reduction diagenetic zone (Curtis, 1980). This zone generally occurs within a few centimetres to about 10m burial depth of sediments (Kaplan et al., 1963; Berner, 1980; Curtis, 1980). In euxinic or poorly aerated/drained surface waters, the existence of strongly reducing conditions (Eh 0 to 0·4 - see Fig. 28) could also facilitate pyrite formation. Experimental works (i.e. Stashchuk, 1972; Deelman, 1975) have, however, shown that sulphate reduction reactions could start in oxidising environments. At sediment/water interfaces conducive reducing conditions could be attained in partially enclosed micro-environments such as fossil shell chambers. Even where pore waters are not anoxic, the existence of reducing micro-environments could facilitate pyrite formation (Kaplan et al., 1963).

The source of iron for pyrite formation is dominantly detrital-free or adsorbed iron oxides (Carroll, 1958). The main source of

Fig.28: Stability Fields of Iron Phases (After Krauskopf,1979 & Berner,1971)



sulphate ions is the sea-water; this can contain up to 2,650 ppm dissolved sulphur (Table 4.2, Garrels & Mackenzie, 1971). River waters are not important because of their low (11 ppm) dissolved S contents. However organisms, whose sulphur content can be as much as 1% (Kaplan et al., 1963), can, on decaying, provide substantial amounts of sulphur. Reduction of sulphur is believed to be effected by microbes such as the Desulfovibrio species (Kuznetsov, 1975). H_2S produced from the sulphate reduction reacts with organically solubilised iron (Fe^{2+}) to form pyrite, possibly through iron monosulphide precursors, greigite (Fe_3S_4) and mackinawite ($Fe\ S_{0.9}$) (Volkov & Oustramov, 1957; Berner, 1964; Rickard, 1975). Abundant reducible sulphate ions and sulphur are required to sustain H_2S production and pyrite formation. In conditions of rapid depletion of H_2S but abundance of iron, the monosulphides become more stable, and would form and persist. Pye (1982) has reported such a situation from a low-lying coastal marsh in Norfolk, England. The marsh contains concretions and cemented layers of greigite, mackinawite and siderite. The pyrite decreases and eventually ceases as reducible sulphate ions become exhausted. This is particularly the situation when sediments are buried to depths where sulphate ions' diffusion from sea-water through overlying sediments becomes difficult to maintain, and ceases (Berner, 1980).

Growth of pyrite has been discussed by several authors, notably Berner (1971, 1980). Pyrite growth essentially occurs around or in the vicinity of microbially decomposing organic matter. Sulphate reduction and iron sulphide precipitations that attend organic decomposition cause lowered concentrations of dissolved sulphate and active iron in the vicinity of the organic matter. Chemical gradients could then become established with both SO_4^{2-} and Fe^{2+} diffusing towards the organic matter. This would account for the widespread occurrence of pyrite in association with organic remains (Love & Murray, 1963; Love, 1970; Fowler et al., 1973; Hudson, 1982).

The sulphate reduction rate, in sediments, is not only dependent on the abundance of organic matter and the state of complexing of the organic matter on its availability for biogenic degradation, but is also influenced by the environment of deposition and the rate of sediment accumulation. The environmental variation of the sulphate ions has been stated earlier. Sea-water contains higher dissolved sulphate and, on diffusion, facilitates higher sulphide precipitation in marine sediments. The diffusion of sulphate ions into sediments is highly affected by the rate of deposition (Berner, 1971). Rapid sedimentation, such as the 46 cm/1000 years in the Cariaco Trench (Toth & Lerman, 1977), would allow substantial metabolisable organic matter to be buried with the sediment, but would cause rapid cessation of sulphate diffusion. The sulphate reduction zone would be limited to very shallow depths close to the sediment-water interface (Lerman, 1980; Berner, 1980). Whereas in environments of slow deposition (i.e. 0•75 cm/1000 yr. in Venezuelan Basin, Toth & Leman, 1977) and/or extensive bioturbational irrigation (Berner, 1980), diffusion of sulphate ion can extend to depths of about 10m; although much of the organic matter could become lost by oxidation prior to burial below the oxic upper layer of the sediments.

Pyrite occurs in a variety of forms, the more common being frambroid and macro-crystals or lumps. Pyrite fromboids are believed to result where iron monosulphide precursors had been involved (Sweeney & Kaplan, 1973; Rickard, 1975). However, micro-crystalline pyrites need no necessarily form via precursors. These could precipitate directly from solutions in conditions of low supersaturation of iron sulphides, whereby the solubility product of pyrite is exceeded but that of iron monosulphides is not (Goldhaber & Kaplan, 1974; Howarth, 1979; Hudson, 1980).

8.2 Distribution

In the Upper Eocene sediment under study, pyrite occurs in amounts varying from trace to 3% (Tables 7a - g). Two samples - BBB2 and BRH8 - however, contain relatively high amounts of 4% and 8% respectively. These are also very carbonaceous and fossiliferous. The mineral is most common in clayey sediments, particularly in the Naish member and Lower Headon Beds on the mainland. Pyrite was not detected in the sandy sediments of the Barton Formation and Lower Headon Beds, with the exception of that in the Leaf Bed at Long Mead End, where trace amounts were recorded. This horizon contains numerous ramifying rootlets that are pyritised in places.

8.3 Petrology

Pyrite generally occurs in the sediments in association with organic remains - fossil shells, tests of foraminifera and dinoflagellates and plant matter. Macroscopic pyrites are often seen partially or completely filling shell chambers (Plate 67) and replacing walls of rootlets. Fowler et al. (1975) observed pyritised cells of a swamp-inhabiting deciduous hardwood in the Leaf Bed, but no similarly well-preserved material was obtained during the present study.

Microscopically, irregularly-shaped pyrite masses were observed within tests of dinoflagellates (Plate 75), foraminiferal tests (Plates 68,75) and chambers of pelecypod and gastropod shells (i.e. Plates 6, 67). Also common are disseminated and aggregated individual pyrite crystals, often in association with fossil remains (Plates 31, 74). Under the SEM, the pyrite crystals were seen to vary in size from about 2 μm to 10 μm. They occur mostly in cube and pyritohedral forms. Many are aggregated into framboids with or without shell enclosures (Plates 72a-e).

8.4 Genesis

The mode of pyrite formation in the Upper Eocene sediments may be considered in terms of the depth of sulphate reduction, and the nature of the water bodies.

Pyrite occurs in small ($< 3\%$) in the Upper Eocene sediments and predominantly in association with fossil materials. Similar pyrite occurrences are common in the literature; an example of those in Recent sediments has been documented by Love & Murray (1966) from Christchurch Harbour in southern England. This mode of occurrence underlines the contribution of organic matter and micro-organisms effecting tissue decay in the formation of pyrite, as has been shown by several workers including Goldhaber & Kaplan (1974).

Pyrite formation generally occurs within the sulphate reduction zone of buried sediment. This zone often extends from the sediment/water interface to depths of about 10m (Curtis, 1980). In the Upper Eocene sediments, the sulphate reduction zone is thought to have been within very shallow depths, poasibly a depth of a few centimetres. The major evidence for this, in the Barton Clay Formation, is deduced from the pyrite-containing shell encrustations on calcareous concretions that were exposed contemporaneously in the Barton Sea (Plate 6). The concretions, as shown in other parts of this study, have grown in host sediments with about 65-80% porosity - porosities that are mainly attainable within very shallow depths. Similar very shallow depths of formation deduced for the sideritic nodules and concretaions, in all divisions of the Upper Eocene deposits, also suggest rapid depletion of reducible sulphate ions in the sediments.

Apparently finely disseminated organic matter has not contributed much to the pyrites, rather the pyrite formation was mainly within reducing, semi-enclosed micro-environments provided by fossil shell chambers and cavities in plant matter. Pyrite formation in these materials would best be achieved at, or close to, the sediment/water interface where ionic diffusion from the water bodies is greater (Berner, 1971; Lerman, 1979). This will particularly be the case for the marine Barton Clay. The Barton Sea was possibly muddy during deposition of much of the Barton Clay, but the abundance of benthic foraminiferids in the sediments (Murray & Wright, 1974) would not suggest an oxygen-depleted water bottom condition. However, the water is apparently not well aerated compared to the clear waters in which the bulk of the Barton Sands are deposited. Also reducing conditions prevailing in the muddy sediments of the Barton Clay quite differed from the apparently oxygenating conditions in the porous sand bodies of the Barton Sand, as this lacks pyrite but contains disseminated goethite and goethitic sand moulds of plant matter. In the case of the carbonaceous sediments of the Lower Headon Beds, reducing conditions would have been induced by poor aeration and drainage of water bodies, and the existence of swamps.

Pyrite in many parts of the exposed succession has suffered alteration to goethite, gypsum and favosite. Although many of these exogenous minerals are believed to be largely due to recent weatherings, yet there are palaeosols in the succession that also suggest some contemporaneous surficial processes. This problem is considered further in succeeding Chapters.

CHAPTER 9

IRON-OXIDES - GOETHITE AND LEPIDOCROCITE

9.1 Introduction

Iron oxide phases in the Upper Eocene sediments predominantly comprise crystalline goethite and lepidocrocite, and there is no widespread occurrence of amorphous phases such as limonite. The general distribution of goethite and lepidocrocite in the sediments has been studied, whilst detailed crystal morphologies of some selected materials were investigated towards elucidating the modes and times (recent or contemporaneous) of formation of the minerals. To facilitate discussion of the obtained data, a brief review of the iron-oxide phases is made below.

9.2 Review of Iron-Oxide Phases

9.2.1 Modes of Formation

The study of natural and synthetic iron-oxide phases has preoccupied many authors, including Deb (1950), Norrish & Taylor (1961), De Villiers (1969), Hsu & Ragone (1972), Chukrov et al. (1975), Kühnel et al. (1975), Schwertmann & Taylor (1977) and Goodman & Lewis (1981). The factors found to be important with regard to the occurrence of the various phases are: concentration of iron in solutions; pH; PCO_2; PO_2; rate of oxidation; presence of various dissolved cations; and the presence and abundance of nucleating surfaces (nucleii or seed).

Laboratory synthesis usually involves alkali hydrolysis of solutions of iron compounds under controlled oxidation rates and pH. In nature, iron could be made available from decomposed iron minerals, oxidation of organo-Fe complexes (Van Schuylenborg, 1965; Schwertmann & Fisher, 1965), or from microbial activities (Deb, 1950). Hydrolysis of iron compounds leads to the production of ferric-hydroxide $[Fe(OH)_3]$ monomers which would polymerise further into positively-charged Fe_nO_{3n} polymers (Hsu & Ragone, 1972). The polymers, growing bigger, will attract OH^- ions, lose their charges and settle out of solution as amorphous or crystalline hydrated iron-oxide, FeOOH. This may pass through an intervening, morphologically-distinct globular or spherical amorphous iron hydroxide phase (Hsu & Ragone, 1972; De Villiers, 1969). Early-formed hydroxides and/or hydrous iron-oxide might act as nucleii or seeds for later precipitates. Negatively-charged surfaces of minerals such as clays, might also act as adsorbing surfaces upon which the iron polymers could grow and have their charge-density changed and satisfied. This could account for iron-oxide coatings on clays and other mineral grains.

At neutral pH (i.e. OH^- or HCO_3^-/Fe^{3+} ratios $<$ 1), goethite and lepidocrocite could be precipitated; whilst in more acidic conditions, high iron concentrations and slow oxidation rates, goethite would mainly precipitate. At high alkalinity and low iron concentrations, rapid hydrolysis and polymerisation may ensure and lead to precipitation of amorphous iron gels and/or poorly-crystallised acicular crystals (Hsu & Ragone, 1972).

The presence of cations other than iron may not only cause substitution of iron, but could also have inhibitory effects on crystal growth. The important cations are Al^{3+} (Norrish & Taylor, 1961; Schwertmann & Taylor, 1972 ; Taylor & Schwertmann, 1980), and Si^{4+} (Schwertmann & Thalman, 1976; Kühnel et al., 1975). Others include Ni, Co, Cr and Mn (Brown, 1980). Goethite is isomorphous with diaspore (α AlOOH) and the progressive substitution of the 0·57Å Al^{3+} for 0·67Å Fe^{3+} would continuously reduce the goethite cell-dimensions and crystallinity. The substitution is most reflected by the goethite (111) reflection that changes from 2·453Å of pure phase to lower d-spacings (Thiel, 1963; Brown, 1980). Silica does not substitute for iron, but could arrest the growth of goethite crystals, possibly as a result of thin films of amorphous silica precipitations blocking the nucleation sites of goethite (Kühnel et al., 1975). In contrast, lepidocrocite does not have an isomorphic relationship with the structurally-similar boehmite (γAlOOH). So incorporation of Al^{3+} into the lepidocrocite structure would be more inhibitory to its development than would silica. Schwertmann & Thalman (1976) experimentally deduced that the formation of lepidocrocite is obtainable at Si/Fe concentration ratio $< 15 \times 10^{-3}$. At higher concentration ratios, precipitation of lepidocrocite may completely be blocked at concentration ratios greater than 50×10^{-3}. Cations of Cr, Co, Ni, Mn, Ti and Sn are also thought to have similar inhibitory effects as Al^{3+}, although the mechanisms involved are still less understood (Detournay et al., 1978; Taylor & Schwertmann, 1978 ; Brown, 1980).

9.2.2 Stability and Occurrence

The stability field of hydrous iron-oxides is much the same as that for haematite, shown in Figure 28. They are generally stable under oxic conditions and over wide pH values. There are, however, relative differences in the phases' stability, thermodynanically. Depending on factors similar to those controlling precipitation, the phases often transform from one to the other, usually through intermediate solution phase (Oosterheut, 1967; Atkinson et al., 1977).

Of the two phases under study, goethite is thermodynamically more stable. Goethite (and limonite) is very common in soils and weathering profiles of present-day humid tropical to warm temperate regions. The mineral is particularly important in latosols and podzols, where it often occurs as a crust or indurating material (Gidigasu, 1976). As an exogenous mineral, goethite commonly forms from the alteration and decomposition of iron-bearing minerals under surficial action of water, carbon dioxide, oxygen and humic substances (Deer et al., 1962; Beutelsphacher & van der Marel, 1968). The mineral can also form directly from slowly oxidised jarosite (Chukrov et al., 1975). Goethite in some soils may be Al-substituted and may contain up to 30 mol% Al (Norrish & Taylor, 1961). These are generally poorly-crystalline, often occurring as acicular or lath-shaped crystals with variable lengths and thicknesses (Norrish & Taylor, 1961; Taylor & Schwertmann, 1974). In contrast, pure goethite is usually well crystallised with platy or prismatic morphology (Deer et al., 1962). Goethite crystals occur as discrete crystals or as intricately interwoven forms. The latter typically occur where iron has been concentrated considerably, e.g. indurated soil horizons (Alexander & Cady, 1962). The crystals often exhibit edge to edge contact and face to face stacking so as to appear as star or leaf-like aggregations (Mackenzie et al., 1971). Goethite could transform to ferrihydrite and haematite when subjected to dissolution and intense oxidation in seasonally-alternating wet and very warm climatic regions (Chukrov et al., 1975). The reverse can also occur in conditions of high acidity or alkalinity with probable participation of micro-organisms, and particularly when climatic conditions change from very warm to a colder one (Schwertmann, 1971; Chukrov et al., 1975).

Lepidocrocite is relatively rare, and is mostly found in present-day poorly-drained hydromorphic or gley soils, in particular swamps and marshes (Brown, 1953; Chukrov et al., 1975; Schwertmann & Taylor, 1977; Niederbudde & Schwertmann, 1980). The occurrence reported by Chukrov et al. (1975) from the USSR was, in fact, a product of siderite transformation. The phase has also been reported as forming in well-drained soils developing on acid crystalline rocks in Ontario, Canada (Tarzi & Protz, 1978b). Soil lepidocrocite occurs as scales, crusts and fibrous or flaky aggregates (Mackenzie et al., 1971; Schwertmann & Fitzpatrick, 1971; Niederbudde & Schwertmann, 1980). Lepidocrocite crystals are often well crystallized with platy and lath-like morphologies. They are apparently flexible and can become bent or stacked into lamellae (Mackenzie & Meldau, 1959). Lepidocrocite is liable, on exposure to higher PO_2, and can transform to goethite or maghemite via solution phase (Oosterheut, 1967; Taylor & Schwertmann, 1980). The mineral can also transform to haematite under alternating reducing and oxidising conditions (Chukrov et al., 1975). The rare instances in which lepidocrocite persists in soils has been attributed to some factors such as (i) stabilisation by organic matter (Schwertmann & Taylor, 1979); (ii) the presence of silica that would inhibit goethite crystallization (Taylor & Schwertmann, 1972a,b and 1980); and (iii) the maintenance of oxic conditions with drainage loss of Fe^{3+} (Tarzi & Protz, 1978b).

9.3 Goethite and Lepidocrocite in the Upper Eocene Hampshire Basin

9.3.1 Distribution

Substantial occurrences of goethite and lepidocrocite are limited to a few horizons in the succession studied (Tables 7a - g). On the basis of their probable time of formation or derivation, the occurrences can be grouped into:

i) Goethite contemporaneously accumulated in palaeosols and related horizons. Details of the palaeosols are given in Chapter 16. Most important are the sandy red-yellow podzols at the top of the Barton Sand (Fig. 6b) and the Pebble Bed at the base of the succession at Alum Bay. These contain goethite in amounts ranging from trace to 44%, the high amounts (> 20%) being in the indurated horizons, vesons or B2ir (Table 7e, cf. Fig. 6b). Very few horizons of the hydromorphic (swamp) palaeosols (Fig. 48) contain goethite. These are on the Hordle Cliff and at Whitecliff Bay. The indurated sand, BLH12, at the base of the Chara Bed on Hordle Cliff contains about 10% goethite as well as 7% lepidocrocite. At Whitecliff Bay, between 6% and 14% goethite was recorded in some of the mottled clays in the Lower Headon Bed sections, whilst goethite in the ferruginous top of the Barton Sand is between 4% and 10%.

(ii) Disseminated goethite of possible detrital derivation occurring in the freshwater limestones at Heatherwood Point, and the Barton Sand on the Isle of Wight. The acid insoluble residue of the limestones contains 12% to 15% goethite, although this amounts to < 1% of the bulk composition (Table 18). With the exception of the uppermost part of the Barton Sand at Whitecliff Bay with high (4%-10%) goethite contents, goethite occurs only in traces in very few parts of the Barton Sands. Visual and optical observations show that the goethite contents of the goethitic sand moulds of plant materials, in the Barton Sand on the Isle of Wight, vary considerably from poor to abundant, in sympathy with their extent of induration.

(iii) Scales and crusts of goethites and lepidocrocite on oxidised and altered sideritic ironstones. These are prominent in the horizons of samples WBLH-10 and WBLH-6 at Whitecliff Bay, and ABLH-8 and ABBB-13 at Alum Bay. They occur less prominently in the horizons of BLH-36, BBB-23 and BBB-50 on the mainland. Although the scales and crusts could be penecontemporaneous with deposition, they are very likely to have formed after the uplift of the Palaeogene sediments in the Hampshire Basin. The uplift was believed to be during the Miocene (White, 1921). The relative abundance of the phases in the scales and crusts was not determined, but the crystal morphology of samples from WBLH-10 and BLH-12 was studied. In WBLH-10 the steel grey scales are wholly composed of goethite with traces of lepidocrocite. Coating the scales are orange-brown crusts dominantly composed of lepidocrocite plus some small amounts of goethite. The dark-brown scales on BLH-12 are an admixture of goethite and lepidocrocite.

9.3.2 Crystal Characteristics

Aspects of the purity of the phases were investigated by X-ray diffraction, whilst optical and SEM method were employed for crystal morphology. Materials from the podzol palaeosols, and the scales and crusts on altered ironstones WBLH-10 and BLH-2 only were studied in some detail.

9.3.2A Phase Purity

Goethites from all sampled materials appear to be highly crystallized phases; their reflection peaks being sharp but slightly broader at the base. The (111) reflection occurs between 2·45Å and 2·43Å. Using Vergard's rule with respect to the relationship between goethite and isomorphous diaspore, those d-spacings correspond to relatively pure goethite phases with < 10 mol% Al. They thus differ from aluminian-goethites thought to be most common in present-day soils (Norrish & Taylor, 1961).

The lepidocrocite is also relatively well crystallized; the basal (020) reflection being sharp and symmetrical. In order to confirm that the phase was in fact lepidocrocite and not the structurally-similar boehmite (γAlOOH), the sample materials were heated to 300°C. The (020) reflection at 6·26 - 6·28Å collapsed completely. This confirms the presence of lepidocrocite because boehmite would have persisted to relatively higher (~400°C) temperatures (Mackenzie, 1957).

9.3.2B Crystal Morphology

In thin sections, goethite in the podzols occurs mainly as an opaque matrix material coating and cementing quartz grains (Plates 40, 41,45-50). In pedological terms of Brewer (1964), the quartz grains would be 'skeletal grains', whilst the goethite would be 'voidan goethite'. A similar fabric feature is possessed by the sand moulds of plant material in the Barton Sands on the Isle of Wight. Other forms common in parts of the podzols are discrete millimetre-sized glaebular concentrates of goethite (i.e. Plate 46). They are the red iron mottles in the soil profiles. In the carbonaceous clays and lignites, iron-oxide occurs intimately admixed with organic matter and/or clays (Plate 32), and cannot be differentiated convincingly.

Under the SEM, diverse crystal morphologies were observed. These, for samples of the palaeosols and crusts and scales studied, are considered separately as follows:

a) Palaeosols:

1) Laths or acicular goethites. These measure 0·2 - 2 µm in length but ≤ 0·2 µm thick, and occur as discrete crystals or admixed with clay

floccules and coating quartz grains (Plates 51a;52d,e). The acicular form is the commonest iron-oxide form in the podzol profiles, except where indurated.

2) Glaebular goethites. They are the dominant form in the indurated horizons, filling pores and coating quartz grains (Plates 51f;52f-h; 53a-e). The glaebules are spherical or rounded with 2-5 µm diameters, and appear to be made up of cryptocrystalline materials and very fine-sized acicular crystals. Many have smooth external surfaces (Plate 53d) but some are roughened like 'balls of wool' (Plate 53c)

3) Honeycombed spheres (Plates 51i,j;53f,g).These are < 5µm-sized spheres made up of platy crystals intricately interwoven with edge to edge contacts. This form mainly occurs in the indurated horizons.

4) Radiating Laths (Plates 51h;53h). These consist of very thin laths radiating from a 1-3 µm sized central core. They also only occur mainly in the indurated horizons.

5) Crusty spheres (Plates 51c; 53f). They are 5-10 µm-sized bodies composed of poorly-differentiated < 0·1 µm-sized plates or laths. The bodies occur only in patches in the indurated horizons.

b) Scales and Crusts:

The iron-oxide forms on the scales and crust developed on altered sideritic ironstones comprise -

6) Spherules of platy goethites (Plates 88a-e). These occur in the scales on WBLH-10 and are composed of thin (< 0·01 µm) but broad (1-2 µm) crystals with serrated edges. The crystals are generally stacked face to face and, in places, bundled into flowery masses.

7) Books of rhomb-like goethite (Plates 88f,g). These also occur only in the scales on WBLH-10. They consist of 1-3 µm wide but < 0·02 µm thick crystals of rhombic outlines with serrated edges that have been stacked face to face into books. The books are, however, arranged edge to edge. These book forms are few, and occur in patches above the spherulitic forms; they could have formed by re-crystallization of the spherules.

8) Mixed masses or aggregates of goethite and lepidocrocite. These occur in the scales on both the WBLH-10 and BLH-12. It is difficult

asserting to which phase each of the crystals belongs. Considering the WBLH-10 first: spherulitic aggregations occur in patches, which, unlike (6) described above, comprise a mixture of what is probably platy lepidocrocite and prismatic laths of goethite (Plates 88h,i). The plates are about 0·5 μm thick, whilst the laths are up to 10 μm long. Also present are very small (< 2 μm-sized) glaebular bodies.

The scales on BLH-12 dominantly comprise flowery masses of platy lepidocrocite and prismatic goethite laths (Plates 90a - c). The lepicocrocite plates are 4-8 μm wide and 0·5 to 1 μm thick. Most have prismatic terminations (Plate 90d), whilst many appear to be bent (Plates 90c,d). They are also often arranged to form star-like or sheaf-like aggregates. The goethite (?) laths are slender, 10-20 μm long and 1-2 μm thick. Laths within a bunch often have star-like edge to edge contact at their basal ends.

9) Euhedral prismatic crystals of goethite (?) (Plates 90g,i,j). These occur sparsely in the scales on BLH-12 only. They consist of pseudo-hexagonal prisms with pinacoidal terminations,and measure up to 5 μm.

10) Clods of lepidocrocite plates (Plates 89a - c). These occur mainly in the orange-brown crusts on WBLH-10. The clods are 2-10 μm in size and generally consist of < 1 μm-sized plates. In some clods the plates are poorly differentiated and may appear to be cryptocrystalline (Plates 89a,b).

11) Matted interwoven lepidocrocite plates (Plates 89f - i). They also occur mainly in the orange-brown crusts. They consist of stacks of thin (< 0·1 μm) 1-2 μm-sized serrated-edged platy crystals that have interwoven,edge to edge, into star-like twins. These crystals closely resemble those of the honeycomb forms (3) in the podzol palaeosols.

12) Vuggy mounds or clods of lepidocrocite (?) (Plates 89f,h,j; 90b). These were observed in BLH 12 and in the orange-brown crust on WBLH-10. They generally consist of undifferentiated convoluted masses. These in parts of BLH-12 have, however, been partially differentiated into platy crystals (Plates 90c,e,h).

13) Crusty spheres (Plate 88j) similar to those (5) described in the palaeosols also occur in all the scales and crusts investigated.

9.4 Discussion - Derivation and Formation

The occurrence of iron-oxide phases in the Upper Eocene sediments raises a number of question with regard to their derivation (detritally-derived or authigenic) and dating (contemporaneous or Recent). These are considered below with respect to factors such as the nature of the source rocks; modes of transportation and precipitation; and post-depositional alterations; regarded by many authors, including Krauskopf (1967) and Pettijohn (1975), to be important for iron-oxide occurrences in sediments.

9.4.1 Detrital Derivation

Under the humid climatic conditions believed to prevail in Britain during the Eocene (Daley, 1972; Hubbard & Boulter, 1983), materials derived from surficially weathered source rocks and supplied to the Hampshire Basin would have included iron, both in solution and adsorbed. Iron-rich sediment sources probably included the glauconitic Cretaceous-age 'Greensands' and early Palaeogene sediments. Perhaps also important were lateritic palaeosols, which Isaac (1981, 1983) described from south-west England, and dated as Upper Cretaceous to Miocene.

The distribution of discrete iron-oxides in the succession is, however, limited; being largely undetected in the Barton Clay, most parts of the Lower Headon Beds, and only occurring in trace amounts in some of the sand sediments, notably the Barton Sand on the Isle of Wight. This distribution was most likely caused by differential Eh conditions that prevailed in the succession upon the sediments' burial. Where undetected, any free iron oxide phases deposited with the sediments may have become subjected to reducing (-ve Eh) conditions, so as to consequently become reduced to Fe^{2+} and mobilised for sulphide and/or carbonate diagenesis. The diagenetic phases are discussed elsewhere. Reducing conditions often rapidly become established in clayey (fine-grained) sediments within a few millimetres of the sediment/water interface (i.e. Degens, 1965; Goldhaber <u>et al.</u>, 1977). In contrast, higher permeability and greater interstitial fluid circulation in sand sediments may have ensured the maintenance of oxidising (high PO_2; +ve or 0 Eh) conditions (i.e. Curtis, 1978).

In addition to detritus sources, localised and in-situ pedogenically formed goethite has most likely contributed to the disseminated iron-oxides in the Barton Sand. As stated previously, penecontemporaneous goethite-kaolinite facie pedogenesis (cf. Chesworth, 1975) occurred on the emerged uppermost part of the Barton Sand on the Isle of Wight. Goethite could have become caught up in meteoric waters flushing through the soil into the sand deposit. Mineral grains, clays and iron-oxides earlier deposited for the sands can then adsorb and/or induce precipitation of the fluid-borne goethites. Indeed, precipitations from flushing waters would help explain the goethitic Liesegang rings in the Barton Sand at Alum Bay. Liesegang rings are diffusion phenomena due to a periodic alteration between solution mobility (diffusion) and supersaturation (nucleation and precipitation (Liesegang, 1913). Iron-oxide Liesegang rings are not uncommon in sands and sandstones where they may form by the mixing of Fe^{2+}-bearing waters (from anoxic sources) and oxygenated waters (from oxic sources) (Berner, 1980). This mode of formation is considered more common in the ocean (Stern, 1954) and saline lakes (Sugawara, 1934).

It is difficult to establish the origin of goethite in the sand moulds of plant materials in the Barton Sand at Alum Bay and Whitecliff Bay. First of all, the limitation of these materials to deposits on the Isle of Wight suggests very localised derivation. The moulds were plant matters whose decay was followed by infiltration of sand grains into the spaces ensuing. For the moulds to be preserved, the decaying and iron precipitation would possibly have occurred contemporaneously with deposition; otherwise the plants, on decaying, could have been crushed by the weight of the overlying sediments.

Finally, it is thought that iron-oxides disseminated in the How-Ledge Limestone at Heatherwood Point had possibly flocculated and settled down from suspension in the low-energy freshwater body in which the limestone accumulated. With virtually no detritus supply to the quiet water body, goethite had settled and, with clays, became admixed with the precipitating lime-mud of the limestone.

The origin of iron-oxides in the palaeosols, and on altered ironstones, is different from those described above. They are believed to have authigenically formed under oxic pedogenous conditions. This is considered as follows:

9.4.2 Pedogenous Authigenesis of Iron-Oxides

In surface conditions, iron-bearing minerals do suffer alteration and decomposition under the actions of water, carbon dioxide, oxygen and, possibly, humic substances (Deer et al., 1962). Where reducing (-ve Eh) conditions prevail, iron may be taken into solution and be stabilised as Fe^{2+}. Such reducing conditions typify or often occur in water-logged, poorly drained and/or poorly aerated environments. It may also exist below the lowest ground-water of soils, where water saturation is apparently permanent. However, when the drainage and aeration improves or the ferrous solution is brought into oxidising conditions, Fe^{2+} will oxidise and precipitate as Fe^{3+}. This mode of formation would account for the goethite in the palaeosols. Aeration in those soils would have been effected by or occur within the large voids between the sand grains, along root paths and/or animal burrows; these being typical aeration elements in soils (Brewer, 1964). Apparently, iron mobilisation and precipitation had been greatest in the sandy acid podzols, where aeration and ground-water movements would have been considerably enhanced. The indurated horizons would have been the horizons of highest ground-water table; hence the high goethite precipitation would be there. Conditions in the hydromorphic profiles have been less acidic and, hence there was little alteration of the mineral; nor was mobilisation of iron substantial.

Variations in the crystal morphologies of goethite in the podzol palaeosols show an apparently strong relationship to abundance of iron; although other factors, such as oxidation rates (or PO_2) and the presence of inhibiting cations such as Al^{3+} and Si^{4+}, could have been equally important. The precipitation of goethite indicates the absence or presence of insignificant amounts of silica in the soil solutions, as that could have blocked crystallization (Taylor & Schwertmann, 1980). Apparently there had been some Al^{3+} in the solutions so as to induce restrictive growths on the b-axis and hence precipitation of the acicular laths and thin platy crystals. However, the amounts of Al^{3+} involved would have been very small, since the goethite contains $<$ 10 mol% Al. Indeed, much of the released Al^{3+} and Si^{4+} in the podzols had either been combined to form the enriched authigenic kaolinite or probably lost in the ground-water drainage. The commonest goethite acicular or lath crystals have mainly formed in horizons where iron concentrations and oxidation rates have respectively been low and slower. In contrast, the glaebules and the variously interwoven plates and laths have precipitated mainly in the horizons of the uppermost water tables. Here, the iron concentrations would have been higher and oxidation more intense, and the predominance of the glaebules would suggest that it is the earliest form formed. It was probably initially precipitated as amorphous hydroxide, but,with time, grew in size and transformed to crystalline forms. Glaebular iron-oxides have been synthetised by Hsu & Ragone (1972), whilst in present-day soils they do occur as amorphous iron-oxide (Eswaran & De Connick, 1971). Glaebular goethite has also been described from a ferruginous palaeosol of Lower Cretaceous (Wealden) age in the Paris Basin (Meyer, 1976). The occurrence of interwoven forms above the glaebules would suggest they formed from the constructive recrystallization (McKay, 1960) of the glaebules. Alternatively, the interwoven forms could have formed when the iron-bearing solution became less rich in inhibitory cations and/or contain lesser nucleating centres or seeds.

9.4.3 Surficial Oxidation and Alteration of Sideritic Ironstones

The development of the sideritic ironstones is discussed in Chapter 14. They are believed to have diagenetically-formed at shallow depths of burial in the Upper Eocene sediments. The stability field of siderite, shown in Figure 28 , extends over reducing (-ve Eh) conditions, low PO_2, high PCO_2 and high PS^{2-}. When brought into oxidising conditions, siderite suffers oxidation and alteration, with iron-oxide crusts and coatings developing on the ironstones. The crusts in the present study comprise goethite and/or lepidocrocite. Similarly altered ironstones are common; they have been reported from Britain (Greensmith, 1971; Gad et al., 1969); Japan (Matsumoto & Ijima, 1975); and New Zealand (Childs et al., 1972).

In WBLH-10 the initial very thin, platy goethite crystals apparently pseudomorphed on siderite rhombs and spherules (Plates 88a-d). The rhombs and spherules had acted as sources of iron and, in addition, sites of goethite precipitation. This suggests no translocation or mobilisation of iron from or to the ironstones; probably no ground water or percolating meteoric water has been involved nor have the ironstone horizons constituted soil units. It could be said that the siderite oxidation and alteration have mainly been effected by atmospheric oxygen, and carbon dioxide and moisture (i.e. carbonic acid, H_2CO_3). The volume of the acidic moisture involved would be very small in comparison with the high concentration of iron that would have been released - and precipitated as Fe^{3+}. The close packing of these platy goethite crystals has thus resulted from, or is reflecting, the close spacings of the points of acid attack on the siderite. Competition amongst the crystallites for the available iron has resulted in their extreme thinness; although the presence of growth-inhibiting cations, such as Mn, Co and Cr, released from the siderites could have contributed to the growth inhibitions. All the other goethite forms occurring above the spherulitic aggregates (Plates 88a - d) would have developed from the spherules, possibly by what McKay (1960) termed 'constructive recrystallization'.

In comparison with goethite which could have formed under rapid oxidation, lepidocrocite is considered to form and be stable in conditions of slow oxidation, the presence of organic matter, high alkalinity, and the presence of cations (i.e. Si^{4+}) that can retard or inhibit the growth of goethite (Chukrov et al., 1975; Schwertmann & Taylor, 1977; Taylor & Schwertmann, 1980). Although a slow oxidation rate would often be attained in water-logged or poorly-drained horizons, it is unlikely that this was the case in the horizon of WBLH-10. It has been suggested earlier that the horizon does not constitute a soil unit, nor was it exposed under a surface water body. It has also been suggested that the alterations were mainly by atmospheric elements. Changes in atmospheric conditions with seasonal climatic fluctuations need to be considered for the lepidocrocite formation. It is probable that seasonal changes in the atmospheric humidity (especially rainfall) had some influence on the iron-oxide phase precipitation. The goethites had possibly formed in the dry seasons when humidity (and rainfall) was low; whilst the lepidocrocite crusts formed in the wetter periods when the solutions generated would have been greater in volume and less acidic. These modes of formation would help to explain the layering of the weathered crust and, in particular, the consistent occurrence of the lepidocrocite crust over each goethite scale. Each is a distinct precipitated phase with no indication of inter-phase transformation. It is, however, difficult to ascertain whether organic matter and growth-influencing cations made any significant contributions to the formation of the iron-oxide phases. But rather than organic matter, it was clays that were observed admixed with the lepidocrocite in the orange-brown crusts on WBLH-10. Perhaps this was what induced the clod-form of the lepidocrocite (Plates 89a - d).

In contrast to WBLH-10, the horizon of BLH-12 appears to be a palaeosol, not only because of its induration by the iron-oxides, but also because of the presence of rootlets and related aeration channel. The horizon is considered in detail with the palaeosols in Chapter 16. But of concern at present are the goethite-lepidocrocite scales on the indurated sand. The vuggy cryptocrystalline masses (i.e. Plate 90c) appear to be the initial precipitate. These were seen differentiating into lepidocrocite of distinctly good, platy crystal morphologies (Plate 90h). The mode of formation of the goethite content of the scales is less easy to discern. The intricate associations of both the goethite and lepidocrocite as distinct crystals in most parts of the scales (Plates 90a, b) may only be interpreted as resulting from 'simultaneous precipitation or formation'. The possibility of this type of formation in nature is given by laboratory synthesis of admixed phases such as those obtained by Taylor & Schwertmann (1972, 1978) using Fe(11) - Fe(111) and Fe(11)CO_3 solutions within the range of pH 5·9 and 7, but variable oxidation rates. Other iron-oxide phases also form during the synthesis. These include 'green-rust', maghemite and ferrihydrite. But these were not observed in the material under study; either their formation was disfavoured or suppressed or, if formed, had largely transformed on ageing and/or continuous oxidation.

9.4.4 Time of Formation of Iron-oxide Crusts and Scales

The time of formation of the iron-oxide crusts and scales would possibly be 'post Miocene' and, less probably, penecontemporaneous.

The possibility of ironstones in the Upper Eocene sediments having formed at very shallow burial depths of sediments has been discussed in Chapter 14. These, in the non-marine Lower Headon Beds, were at near-surface conditions; perhaps including marsh (or swamp) soils. In these settings, as in many present-day soils, e.g. Cat Clays, there could have been changes from reducing conditions conducive for siderite stability to relatively oxidising conditions, whereby the ironstones got altered. Hence a penecontemporaneous development of the iron-oxide crusts and scales is probable, at least in the non-marine parts of the succession.

In many respects, weathered crusts on marine ironstones from Highcliffe and Alum Bay would most certainly have been a result of exposure to atmospheric conditions. It is extremely unlikely that oxidation at depth, or on contemporaneous exposure in the sea, would cause what appears to be seasonal layered weatherings of the ironstones.

In general, the alteration of the ironstones would possibly be after the Miocene times uplift of the Palaeogene sediments in the Hampshire Basin (White, 1921; Daley & Edward 1971), and the development of the coast-line during the Holocene (Melville & Freshney, 1982). Similar surficial alteration is believed to have affected the other iron-bearing minerals - pyrite and glauconite in the exposed parts of the succession; leading to the formation of iron-oxides, gypsum and jarosite.

Convincing evidence for recent alterations was obtained during the course of the present study. Ironstones sampled fresh in the field became oxidised and altered to goethite within a few days (< one week) of storage in polythene bags under ordinary laboratory conditions. The ironstones are greyish-white or greenish when fresh, but turn brown-red from films of iron-oxide on exposure. Therefore it is very possible that alterations on sediment faces could have occurred within a very short time of exposure. The study of borehole samples, not available during the present study, could confirm when the exogenous minerals form.

9.5 Summary

Goethite and lepidocrocite are the only free iron-oxide phases found in the Upper Eocene succession of the Hampshire Basin. Their occurrences are restricted, whereas their origin is very diverse. Goethite is disseminated in the Barton Sand and the freshwater limestone, particularly on the Isle of Wight sections; this is believed to be detritally derived. Goethite in the palaeosols, particularly the red-yellow podzols, is pore-filling and grain-coating; it is of pedogenic origin. There are also crusts and scales of goethite and/or lepidocrocite on sideritic ironstones; these would have resulted from the alteration of siderite on exposure in Recent times.

The iron-oxide phase phases are low aluminian varieties and possess good crystallinities. Their morphology is, however, very diverse. Thin goethite laths are common in most parts of the podzols and related soils; but glaebules and variously interwoven lath forms characterise the indurated podzol horizons, including the pebble bed at Alum Bay. Thin platy crystals in dense, flowery aggregation pseudomorph siderites altered in the ironstones. Other forms on the ironstones include rhomb-like books of goethite, clods of lepidocrocite, and prismatic and platy crystals with edge to edge star-like twinning.

CHAPTER 10

EXOGENOUS MINERALS - GYPSUM AND JAROSITE

10.1 Gypsum

10.1.1 Introduction

Gypsum is a sulphate mineral whose occurrence is very limited in the Upper Eocene succession under study, and is thought to have formed largely by surficial alteration of pyrites in Recent times. Its occurrence and morphology have been studied and genesis discussed.

In sediments, gypsum commonly occurs either as a diagenetic precipitate in hypersaline waters ($>125‰$) and arid conditions, or as a product of surficial alteration of sulphide phases such as pyrite. The former is more common with the mineral being a primary or secondary precipitate in evaporitic deposits of playa lakes and sabkhas (Blatt et al., 1972; Leeder, 1981) and also in saline soils of arid regions (Fitzpatrick, 1971). In these, gypsum often occurs in a variety of forms, including lenticular masses and satin spar. It can also be replaced or pseudomorphed by other salt minerals (i.e. anhydrite and halite), and carbonate minerals (calcite and dolomite).

Exogenously formed gypsum occurs extensively in Cat-Clays (acid sulphate soils or Thiosols - Fitzpatrick, 1971). Cat-clays are subjected to alternate wetting and drying. Pyrite formed in the initial reducing conditions oxidises later as a result of aeration. Gypsum precipitates when sulphate ions from the altered sulphide and Ca^{2+} from clays and invertebrate shells exceed the solubility product of gypsum $K_{gypsum} = 2 \cdot 5 \times 10^{-5}$ (Berner, 1971). Also widespread is gypsum formed from the surficial alteration of pyrites in exposed sediments (Spear, 1982). Such recently formed exogenous products commonly occur as finely disseminated prismatic and lenticular crystals. Selenites formed by this mode are common on the exposed faces of the Upper Eocene sediments under study.

Gypsum does not commonly form in normal marine and freshwater environments because of under-saturation with respect to the constituent ions. However, in rare instances, such as that described by Siesser & Rogers (1976), authigenic gypsum may form in marine sediments. Siesser

& Rogers (op.cit.) observed gypsum encrustations on pyrites, and disseminated lenticular gypsum crystals in Upper Miocene - Lower Pliocene sediments off the south-west African coast. The authors attributed the gypsum to oxidation of pyrite at depth and localised super-saturation of the interstitial water. They suggested that calcium came from dissolved planktonic calcareous organisms.

10.1.2 Distribution

Gypsum occurrence in the presently studied sediments is limited. It is most common in the lignitic and carbonaceous clays in the non-marine sediments, especially on the mainland sections. These contain trace to 6% gypsum. The lignitic clay sample WBLH-9 at Whitecliff Bay, and the basal part of the Chana Bed (Sample BLH-12) on Hordle Cliff, however, contain substantially high amounts - 12% and 21% gypsum respectively. The occurrence of small gypsiferous bodies, especially in the Chana Bed, could account for those high gypsum contents. Gypsum was also recorded in some samples from the Naish member of the Barton Clay at Barton and Alum Bay in amounts of up to 6%.

Gypsum occurring in the lignites and associated clays is possibly recent, although a penecontemporaneous age cannot be ruled out. Gypsum in the Barton Clay would, however, be due to recently formed selenites, as a result of surface weathering of pyrite in the exposed sediments.

10.1.3 Morphology

Gypsum, in the lignitic clays, appears to be an integral constituent of the sediments; mainly occurring as prismatic crystals often in association with iron-oxides in altered plant structures (Plates 35,36) or admixed with organic matter and/or clays (Plates 34a, b). Aggregation into rosettes (Plate 34b) is also very common. These occur within cavities in altered pyritised roots and voids rimmed by organic matter. The rosettes consist of twinned, prismatic crystals crystallographically arranged with the major axes aligned approximately parallel to walls of the voids or cavities. The crystal sizes decrease from about 250 µm near the void walls to < 20 µm at the centres, with the central crystals also being more anhedral and randomly arranged. Gypsum rosettes are solution features commonly observed in soil horizons (Brewer, 1964), indicating precipitation from small volume solutions whose hypersalinity could have been attained in small or localised confined spaces.

Apart from the lignitic and carbonaceous clays, no gypsum crystals were observed in the thin sections of other sediments. This indeed further indicates that gypsums recorded in parts of the Barton Clay were selenite contaminations. The selenites on exposed sediment faces are prismatic with swallow-tail twinning (Plate 39) and vary in size from a few microns to about 1·5 cm.

10.14 Genesis

The occurrence of gypsum in the lignites and associated clays raises the question of conditions and time of formation. In the Hampshire Basin, there is no evidence, sedimentologically or palaeontologically, of the existence of arid climatic conditions or the existence of hypersaline water bodies. The probable climatic conditions during the Upper Eocene times were warm and humid types (Daley, 1972; Hubbard & Boulter, 1983), whilst sedimentation mainly consisted of clastic deposits and freshwater limestone (Melville & Freshney, 1982). So gypsum recorded in the present study is extremely unlikely to be evaporitic or of arid saline soil in origin. This is in contrast to the adjoining Paris Basin in France, where, during the Palaeogene, arid climatic conditions alternated with wetter but also warmer seasons (Chateauneuff, 1980). Hypersaline water bodies existed at times (Murray & Wright, 1974), and gypsiferous sediments are abundant in the Upper Eocene/Oligocene Paris Basin (Pomerol, 1973; Fontes & Lucus, 1968).

The lignitic clays and associated sediments are regarded, in the present study, as primarily hydromorphic (swamp) soils (see Chapter 16). They were probably affected by alternate wetting and drying, as are present-day cat-clays that contain gypsum as one of the alteration products of sulphide phases (Dones & Lynn, 1977). These would explain the association of gypsum with organic matter and goethite in altered pyritised rootlets. The gypsiferous bodies on Hordle Cliff could have formed from altered pyritised fossil shells that are common in the basal part of the Chara Bed. Sulphuric acid from altered pyrites would have been neutralised by calcium carbonate from the shells, and the gypsum precipitated with the other alteration products - goethite and jarosite.

In the above envisaged soil conditions, gypsum can be expected to form contemporaneously. But such dating cannot be strongly justified because of the problem of explaining the mineral's preservation in the humid climatic conditions of the Upper Eocene Hampshire Basin. There is also no mineralogical or petrological evidence that there were highly saline pore waters that would help to stabilise and preserve the gypsum. Equally, dissolution features or partial replacement that could suggest preservation in under-saturated conditions, are absent; whereas such replaced gypsum and gypsum pseudomorphs respectively occur in the Bembridge Limestone, higher up in the Palaeogene succession on the Isle of Wight (Daley, 1971), and some hydromorphic palaeosol in Languedoc in France (Freytet, 1971).

A recent (or post-Miocene) time of formation is more possible. Just as argued for the goethite and lepidocrocite crusts on sideritic ironstones (see Chapter 9), the gypsum could have resulted from weathering of the sediments after their uplift during the Miocene (White, 1921), and coast-line development in the Holocene times (Melville & Freshney, 1982). Alterations of pyrites have certainly produced selenites, iron-oxides and jarosite on exposed sediment faces. Gypsum recorded in the Barton Clay samples suggests that the alteration is much deeper than visually realised in the field, especially in the carbonaceous horizons.

10.2 Jarosite

10.2.1 Introduction

Jarosite occurs in the Upper Eocene sediments as one of the oxogenous alteration products of pyrite and glauconies. The mineral was not studied in great detail; only comments on its distribution and formation are given below.

Jarosite commonly occurs as straw or greenish-yellow efflorescence, flakes and encrustations (Paluche et al., 1957). It has been reported from underclays of coal and lignites (Warshaw, 1956); hydromorphic (pseudogleys) palaeosols (Buurman, 1980); present-day cat-clays (thiosols) (Fitzpatrick, 1971; van Breeman & Harmsen, 1975; Dones & Lynn, 1977); and on exposed pyritic, limonitic and glauconitic sediments (Briggs, 1951; Paluche et al., 1957; Wright & Wilson, 1970 ; Deeson et al., 1973).

The formation of jarosite has been shown (Merwin & Psonjak, 1922 & 1937) to be mainly from oxidised iron-bearing minerals, particularly pyrite, in the presence of sufficient water. It was shown that pyrite oxidation first yielded the acid, ferric sulphate rhomboclase [$HFe(SO_4)_2.4H_2O$]. However, because the oxidation of iron was much lower than sulphur, a mixture of ferric and ferrous sulphates and sulphuric acid was produced. The attack of this acid on other mineral constituents in the sediments, especially clays, would cause the release of alkaline and alkaline-earth cations. These would then react with the iron-sulphate to form jarosite and other related basic sulphates, including natrojarosite.

Jarosite is unstable relative to iron-oxide phases. Chukrov et al. (1975) experimentally found that alteration products of jarosite depend on the rate of oxidation and/or pH. Slow oxidation of jarosite can lead directly to precipitation of goethite; whereas ferrihydrite and then haematite may result under rapid oxidation; whilst lepidocrocite will be favoured in highly alkaline conditions.

10.2.2 Distribution and Genesis

The occurrence of jarosite is very limited in the Upper Eocene sediments. It was recorded in amounts of trace to 8% in the bulk samples of the glauconitic sediments at the base of the succession at Highcliffe and the base of the Chara Bed on Hordle Cliff. In addition, it was recorded in the clay (-2 µm) fractions of the lignitic clays at Alum Bay and Whitcliff Bay. In some altered pyritised plant materials from Hordle Cliff, jarosite also occurs in association with goethite and gypsum. Similar mineral-assemblages predominate in the gypsiferous bodies at the base of the Chara Bed (Plate 36).

On exposed sediment surfaces, straw-yellowish jarosite flakes commonly occur as coatings, along with selenites on both the marine and non-marine sediment sections, and at all localities. On the surface of 'Bed L' at Long Mead End, there are also ash or greyish-white flakes (Plate 7), soluble and acid-tasting. They are probably a soluble precursor of jarosite, e.g. melanterite ($FeSO_4.7H_2O$).

The extensive occurrence of jarosite on the sediment surfaces certainly indicates recent formation from alteration of iron-bearing minerals in the sediments. These are pyrite and glauconite. Wright & Wilson (1970) believed that glauconite in the Barton Clays at Whitecliff Bay is the primary material for jarosite they observed at that locality. These two authors failed to appreciate the importance of pyrite, not only as the main primarily altered material, but also as the predominant source of the sulphate ions in the alteration processes. Most of the jarosite recorded is almost certain to be recently formed material. It should, however, be borne in mind that the jarosite present in the lignites and carbonaceous horizons could, as argued for gypsum, have formed during the contemporaneous development of the horizons as swamp soil. But since no jarosite pseudomorphs on pyrites were observed in the present study, no direct comparison could be made with jarosite that Buurman (1980a) described from pseudogley palaeosols in the Lower Eocene Reading Clay formation at Alum Bay. The description of those palaeosols implies a contemporaneous time of formation of the jarosite; but no discussion of the conditions of its preservation has been made by the author.

CHAPTER 11

BIOGENIC ARAGONITE AND CALCITE

11.1 Introduction

Most horizons of the Upper Eocene succession in the Hampshire Basin are fossiliferous. The coastal cliff exposures, particularly on mainland Hampshire, provide some of the best preserved fossiliferous Tertiary sections in Britain. The fossils have attracted attention since the late eighteenth century (see Gardner et al., 1888) and many extensive palaeontological studies have been undertaken. Many authors, notably Fisher (1862), Tawney & Keeping (1883), Gardner et al. (1888), Burton (1929), Edwards (1967), Keen (1978) and Bujak et al. (1982) have employed the fossil contents for biostratigraphic definition and subdivision of the Upper Eocene succession. This has been discussed in Chapter 1.

There are, however, no known studies on the chemical and mineralogical composition of the fossils in the succession. A knowledge of their composition would be invaluable in deducing the Upper Eocene depositional environments in the Hampshire Basin as well as throwing light on the diagenetic roles the shells had played in the sediments. Therefore, as part of the present study, shells of some pelecypod and gastropod species from marine and non-marine environments were separated and investigated chemically and mineralogically. Details of the experimental procedures are described in Chapter 3, and the analytical results are shown in Table 14 . These are discussed below, preceded by a brief review of the literature on the occurrences and composition of shells.

11.2 Review of Invertebrate Shells

Skeletal parts of invertebrates are usually composed of polymorphs of calcium carbonate - aragonite and calcite; and only rarely do shells contain calcium phosphate (collophanite) and chitino-phosphate (Garrels & Mackenzie, 1971). Portions of shells' constituents may also be separated or enveloped by organic sheaths.

Pelecypods and gastropods, which are of interest in the present study, generally possess shells composed of calcite and/or aragonite in flattened, variously stacked prismatic crystals, or fibrous crystals in cross-lamellar and foliated structured arrangements (Bathurst, 1975). Lowenstram (1954) and Dodd (1967) observed that, in aragonitic and calcitic shells, the inner nacreous layer is usually aragonitic, while the outer prismatic layer is calcitic. Thin aragonitic mycostracal layers in former positions of muscle attachments may also be observed.

Compositional studies of some modern shells have been made by Clarke and Wheeler (1922), Chave (1954), Thompson and Chow (1955), Goldsmith et al. (1955) and many other workers. A summary of some of the results has been made by Garrels and Mackenzie (1971, Table 8.3) and Lippman (1973 - Table 13), and they show that the carbonate contents of pelecypods and gastropods are low magnesian, with $\leq$ 3 mol% $MgCO_3$. The magnesium was incorporated into the calcite structure solely because of the solid-solution relationship between calcite and magnesite ($MgCO_3$). The isomorphism between strontianite ($SrCO_3$) and aragonite has been used to explain Sr incorporation into the aragonite structure (Kinsman, 1969). The 2000 ppm Sr that is biochemically partitioned into aragonite shells is, however, very much lower than the 8000 ppm contained in chemically precipitated aragonites in Recent aragonitic muds and ooids, or the 1·04% expected from sea-water with Sr^{2+}/Ca^{2+} ratio of 10^{-2} and a Sr distribution coefficient of about 1 [that of calcite is 0·14%] (Kinsman, 1969; Kinsman & Holland, 1969).

Factors influencing the formation and composition of invertebrate shells are essentially: the body fluid biochemistry of the organism; the phylogenetic level or physiological state of the organism; environmental temperatures; and salinity (Lowenstram, 1954; Kinsman, 1969). Lippman (1973) has reviewed some studies on the effects of organic compounds on aragonite-calcite precipitation. These show that the absence or presence, in variable amounts, of many organic compounds do have significant and variable influences on which polymorph of $CaCO_3$ precipitates. The mechanisms involved are still the subject of research. In line with the relationship established by Müller et al. (1972) between Mg/Ca ratios of surface and interstitial waters and the type of carbonate phase precipitated, Folk (1974) has suggested that animal body fluids with Mg/Ca ratios $<$ 2 would induce aragonite precipitation. Folk also employed the experimental works of Bischoff & Fyfe (1969) and Vater (1899) on magnesium, and those of Johnston and William (1916) and Schroader (1969) on SO_4^{2-}, Pb, Sr and Zn to explain the precipitation of aragonite and magnesian-calcites with fibrous and/or steep rhombic forms. It was envisaged that growth inhibition and hence lattice distortion of the calcite structure were brought about by the introduction of cations substituting for Ca; the growth inhibition being least or non-operative along the crystallographic 'C' axis.

Most shells of the highly-evolved annelids, pelecypods, gastropods and cephalopods are aragonitic; but in those composed of calcite, the Mg content decreases with physiological development (Chave, 1954; Lowenstram, 1954a & b). The temperature dependency is best exhibited by species with mixed calcite and aragonite shells. In these, the aragonite/calcite ratios and the Mg contents of the calcitic components increase with increase in temperature of the water-habitats of the animals concerned. These would explain the abundance of aragonitic and high-magnesian calcitic shells in modern warm seas (Bathurst, 1971). Moberley (1968) and Weber (1969), however, think that fast growth rates rather than temperature may be responsible for the high Mg contents of skeletal Mg-calcites.

With respect to the Sr content of shells, Lowenstram (1954) believes the low values ($\leq$ 2000 ppm) of the element in molluscs to be a reflection of their high physiological evolution. The temperature dependence of Sr partition is less well established (compared with magnesium). Hallam & Price (1968), however, studied the gastropod <u>Cardium</u> <u>edule</u>, from European localities with mean annual temperatures of 14-27°C, and found that the Sr concentrations in the shells decreased from about 2000 ppm at 14°C to about 1100 ppm at 20°C - i.e. a decrease in Sr with increasing temperature of water-habitat. Salinity, earlier thought to have an influence on shell composition (Chave, 1954) has been found not to be of any significance in recent studies (i.e. Kinsman, 1969; Hallam & Price, 1968).

Using data collected from various sources on the thermodynamics and phase chemistry of calcite and aragonite, Lippman (1973) deduced that at earth-surface conditions chemically precipitated and biogenic aragonites are metastable with respect to calcite. During sediment diagenesis, and in particular during the lithification of carbonate sediments within the realms of phreatic and/or meteoric freshwaters, skeletal aragonite and magnesian calcites will transform through solution phases into sparry calcites (Folk, 1974; Stehli & Hower, 1961; Gavish & Friedman, 1969). From work on Pleistocene carbonate sediments, Matthews (1968, in Barbados) and Gavish & Friedman (1969, in Bermuda) suggested that complete aragonite transformation in lithifying carbonate sediments could be achieved within 100,000 years, depending on the availability and rate of flushing of interstitial fresh-waters. Primary low-magnesian calcite, being the stable polymorph, can resist alteration sediment diagenesis. There may, however, be neomorphic replacement by other minerals.

The preservation of aragonitic shells is not uncommon in sediments older than Pleistocene. Such occurrences include aragonitic ammonite shells in Jurassic shale, Germany (Fuchtbauer & Goldschmidt, 1965; Andalib, 1970 - both quoted in Lippman, 1973; and Bathurst, 1971); mollusc shells in Devonian sediments, Belgium (Grandjean et al., 1964); Lower Carboniferous shales, Scotland (Hallam & O'Hara, 1962); Turonian glauconitic sandstone, India (Richter & Fuchtbauer, 1978); and the Aragonitic Bivalve Beds in the Purbeck Formation of southern England (El-Shahat, 1977; El-Shahat & West, 1983). The preservation of aragonitic shells may be due to:

a) the retarding or inhibiting influences on calcite nucleation by ions which form sparingly soluble salts with Ca^{2+} and CO_3^{2-} (Lippman, 1973). Such materials include SO_4^{2-} and bivalent cations, especially Mg^{2+} and others like Fe^{2+} and Ni^{2+}. The retarding effects of Mg have been observed at concentrations as low as 0·001M (Taft, 1967; Bischoff & Fyfe, 1968). Hence the presence of 0·05M Mg^{2+} in sea-waters may account for the non-dissolution of aragonitic shells in modern seas. Also interstitial waters with substantial Mg^{2+} concentrations or high Mg/Ca ratios would enhance aragonite preservation (Robertson, 1964; Fyfe & Bischoff, 1965).

b) the presence of protective hydrophobic organic compounds like amines, bitumens and oils (Kennedy & Hall, 1967). These compounds protect the shells' mineral constituents from the dissolution and transformation effects of interstitial waters.

c) conditions of low permeability in clayey sediments and restrictions on the availability or circulation of interstitial waters (El-Shahat & West, 1983).

11.3 Aragonitic and Calcitic Fossil Shells in the Upper Eocene Hampshire Basin

11.3.1 Occurrence

Most fossil shells in the Upper Eocene succession occur as water-worn or broken individuals or, in places, current-accumulated into seams and pockets. These could be due to the derivation of some of the shells as river-transported or sea-bottom current re-worked material (Fisher, 1862; Burton, 1929). Their condition might also reflect the fluctuating sea levels on a relatively active or mobile Hampshire Basin. Some of the shells are also extensively bored. Typical are the *Turritella* in the uppermost part of the Naish Member and 'Bed G', which are bored by the minute *Lithodonus* (Burton, 1929). These borings suggest the possible exposure of the shell on the sea bed for a considerable length of time before incorporation in accumulating sediments. The horizons of occurrence of bored shells, such as 'Bed G', would therefore indicate stable sea level conditions, low rate of deposition and/or detrital supply.

11.3.2 Mineralogy

The compositions of the shells analysed are given in Table 14. The shells are almost wholly aragonitic, the exceptions being in the Barton Clay 'Beds F and G', where the presence of trace to 15% calcite was recorded for undifferentiated masses of shells. Analyses of individuals in the masses showed that the calcite contributions mainly came from pelecypods. One such pelecypod was identified as *Ostrea plicata*, and is wholly composed of calcite.

There are few reports in the literature with which to compare the compositions of the fossil species studied. Only that of Lowenstram (1954) on *Chama* shells from California, Japan and some Pacific Ocean localities is of any value. Lowenstram obtained 43-96% aragonite for shells from areas with water temperatures of 16-18°C; whilst shells from warmer (23-28°C) waters with 30-36‰ salinities possessed 100% aragonite. By comparison, the *Chama* shells from the basal parts of the Barton Sand Formation at Barton ('Bed H') with 100% aragonite could be reflective of a warm ($\geq$ 20°C) water during the shallowing-up of the Barton Sea (Curry, 1965).

The dominance of aragonitic forms in the succession is not well indicated in the mineralogical compositions of bulk samples of the clastic sediments. This might be due to reduction in the crystallinity, or even transformation, of aragonite during the Tema-grinding preparation of powdered samples used for compositional analyses. During grinding, localised increase in temperature and pressure might occur (Davies & Hooper, 1963). This, with the presence of thin films of moisture, may be sufficient to induce aragonite transformation (Lippman, 1973). The conditions would have been severe in samples containing very small amounts of aragonite originally.

11.3.3 Petrology

In thin sections, the aragonitic shells were observed to be composed of flattened, prismatic and bladed fibrous crystals. The 'C' axis of the crystals was aligned perpendicular to the shell wall. The prismatic crystals are often found in stacks, whilst the elongated crystals are mostly in cross-lamellar arrangements. Sometimes foliated structures were observed (i.e. Plates 32,63,67,84c). The crystal sizes vary from < 4 μm to about 50 μm. In many broken pieces, the mycostracal layers could be seen as roughened and darkened bands running parallel to shell elongation or wall. The crystals in the mycostracals were microcrystalline. The calcitic shells were mostly composed of flattened, prismatic calcite, also arranged perpendicular to the shell wall.

In stained thin sections (method of Lindholm & Finkelman, 1972) the gastropod shells in the freshwater limestones were seen to stain red (i.e. Plates 63, 64); so they are non-ferroan. A similar staining result was obtained for the shells in the calcareous concretions (Plates 67,68) and most of the sideritic ironstones.

Only in the ironstone samples ABLH-5 and 8, in the 'Lower Headon Beds' at Heatherwood Point, were some of the shells observed to have been partially or completely replaced by cryptocrystalline siderite (Plates 73a, 73b and 83c). In most of such replaced shells the characteristic cross-lamellar and/or foliated structure of the original aragonitic shells could still be observed. In sample ABLH-5, unreplaced, non-ferroan shells were still common and some still enclose micritic-mud calcite inherited from the primary limestone now sideritised in the ironstone. In a part of ABLH-5 there was a solitary occurrence of a shell and its lime-mud content completely recrystallized into non-ferroan sparry calcites (Plate 83a). This is difficult to explain in the poorly lithified and largely uncemented limestone. Perhaps localised freshwater incorporated into the limestone effected the sparry calcite replacements prior to sideritisation.

11.3.4 Fe, Mg, Mn and Sr Contents

i) XRD: Slow scan resolution of the $10\bar{1}4$ peak of the calcites gave d-spacings of 3·025 to 3·034Å, which correspond to low-magnesian calcites with $<$ 3 mol% $MgCO_3$ (Goldsmith et al., 1955).

ii) β-Probe and A.A.S.: β-Probe analyses showed a purity of 96-99% $CaCO_3$ for the shell impurities, there being $<$ 3% silica, $<$ 0·04% TiO_2 and $<$ 0·07% Al_2O_3. The impurities are probably quartz and clays that were not completely separated from the shells when cleaned. It is, however, thought that the presence of the trace to very small amounts of impurities would not have any significant effect on the shell compositions obtained.

Mg: The chemical compositions of the shells confirmed the low-magnesian nature of the skeletal $CaCO_3$ forms in the sediments under study. The Mg contents were very small and mostly below the lower detection limit of the β-Probe. Determinations on the A.A.S., however, gave the presence of 0·14% Mg ($\equiv$ 0·68 mol% $MgCO_3$) in the calcitic Ostrea shell, and about 0·02% Mg ($\equiv$ 0·01 mol% $MgCO_3$) in the various aragonitic shells.

Fe: Substantial amounts, 0·22 - 0·73% Fe were recorded for the shell assemblages on the β-Probe, but the A.A.S. analysis of the individual shells showed the presence of lesser amounts. The aragonitic shells contain 0·03 - 0·1% Fe ($\equiv$ 0·04 - 0·21 mol% $FeCO_3$), while 0·38% Fe ($\equiv$ 0·83 mol% $FeCO_3$) was recorded in the Ostrea. These showed the shells to be low-ferroan and that relatively higher Fe is incorporated in the calcite structure.

Mn: The Mn values in the assemblages and individuals were similar, varying between 100 and 300 ppm. However, very low, 20 ppm and 25 ppm, contents were recorded respectively for the aragonitic Cardita shells in 'Bed G' and the assemblage in 'Bed F'. Such low Mn contents might be due to the physiological capability of the animals concerned to filter

Table 14. Compositions of Fossil Shells from the Upper Eocene Succession, Hampshire Basin.

Division	Lithology and Horizons of Matrix Sediment	Fossil Shells	% Aragonite (and % Calcite)	Compositions (ppm) Sr	Mg	Mn	Fe
'LOWER HEADON BEDS'	Limestone, How-Ledge Limestone Alum Bay	*Galba* (lymnae) *Planorbis* (G)	100	550	160	160	950
	Greenish Clay, Top of Unio Bed/Base of Lymnae Marl, Paddy's Gap.	*Viviparus* (G)	100	750		n.d.	
	Greenish Clay, Overlying the Lymnae Limestone, Hordle Cliff Long Mead End.	*Megalocochlea*? (G)	100	680		n.d.	
	Clayey Sand ; 1.5m below top of Mammal Bed. Beacon Cliff Long Mead End.	*Viviparus lentus* (G)	100	1680	-	323	2215
BARTON SAND FORMATION	Ferruginous Sand. 2m below top of 'Bed K' Beacon Cliff, Long Mead End.	*Cyrena* spp (P)	100	1340	230	120	750
		Battileria concava (G)	100	1730	160	220	720
		Undifferentiated Shell Mass	100	854	-	106	4161
	Clayey Sand ; Chama Bed (Bed H) Barton	*Chama squamosa* (P)	100	1920		n.d.	
	Uncemented Mass of Shells. Shell Band (Bed G) Barton	*Cardita* spp (P)	100	1300	160	20	250
		Ostrea plicata (P)	(100% Cal.)	550	1420	500	3800
		Undifferentiated mass of pelecypods & gastropods	85% Arag. (15% Cal.)	2134	100	183	6308
BARTON CLAY FORMATION	Brownish Clay ; 3m below top of Bed F. Barton	Undifferentiated mass of pelecypods and gastropods	100% Ar. (plus traces of Calcite)	2292	nd	25	7248
	Greyish Clay, Bed E. Barton	*Corbula pisum* (P)	100%	2410		nd	
		Crassatellites sulcata (P)	100	2450			
	Glauconitic Sandy-Clay, Bed C. Barton	*Clavilithes* spp (G)	100%	1705		nd	

(P) - Pelecypod species

(G) - Gastropod species

ND - Not determined

off or exclude Mn from materials secreted in shells. The relatively high, 500 ppm, Mn present in the Ostrea shell may be reflecting the preferential incorporation of manganese in calcitic structures.

Sr: The Sr concentrations in the shells vary widely from 550 ppm to 2450 ppm. These concentrations are very much within the full range of < 2500 ppm Sr biochemically partitioned in molluscan shells (Kinsman, 1969; Hallam & Price, 1968). There was a significant decrease in Sr concentrations of the shells up the succession; significant differences between shells from fresh-water sediments and marine-brackish sediments; as well as a less significant difference between the $CaCO_3$ shell types.

Factors that could affect or influence Sr concentrations in shells are mainly the shells' $CaCO_3$ form; physiological or evolutionary levels of the animal; and habitat conditions, especially temperature and/or salinity (Lowenstram, 1954; Chave, 1954; Hallam & Price, 1968).

Calcitic shells incorporate less Sr; hence the 550 ppm Sr in the Ostrea shell was low in comparison with the higher amounts in the aragonitic shells. Although the shells analysed were of different species, all are of the same evolutionary class - the molluscs. So the recorded Sr variations in the aragonitic shells would possibly be more dependent on the animals' physiological state and/or external factors.

The physiological control of how much of isostructural elements can be incorporated into skeletal $CaCO_3$ is difficult to ascertain, presently unknown and still a subject for research (Lippman, 1973). It is only envisaged that body fluids with Mg/Ca ratio > 2 would favour aragonitic shell formation, while lesser ratio values would favour calcitic forms (Folk, 1974).

The external temperature dependency of Sr incorporation into shells has been studied by Davies (1964), Dodd (1965) and Hallam & Price (1968) using Mytilus or Cardium edule respectively. The authors generally deduced a decrease in Sr concentrations with increase in temperature of the water abodes of the animals. The work of Hallam & Price detailed a decrease of Sr from 2660 to 910 ppm within mean temperatures of 13·5 to 27°C. If it is assumed that the Sr concentrations of shells varied with temperature, then in the succession under study, it might be inferred that:

a) the shells with $\geqslant$ 2000 ppm Sr in the Barton Clay, particularly 'Barton Beds E and F', would be of cool water ($<$ 18°C) forms; hence suggesting a cool Barton Sea water. Such a deduction would be in agreement with the inferences from previous palaeontological and stratigraphical work of Gardner et al. (1888), Burton (1929 & 1933), Murray & Wright (1974), Curry (1965) and others on the 'Barton Beds' and Tertiary sediments of Hampshire and/or the London Basin. The authors deduced a cool Barton Sea with a bottom temperature of between 16° and 18°C (i.e. Murray & Wright, 1974 - using the presence of Cibicides and Q.seminulum in the Barton Clay).

b) the varying 2000 → 1000 ppm Sr in shells from the lower part of the Barton Sand, and lower parts of the succeeding 'Lower Headon Beds' (i.e. Mammal Bed), suggests a fluctuating but general increase in temperature of the water bodies up the section. This might have been related to the gradual silting up and shallowness of the Barton Sea (Curry, 1965). With increased shallowing, the sea-water would progressively be equilibrated with the atmospheric temperatures, which might have been higher than that in which much of the Barton Clay was deposited. Indeed, microflora assemblages in the Barton Clay Formation (Chandler, 1960) indicate the presence of near-by land masses with warm, tropical to sub-tropical type environments.

c) by the time the fresh-water environments became established the water bodies inhabited by the invertebrates had become relatively warmer, so as to induce the efficient physiological exclusion of Sr from the shell materials. Hence the low, 550-750 ppm, Sr in shells from the greater part of the 'Lower Headon Beds'.

Although the higher 1680 ppm Sr of the Viviparus shells in the 'Mammal Bed' might be reflective of temperature differences from that of 750 ppm Sr in the 'Unio Bed'/'Lymnae Marl Bed' higher up the succession, it perhaps draws attention to an alternative explanation for the variation of Sr contents of fossils in the Upper Eocene succession. The alternative could be salinity.

Salinity controls on the Sr content of shells has not been well established; the works of Dodd (1965) and Hallam & Price (1968) deduced no relationship between them. They do not, however, conclusively invalidate the possibility of salinity influence - first suggested by

Lowenstram (1954), although with no experimental proof.

Salinity could not be determined for the exposed sediments studied, but relating the earlier established (previous workers) stratigraphy to the shells' Sr concentrations and variation across the succession, it may be suggested that: a) high Sr– containing aragonitic shells (with > 2000 ppm Sr) dominated the open, normal marine waters of the Barton Clay (i.e. 'Beds E and F'); b) aragonitic shells with ~850 to ~2000 ppm Sr dominated the shallower near-shore, very hyposaline to slightly hypersaline Barton sea-water environments and the brackish 'Mammal Bed' (Edwards, 1967; Keen, 1977); c) low Sr-containing aragonitic shells (with < 800 ppm Sr) dominated the very shallow freshwater horizons of the 'Lower Headon Beds'. In fact, the gastropods of these freshwater sediments (namely Viviparis, Galba, Plonorbis) are grazers (pulmonates), and would have inhabited not only shallow ponds, lakes, margins of sluggish rivers, sheltered bays, etc., but also surrounding wet, vegetated lands. Gastropods adapted for much land life might have physiologically evolved efficient exclusion or minimization of impurities in their shells.

The very low, 550 ppm, Sr in the gastropod shells from the How Ledge Limestone is of particular importance. The limestones occurring in the 'Lower Headon Beds' are poorly lithified, friable and very porous. Their present state of lithification might have been attained soon after their deposition – a feature typical of calcareous sediments formed in freshwater conditions (Lippman, 1973). The limestones in the 'Lower Headon Beds' had not undergone any significant re-crystallization or cementation, and the shells contained are still 100% aragonite, thus indicating that they have not suffered any diagenetic transformation (see Sections on Carbonate sediments). Therefore the low Sr content in the shells in the limestones could not be due to diagenetic losses accompanying transformation of aragonite. It shows, rather, the original Sr content in the shells. That being so, then the water bodies in which the limestones accumulated could be inferred to have been warm and fresh (non-saline). This would be consistent with the conditions of formation and occurrences of calcareous muds and marls in low-energy, shallow water bodies of creeks, lakes, etc. (Terlecky, 1974; Bathurst, 1975).

If the deduced temperature of the Barton Sea and depositional waters of the 'Lower Headon Beds' was correct, then the Upper Eocene palaeo-environment may be equated to present day warm climatic areas. This would very much agree with the prevalence of humid tropical and warm, humid sub-tropical Eocene palaeoclimatics inferred from floral studies (cf. Daley, 1972; Fowler et al., 1973; Hubbard & Boulter, 1983). In fact, the deduced increased warming in the late Barton Sea phase into the non-marine waters of the 'Lower Headon Beds" significantly corresponds closely to the late Eocene 'warm episode' (Palynology Zone e) of Hubbard & Boulter (1983). It would also support warm aerial conditions inferred as necessary for the red-yellow podzol palaeosols in the succession to develop in locally emerged areas (see Chapter 16).

11.4 Summary

Fossil shells in the Upper Eocene sediments of the Hampshire Basin are mostly those of gastropods and pelecypods. The shells are mostly of aragonitic form; only very few, particularly the pelecypods such as Ostrea plicata, are calcitic.

The shells are low-magnesian and low-ferroan. They contain < 1 mol% $MgCO_3$, ≤ 1 mol% $FeCO_3$ and ≤ 500 ppm Mn. The higher amounts of these components are possessed by the calcitic shells. The Sr contents are very variable but well within the amounts previously recorded (≤ 2500 ppm) in molluscan shells. The calcitic Ostrea contained 550 ppm Sr, while the individual aragonitic shells possess Sr varying from 550 ppm to 2450 ppm. Those shells with > 1000 ppm Sr might be reflecting marine-brackish waters with cool ($\sim 14-20^{\circ}C$) water temperatures. They typify the conditions of the Barton Sea and parts of the 'Lower Headon Beds'. Shells with < 800 ppm Sr would, alternatively, reflect the relatively warmer and shallower Lower Headon freshwater bodies and environments. Equivalent palaeoclimates might be the wet and dry tropics to humid sub-tropics.

The preservation of aragonitic shells, even in the carbonate sediments, showed that the sediments in the succession have not undergone advanced or intensive burial diagenesis and cementation. Only in some sideritic ironstones are occasional partial or complete replacements of the aragonitic shells by cryptocrystalline siderites observed.

CHAPTER 12

MAJOR ELEMENT GEOCHEMISTRY OF THE CLASTIC SEDIMENTS

12.1 Introduction

The commonly occurring minerals in the Upper Eocene succession of the Hampshire Basin are those described in the previous chapters. These minerals - quartz, feldspars, clays, pyrite, goethite, and biogenic calcite and aragonite - are the predominant constituents of the clastic sediments. There are, however, a few more minerals in the succession not yet considered. They are limited to the carbonate sediments, and consist of physico-chemically precipitated lime-mud calcites in the freshwater limestones, the diagenetic calcites in the calcareous concretions and siderites in clay ironstones. These are discussed in Chapters 13 and 14.

The main purpose of this chapter is the presentation and discussion of the major element compositions of the clastic sediments with respect to their differential lithology and mineralogy. The chemical compositions of the sediment samples are given in Tables 15a - g, and their stratigraphic distribution shown in Figures 20a - c. Attention needs to be drawn to the subtlety of the lithological descriptions and differentiation of the sediments into clays and sands because of the continuity of their quartz-clay contents (Fig. 22 ; Chapter 4). In the absence of particle-size analysis not performed during the course of the present study, relative objective differentiation criteria of quartz (+ feldspar)/total clays ratio of 5:1 was employed as a lower compositional limit for the sand sediments (cf. Krumbein & Sloss, 1963, Ch.5; Pettijohn, 1975). That ratio value gave the closest approximation to lithologies used in the field descriptions of the sediments (Chapter 2; Appendix 1). It should also be stated that the lignitic clays and the goethite-rich horizons have not been considered in detail because of their peculiar nature - the possession of pedogenous features. Their consideration as palaeosols is made later in Chapter 16.

12.2 Elemental Abundances

The compositions of the clastic sediments are dominated by silica and alumina, with iron-oxides, magnesia, lime, potash and sulphur occurring in smaller amounts; whilst soda, titania and phosphorous mainly occur in insignificant amounts. Details of the elements abundance and variation are as follows.

Table 15a : Chemical Composition of the 'Lower Headon Beds', Mainland Hampshire.

	MAJOR ELEMENT CHEMICAL COMPOSITION (%)														
.	SiO_2	TiO_2	Al_2O_3	EeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	L.O.I.	TOTAL
BLH 1	87·05	1·04	6·23	0·20	1·64	0·52	0·27	0·10	1·28	0·06	0·01	1·50	2·00		101·90
2	63·70	0·90	11·57	1·01	3·44	0·83	3·76	0·20	1·86	0·02	1·41	8·18	4·78		101·66
3	56·44	0·78	12·36	0·77	5·43	0·82	3·79	0·18	1·97	0·02	3·25	13·19	2·81		101·81
4	67·86	0·86	7·21	1·08	3·15	0·59	6·26	0·01	1·38	0·03	2·12	8·84	1·76		101·15
5	46·51	0·82	9·92	0·52	16·19	0·83	11·22	1·18	1·61	0·10	0·30	7·42	1·63		98·25
6	91·25	0·72	3·90	0·14	0·77	0·32	0·25	0·01	0·95	0·04	-	-	2·00		100·35
7	43·60	0·65	14·20	0·58	3·11	0·91	15·81	0·27	2·11	0·10	0·44	14·95	3·41		100·14
8	68·75	0·84	11·56	0·60	3·59	0·70	0·53	-	1·75	-	0·50	7·07	5·15		101·11
9	89·81	0·51	3·47	0·32	0·89	0·27	0·16	0·13	0·45	0·02	0·08	1·40	0·93		98·44
10	65·44	1·06	13·62	1·20	1·45	0·59	0·19	0·22	1·86	-	0·86	9·73	5·67		101·89
11	50·61	0·38	9·42	0·20	8·46	0·24	10·74	0·05	0·56	0·01	5·17	3·04	6·78		99·95
12	75·58	0·22	1·04	1·9	16·44	0·90	0·86	0·29	0·08	0·02	0·68	2·15	1·33		101·49
14	76·12	1·12	12·21	0·12	2·71	0·30	2·94	0·20	1·81	0·03	0·09	1·40	1·53		100·58
15	73·76	0·70	14·49	0·36	2·72	0·16	0·68	0·84	1·25	0·03	0·09	3·38	3·64		98·71
16	88·31	0·88	4·52	0·14	0·86	0·34	0·54	0·20	0·82	0·02	0·01	0·72	0·97		98·34
18	73·55	0·93	13·32	0·29	5·06	0·38	0·63	0·43	2·28	0·04	0·09	1·40	1·9		100·30
19	11·28	0·18	3·20	0·58	0·86	1·24	44·54	0·12	0·24	0·03	0·26	35·85	1·85		100·23
20	51·38	0·68	13·59	0·58	2·40	0·56	5·12	-	1·08	-	0·16	21·71	4·06		101·82
21	75·57	0·95	12·45	0·30	4·20	0·76	0·84	0·25	1·97	0·04	0·05	2·15	2·79		101·72
22	69·94	0·61	4·18	3·40	7·41	0·51	5·71	-	0·79	0·06	0·04	8·42	0·87		101·94
BLH 24	92·60	0·82	2·43	0·11	0·39	0·27	0·45	0·48	0·50	0·04	0·11	0·90	0·50		99·61
25	54·60	0·77	15·54	0·79	3·98	0·88	7·47	0·87	2·56	0·09	0·82	6·77	5·10		98·57
26	94·62	0·21	1·25	0·10	0·36	0·16	0·26	0·34	0·57	0·06	0·03	1·43	0·38		99·77
27	52·64	0·68	16·07	0·84	3·94	0·81	8·63	0·28	2·69	0·11	1·17	8·74	5·32		101·92
28	58·76	1·10	18·29	1·62	2·52	0·56	0·30	0·82	2·36	-	1·99	7·61	3·09		98·77
29	90·47	0·42	3·94	0·13	0·84	0·25	0·15	0·15	0·46	0·03	0·25	1·38	0·55		99·00
30	92·48	0·53	2·63	0·10	0·41	0·20	0·10	0·07	0·38	0·02	0·03	1·73	1·35		100·00
31	88·47	1·17	5·25	0·20	0·95	0·29	0·14	0·10	0·76	0·03	0·33	1·75	1·75		100·31
32	68·22	1·08	16·64	0·12	4·60	0·69	0·48	0·23	2·59	0·05	0·18	1·38	4·88		101·13
33	58·39	0·42	3·02	13·82	6·12	0·58	3·81	-	0·63	0·07	0·16	13·14	1·13		101·29
35	87·01	0·63	2·39	0·18	0·39	0·22	4·96	0·19	0·64	0·11	0·39	4·15	0·52		101·78
36	9·14	0·24	4·46	37·7	6·48	0·69	7·58	0·03	0·55	0·12	0·10	30·35	0·87		98·31
37	73·46	1·00	12·22	0·30	3·42	0·35	1·56	0·12	2·32	0·04	0·11	1·02	2·91		98·82
39	66·01	0·84	14·15	0·20	2·90	0·55	0·76	0·23	1·84	-	0·40	9·06	4·80		101·74

Table **15b** Chemical Compositions of the Barton Sand Formation, Barton-on-Sea

	MAJOR ELEMENT CHEMICAL COMPOSITION (%)														
Samples	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	L.O.I.	Total
BBB															
1	34.74	0.26	16.53	1.58	7.65	0.46	0.29	0.21	1.01	0.01	0.59	71.92	8.91	35.95	98.69
2	64.63	1.09	11.62	0.66	5.65	0.23	0.27	0.01	2.01	0.04	3.10	6.15	5.06		100.52
3	43.74	0.56	17.26	3.81	2.55	0.58	0.19	0.34	1.55	0.01	0.65	47.71	7.89	28.18	98.76
4	90.25	0.22	3.18	0.13	0.85	0.27	0.10	0.11	0.80	0.02	0.11	1.78	0.90		98.71
5	76.18	0.61	9.95	0.29	4.74	0.40	0.16	0.05	2.49	0.03	1.17	1.42	2.90		100.38
6	90.19	0.24	3.06	0.14	0.89	0.27	0.09	0.16	0.81	0.02	0.13	1.42	0.50		100.33
8	90.35	0.17	2.08	0.06	1.23	0.15	0.08	0.36	0.86	0.02	0.17	1.96	0.67		98.14
9	88.52	0.43	4.20	0.14	1.46	0.34	0.09	0.27	1.35	0.03	0.07	1.07	0.55		98.52
10	78.45	0.68	8.89	0.23	3.25	0.51	0.08	0.30	1.82	0.01	0.98	3.20	0.61		99.66
12	69.57	0.79	12.93	0.66	4.39	1.02	1.00	-	2.57	0.05	0.98	3.20	3.16		100.33
13	67.73	0.82	14.01	0.59	5.06	1.20	0.98	-	2.61	0.06	1.10	3.83	2.48		100.48
14	87.48	0.26	4.80	0.20	1.97	0.49	0.17	0.07	1.15	0.04	0.07	1.42	0.51		98.64
16	92.39	0.12	2.19	0.09	0.23	0.20	0.11	0.12	1.07	0.02	0.02	1.96	0.15		98.67
18	90.68	0.15	3.17	0.22	0.29	0.25	0.14	0.18	1.45	0.02	0.04	-	0.76		97.34
20	88.56	0.24	3.61	0.16	1.70	0.38	0.23	0.13	1.42	0.03	0.44	1.07	1.75		99.72
22	79.37	0.46	8.15	0.35	3.25	0.66	0.57	0.11	2.12	0.02	0.68	1.42	2.95		100.11
23	22.11	0.47	7.12	28.49	5.75	2.18	5.42	0.10	0.55	0.06	0.32	25.73	1.41		99.71

Table 15c : Chemical Composition of the Barton Clay Formation, Mainland Hampshire.

	MAJOR ELEMENT CHEMICAL COMPOSITION (%)													
Samples	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	L.O.I.	Total
BBB															
24	52.06	0.86	17.82	1.74	5.24	1.83	5.46	0.09	2.85	0.07	0.73	6.77	4.99		100.52
25	15.88	0.30	5.50	2.64	1.97	1.55	38.01	0.02	0.38	0.09	0.16	32.76	1.44		101.15
26	32.83	0.61	10.51	18.65	2.02	2.33	7.63	0.16	0.76	0.06	0.56	20.82	2.73		98.92
27	51.60	0.85	17.77	1.47	4.95	1.88	5.95	0.12	2.95	0.08	0.93	6.77	3.48		98.79
30	56.25	0.80	17.11	1.26	5.60	1.61	4.28	0.21	2.81	0.03	1.20	5.42	3.72		100.30
31	10.74	0.20	3.47	1.98	1.78	1.37	43.06	0.01	0.27	0.10	0.21	35.06	0.75		99.36
32	58.54	0.84	15.03	1.18	4.58	1.31	4.76	0.18	2.73	0.07	1.21	6.06	5.01		101.49
34	71.27	0.91	11.86	0.68	4.86	1.39	0.43	0.25	1.95	0.09	0.75	3.92	3.57		101.93
35	64.65	0.75	13.93	1.43	4.94	1.23	1.54	0.18	2.61	0.01	1.06	3.57	4.01		99.91
36	15.20	0.21	3.37	1.87	2.26	1.28	40.87	0.02	0.39	0.10	0.41	32.44	1.87		100.28
37	63.51	0.75	13.62	1.64	6.00	1.40	1.65	0.19	3.18	0.06	1.09	4.28	3.76		101.12
39	16.36	0.21	3.29	1.87	2.17	1.26	39.98	0.06	0.11	0.35	0.33	34.05	1.30		100.34
40	63.31	0.57	11.84	1.41	7.75	1.60	1.76	-	3.43	0.09	1.03	4.28	5.85		101.16
41	76.12	0.90	11.21	0.41	3.98	0.57	0.41	0.08	2.01	0.07	0.66	2.75	2.52		101.68
42	22.44	0.37	6.71	2.36	2.66	1.48	33.55	0.11	0.53	0.16	0.37	26.35	1.31		98.19
43	39.57	0.65	11.23	17.95	2.22	1.09	3.33	0.15	1.99	0.32	0.57	16.08	3.36		98.51
44	59.88	0.82	18.05	0.14	6.34	1.58	1.53	0.23	3.43	0.07	0.87	3.03	3.06		99.03
45	64.07	0.91	17.34	0.66	4.52	1.12	0.14	-	3.14	0.08	0.44	2.40	4.57		99.39
46	60.52	0.70	13.00	1.29	10.37	1.90	0.22	0.15	4.20	0.10	0.17	3.00	6.03		101.75
47	63.23	0.79	16.23	1.01	6.84	1.42	0.20	0.07	3.77	0.09	0.56	2.74	1.70		98.65
48	59.76	0.91	19.20	1.24	7.84	1.77	0.14	0.23	3.44	0.12	0.42	2.33	6.07		101.14
49	56.84	0.62	11.92	1.03	15.71	2.13	0.09	0.10	4.90	0.12	0.20	2.00	5.61		100.82
50	51.52	0.55	9.84	4.43	16.79	1.00	0.69	-	2.94	0.11	0.56	4.99	5.16		98.37
BHC															
1	58.93	0.40	9.60	1.38	13.64	1.77	0.20	0.04	5.40	0.09	0.89	2.40	5.95		100.68
2	69.95	0.59	10.22	0.96	9.61	0.91	0.14	0.02	3.40	0.08	0.43	2.20	3.10		101.61
BPB															
1	88.96	0.94	4.06	0.35	2.04	0.46	0.11	0.23	0.94	0.04	0.04	2.31	1.32		101.84
Septarian Calcite (BBB 36)															
	-	0.03	0.04	n.d.	4.13	1.03	52.63	-	-	-	-	41.95			99.81

Table **15d** Chemical Composition of the 'Lower Headon Beds', Heatherwood Point, Isle of Wight.

	MAJOR ELEMENT CHEMICAL COMPOSITIONS (%)														
Sample	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	L.O.I.	Total
ABLH															
1	0.07	0.03	0.13	0.52	0.98	0.91	53.31	0.12	-	0.08	0.09	43.79	0.79		100.72
2	1.75	0.04	0.61	0.50	0.49	0.86	51.83	0.21	0.02	0.31	0.29	43.60	0.41		101.61
3	0.25	0.02	0.14	0.45	0.59	0.90	54.22	0.04	-	0.05	0.19	43.05	0.95		100.67
4	35.59	0.42	5.89	0.73	1.64	1.26	28.62	0.17	1.27	0.05	0.33	22.17	1.78		99.92
5	10.98	0.23	2.59	42.16	2.24	-	6.65	-	0.42	0.10	0.26	32.82	0.44		99.39
6	0.86	0.03	0.30	0.39	0.72	0.90	53.40	0.37	0.02	0.06	0.26	42.86	0.48		100.65
7	10.20	0.12	1.64	0.39	0.43	0.74	48.48	0.03	0.04	0.03	0.12	37.98	1.10		101.12
8	12.71	0.23	2.87	42.84	5.34	-	2.95	0.02	0.53	0.13	0.16	30.31	1.31		99.40
9	78.61	0.83	9.94	0.13	2.39	0.53	0.28	-	1.56	-	0.19	1.85	3.08		99.39
10	85.07	0.99	8.25	0.10	1.07	-	0.21	0.09	1.37	0.01	0.09	0.67	2.20		100.13
11	31.19	0.28	14.25	3.09	4.68	0.22	0.73	-	0.65	0.01	1.23	85.59	10.65	44.35	99.44
12	86.35	0.29	6.10	0.24	0.87	0.14	0.13	0.06	1.23	-	0.04	1.50	1.80		98.75
13	56.51	0.36	5.77	0.20	3.06	0.19	0.40	-	0.84	-	1.27	63.85	6.08	32.29	100.89
14	95.56	0.10	2.22	-	0.14	0.06	0.06	-	-	0.01	0.05	0.81	0.96		99.96
15	90.63	0.29	4.84	0.07	1.11	0.25	0.13	0.05	0.48	0.02	0.03	1.70	1.30		100.96
16	73.52	0.94	14.61	0.19	3.82	0.03	0.20	0.19	2.88	0.04	0.11	1.88	2.37		100.78

Table **15e** Chemical Composition of the Barton Sand Formation and Palaeosols, Alum Bay, Isle of Wight.

	MAJOR ELEMENT CHEMICAL COMPOSITIONS (%)													
Samples	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	L.O.I.	Total
ABBB/FS															
1a	84.37	0.49	8.82	0.16	2.84	0.26	0.12	0.09	0.51	0.03	0.09		-	3.91	101.69
2a	77.95	0.78	11.27	0.10	4.89	0.40	0.17	0.12	1.06	0.04	0.15		-	5.16	101.64
3a	48.15	0.09	8.39	0.34	34.27	-	0.22	0.04	0.16	0.38	0.04		3.00	6.29	100.37
4a	89.28	0.03	3.29	0.40	5.15	0.05	0.06						1.50	0.29	100.05
ABBB/FS															
1b	81.91	0.54	6.70	0.20	6.92	0.22	0.12	0.04	0.43	0.07	0.09	-		4.66	101.9
2b	82.35	0.67	7.08	0.23	5.06	0.25	0.13	0.06	0.56	0.06	0.10			4.48	101.02
3b	83.54	0.41	6.18	0.16	6.64	0.20	0.14	0.03	0.31	0.06	0.09			4.16	101.91
4b	83.10	0.19	4.37	0.17	9.17	0.14	0.12	0.02	0.03	0.10	0.07		1.33	2.41	101.21
5b	83.13	0.17	3.87	0.16	11.29	0.12	0.10	0.02	-	0.13	0.08				99.01
6b	67.99	0.17	4.08	0.12	22.81	0.10	0.12	0.02	-	0.16	0.11		0.30	4.02	100.01
7b	83.75	0.13	3.86	0.12	10.22	0.11	0.09	0.02	-	0.08	0.07			3.22	101.78
8b	90.57	0.41	5.28	0.14	1.20	0.17	0.08	0.01	0.10	0.02	0.06			2.64	100.99
ABBB															
19	96.98	0.02	1.18	-	-	0.05	0.03	-	-	-	-	1.50	0.28		100.04
18	98.23	0.03	2.32	-	-	0.07	0.04	-	-	-	-	0.38	0.42		101.49
17	59.55	1.17	24.73	0.04	3.11	1.09	0.40	0.27	2.46	0.07	0.04	0.62	7.68		101.17
16	95.67	0.11	2.80	-	-	0.10	0.04	-	0.19	-	-	0.38	0.74		100.03
15	84.51	0.63	8.83	0.16	1.00	0.45	0.14	0.14	1.50	0.02	0.08	1.40	2.24		97.39

Table 15f Chemical Composition of the Barton Clay Formation, Alum Bay.

	MAJOR ELEMENTS CHEMICAL COMPOSITIONS (%)													
Samples ABBB	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	Total
14	70.46	0.84	13.54	0.79	3.09	0.36	0.53	0.17	2.2	0.05	1.10	3.38	4.50	101.58
13	10.34	0.36	6.74	41.7	3.74	0.20	3.09	-	0.94	0.11	0.37	31.16	1.26	99.57
12	63.17	1.12	18.03	1.09	4.87	1.48	0.47	0.20	2.82	0.06	0.51	3.11	4.66	101.59
11	59.06	0.87	16.92	0.61	5.77	1.27	0.46	0.16	2.86	0.05	1.79	5.73	2.60	98.15
10	55.29	0.79	13.30	1.62	3.73	0.81	7.62	0.20	2.36	0.09	1.08	8,87	4.90	100.18
9	77.93	0.74	7.37	0.31	5.15	0.78	0.30	-	1.34	0.01	0.57	2.96	2.12	100.95
8	18.30	0.20	2.91	2.15	1.39	1.24	40.22	-	0.27	0.10	0.8	30.45	2.09	100.12
7	72.21	0.70	9.03	0.92	6.69	1.49	1.40	0.07	2.40	0.07	0.60	2.90	3.31	101.49
6	64.85	1.18	16.96	0.43	4.08	1.61	0.85	0.32	2.60	0.05	0.80	2.33	6.63	101.97
5	16.35	0.16	3.59	1.67	1.47	-	40.79	0.01	0.94	0.13	0.38	32.33	1.24	99.06
4	16.67	0.25	4.68	1.87	1.90	1.29	39.39	-	0.33	0.13	0.66	29.83	2.07	98.97
3	75.72	0.92	11.55	0.39	2.85	0.83	0.59	-	1.77	0.02	0.37	2.96	2.12	100.08
2	66.74	0.81	13.17	1.04	3.24	0.71	3.89	0.17	2.33	0.06	0.70	4.80	3.29	100.95
1	63.31	0.57	11.60	1.16	6.74	1.28	3.48	0.19	2.94	0.07	1.14	6.28	2.41	101.17
ABHC														
1	78.42	0.72	8.00	0.36	5.25	1.03	0.43	-	1.85	0.04	0.51	2.59	2.13	101.33
2	78.53	0.73	8.84	0.09	3.58	0.57	0.27	-	1.32	0.01	0.72	3.33	1.46	99.45
ABPB														
1	73.17	0.08	5.90	0.31	17.65	0.06	0.09	-	-	0.34	0.02	0.74	3.14	101.5

Table 15g :Chemical Composion of the Upper Eocene Succession,Whitecliff Bay.

MAJOR ELEMENTS CHEMICAL COMPOSITION %

		SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O	L.I.O.	TOTAL
WBLH	1	58·89	0·80	16·42	0·37	6·19	0·97	3·43	0·20	3·29	0·32	0·37	4·52	4·61		100·06
	2	55·15	0·80	15·73	0·49	7·62	0·58	5·51	0·25	2·96	0·10	0·78	5·46	3·21		98·64
	3	68·30	0·83	12·88	0·40	8·53	0·14	0·67	0·19	2·05	0·08	0·12	2·92	4·53		101·64
	4	82·14	0·95	8·08	0·12	1·91	-	0·29	0·15	1·35	0·01	0·01	1·13	3·06		99·20
	5	86·84	0·80	6·84	0·07	1·50	0·45	0·10	-	0·86	-	0·02	0·47	2·14		100·09
	6	39·49	0·43	3·15	23·58	11·06	-	1·60	0·03	0·72	0·05	0·46	18·83	1·15		99·40
	7	55·12	0·84	20·24	0·54	3·34	0·45	1·10	0·41	3·14	0·02	0·68	8·28	7·27		101·57
	8	69·75	0·78	15·40	0·23	3·79	1·06	0·56	-	2·33	-	0·10	2·26	3·06		99·32
	9	22·35	0·22	5·80	3·52	1·13	0·28	1·71	-	0·71	-	3·82	114·30	10.18	63.18	98.90
	10	3·96	0·14	1·51	49·61	10·48	-	1·03	0·01	0·31	0·10	0·14	34·27	0·75		99·88
	11	72·33	1·01	11·43	0·40	6·21	0·13	0·58	0·13	2·13	0·03	0·02	2·26	2·12		98·74
	12	55·37	0·77	16·95	0·72	6·82	0·75	1·06	0·23	2·84	0·05	0·75	7·75	7·78		101·22
	13	63·28	0·80	14·82	0·18	9·12	1·22	0·66	0·20	3·95	0·07	0·06	1·51	4·56		100·43
WBBB	9	78·30	0·25	4·90	0·11	11·12	0·39	0·36	-	1·23	0·22	-	1·15	1·63		99·68
	8	89·95	0·21	4·28	0·06	1·93	0·34	0·17	-	1·0	-	-	1·15	0·92		100·01
	7	90·55	0·26	5·36	0·06	1·83	0·55	0·15	-	1·22	-	-	0·77	0·73		101·48
	6	90·87	0·28	5·01	0·07	1·20	0·54	0·19	0·22	1·37	-	0·05	0·38	1·07		100·97
	5	87·54	0·35	5·72	0·09	1·77	0·63	0·16	0·15	1·44	-	0·01	0·77	1·71		100·24
	4	75·35	0·57	9·32	1·15	4·95	1·23	0·26	0·21	2·32	0·02	1·01	2·68	2·42		100·36
	3	78·13	0·65	10·23	0·20	3·18	1·02	0·08	0·25	2·39	-	0·41	1·53	2·44		99·85
	2	32.69	0·31	6·40	24·01	5·44	0·53	3·31	0·09	1·13	0·67	0·31	21·84	2·11		98·52
	1	64·69	0·57	12·25	0·66	4·05	2·01	3·77	0·26	2·75	0·04	1·16	4·98	4·64		101·83

Fig.29a :Stratigraphical Variation of the Major Element Composition; Highcliffe-Milford-on-Sea, Mainland Hampshire

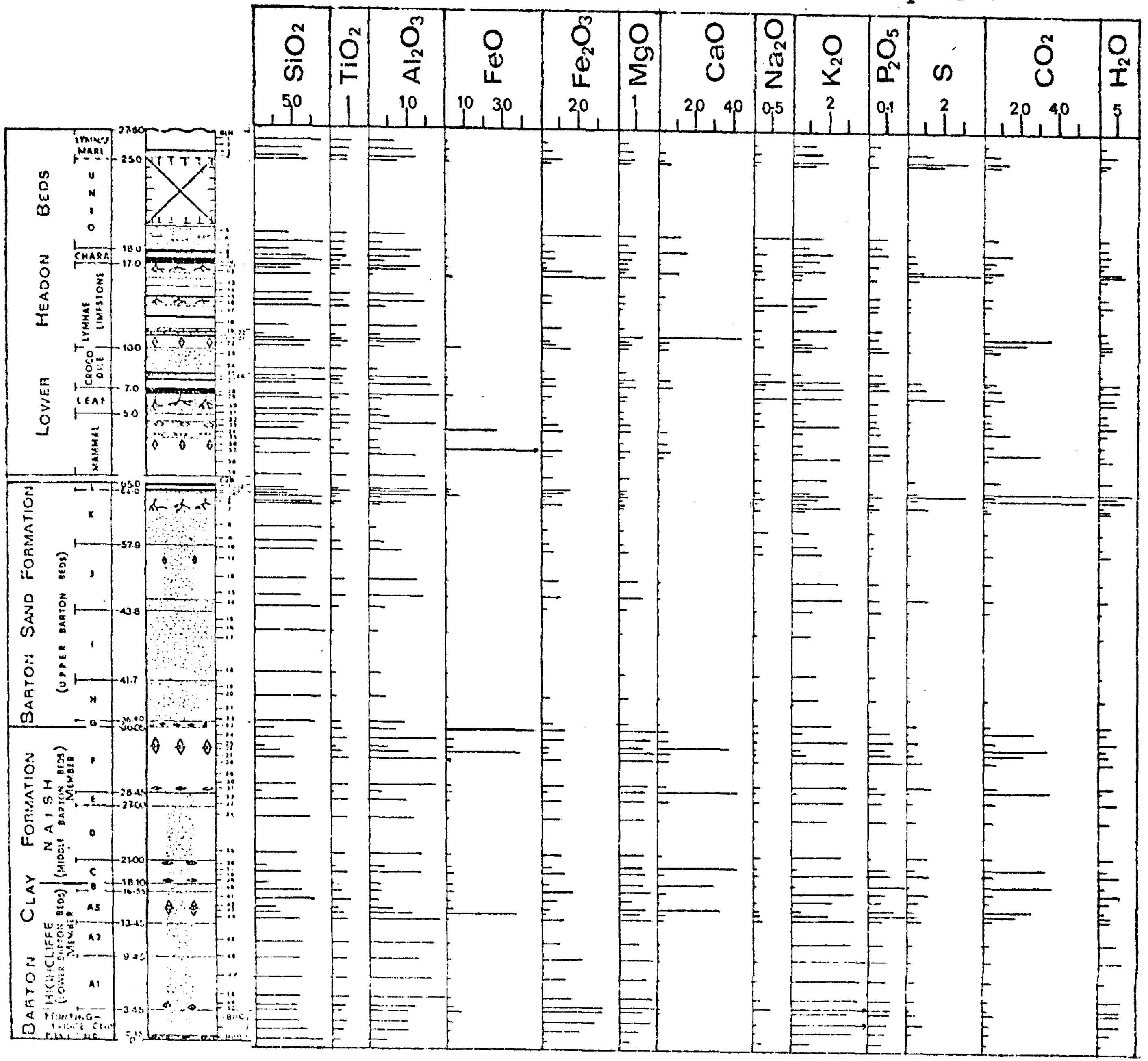


Fig.29b :Stratigraphical Variation of the Major Element Composition; Alum Bay-Heatherwood Point, Isle of Wight.

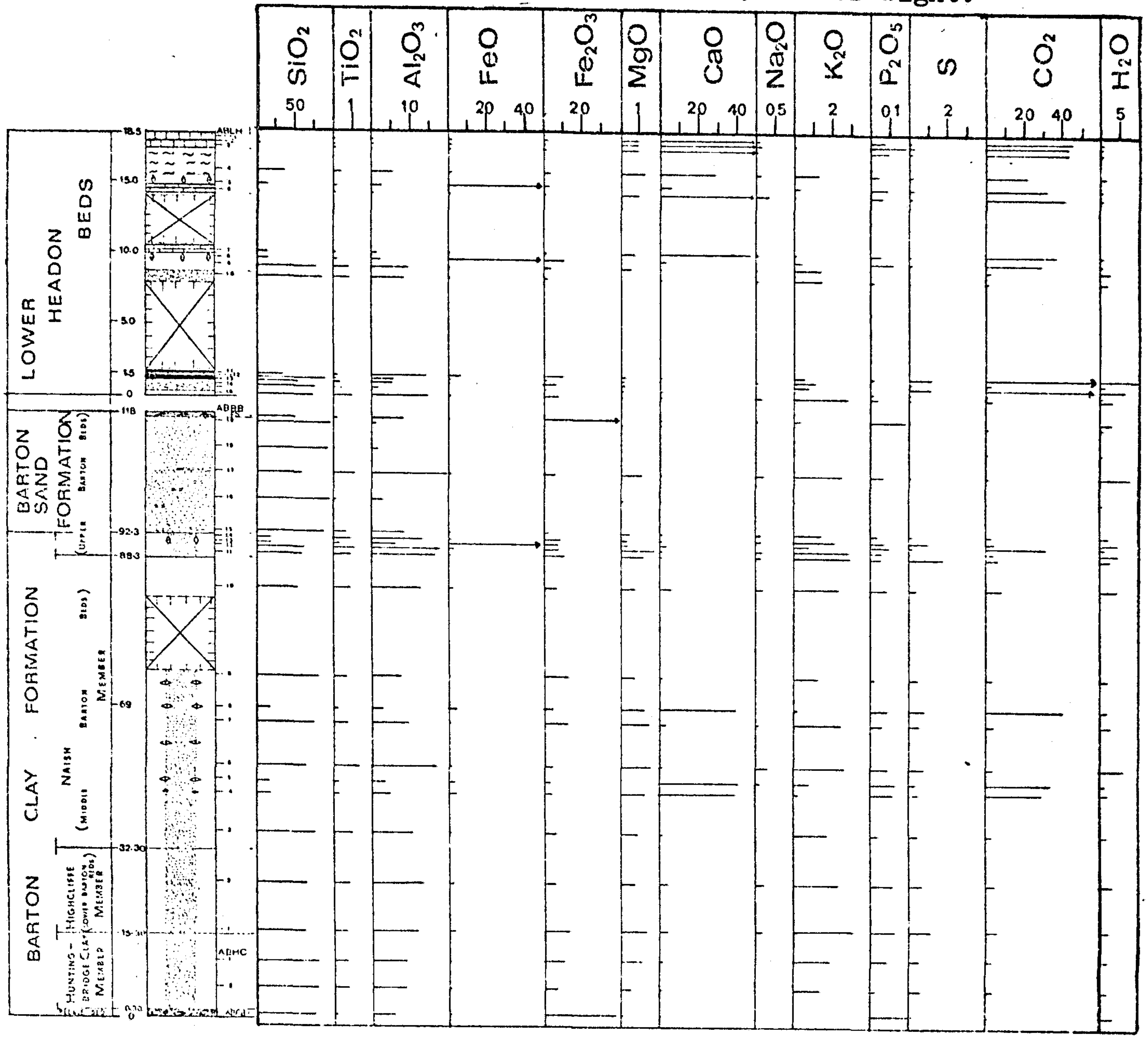
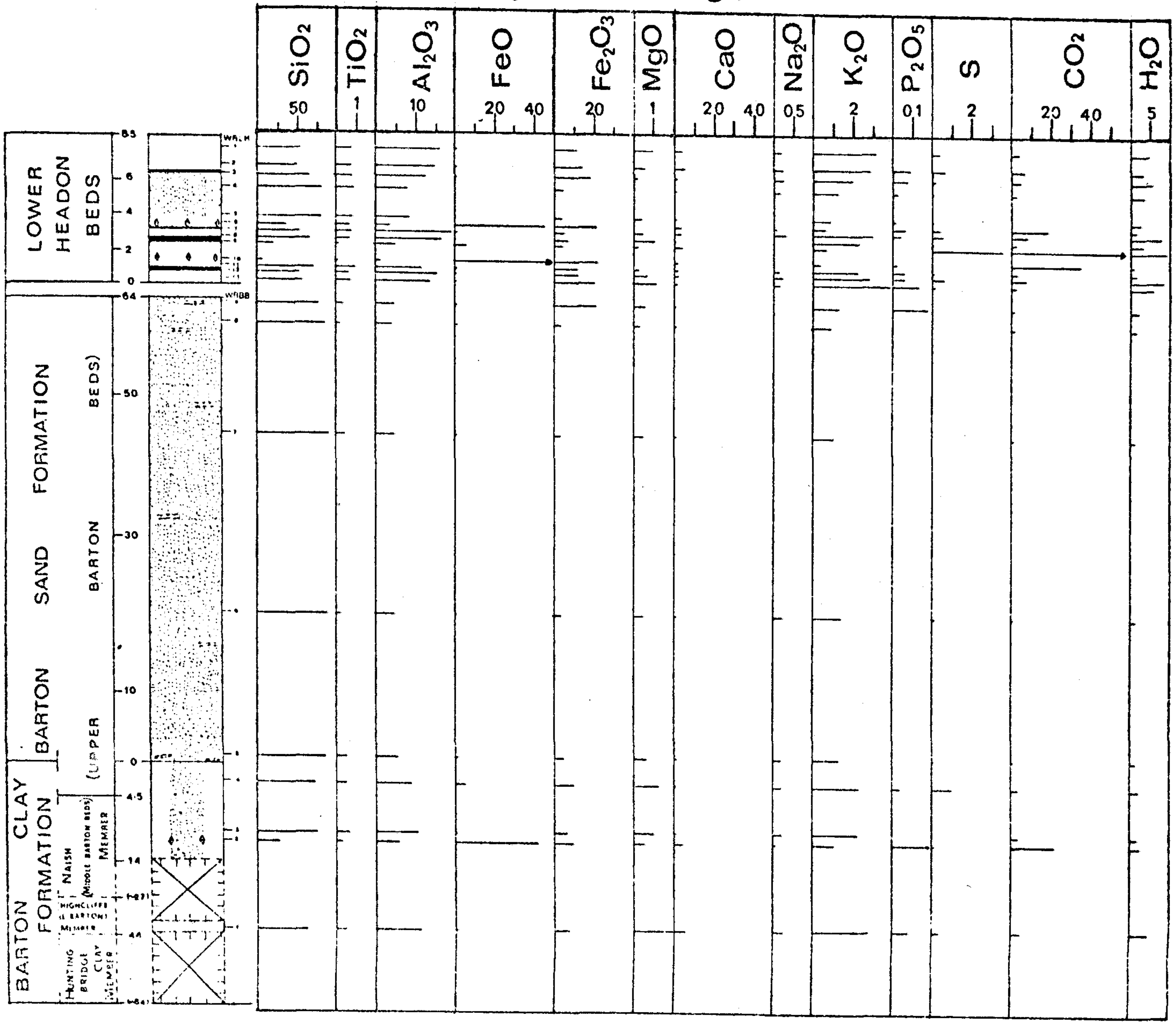


Fig.29c :Stratigraphical Variation of the Major Element Composition; Whitecliff Bay, Isle of Wight.



12.2.1 SiO_2 and Al_2O_3

The variations of the average amounts of silica and alumina in the sediments from different divisions of the succession are shown in Table 16 overleaf. Little differences exist between the clayey sediments. Their silica contents vary from 50 to 70% averaging 66·85 ± 8%, whilst the alumina, which varies a little more widely from 7 to 24%, averages 9·17 ± 1% in the Huntingbridge Clays, 13·7 ± 2·7% in the rest of the Barton Clay and 12·97 ± 3·2% in the 'Lower Headon Beds'. When compared to the reported compositions of average clays and shales in the literature (Table 17), the clayey sediments under study are seen to be generally more siliceous. This is also reflected in their quartz contents discussed in Chapter 4. The very siliceous clays are characterised by SiO_2/Al_2O_3 ratio values of between 6 and 10 (Figs. 22a, b). They include the Huntingbridge Clays and some parts of the Highcliffe and Naish Members of the Barton Clay at Barton (i.e. BBB-34 at the top of 'Bed D' and BBB-41 at the top of 'Bed A_3') and Alum Bay (ABBB-9). The few in the 'Lower Headon Beds' are those of Samples BLH-4, 14 and 37 at Long Mead End, and ABLH-9 at Heatherwood Point. These sediments would have been deposited in relatively shallower waters with strong current energies and/or more quartz-rich detritus.compared with the less siliceous clays whose SiO_2/Al_2O_3 ratio values are about 3. The less siliceous clays include the brown clays near the top of the Barton Clay at Barton ('Beds E and F') and Alum Bay, the pipe clays in the Barton Sands (ABBB-17) on the Isle of Wight, and most of the green clays in the 'Lower Headon Beds'.

The sand sediments possess compositions that are similarly dominated by silica in amounts of between 78 and 98%, and which average 89·66 ± 4·2%. Their alumina content is small, < 10%, and averages only about 4%. The very siliceous nature of the sands is an attribute of their high ($\gtrsim$ 80%) quartz contents and relatively very good sortings. The SiO_2/Al_2O_3 ratios allow some differentiation of very siliceous sands from those that are relatively more clayey or aluminous. The most siliceous sands possess $SiO_2/Al_2O_3 > 20$, and constitute the bulk of the Barton Sands at Alum Bay and many parts of the equivalent deposit at Barton (i.e. top of 'Bed H', the whole of 'Bed I', base of 'Bed J' and much of 'Bed K'). Sands in the 'Lower Headon Beds' and the matrix to the pebbles in the pebble beds are also similarly very siliceous. In contrast, lower SiO_2/Al_2O_3 ratio values (10-20) characterise the basal parts of the

TABLE 16: The Average Silica and Alumina Contents of Clastic Sediments in the Upper Eocene Hampshire Basin

Division		LOCALITY			
		Barton-on-Sea	Alum Bay	Whitecliff Bay	All Localities
A. Clayey Sediments					
Lower Headon Beds	% SiO_2	68·30	76·07	63·88	67·91± 7·7
	Al_2O_3	12·13	12·28	14·76	12·97± 3·2
Barton Sand Fm.	SiO_2	72·66	63·06 (pipe clay)		69·4 ± 7·3
	Al_2O_3	10·93	18·31		13·46± 3·5
Naish Member	SiO_2	59·70	69·19	↑	63·9 ± 9·4
	Al_2O_3	15·31	11·64	72·72	13·77± 3·5
Highcliffe Member	SiO_2	62·97	65·03	10·6	64·5 ± 6
	Al_2O_3	14·85	12·39	↓	13·95± 2·9
Huntingbridge Clay Member	SiO_2	64·44	78·48		71·46± 9·3
	Al_2O_3	9·91	8·82		9·17± 1
B. Sands					
'Lower Headon Beds'	SiO_2	87·5±6·6	90·42±5·3	84·49	89·20± 3·7
	Al_2O_3	3·9±2·3	5·1± 3·0	5·0	4·5 ± 2·2
Barton Sand Fm.	SiO_2		[79·36±11·9	(Palaeosols)]	
	Al_2O_3		6·30± 2·5		
	SiO_2	89·9±1·6	93·85±6·3	87·44±5·3	90·06± 4·1
	Al_2O_3	3·2±1·0	3·8 ±3·0	5·05±0·5	3·92+ 1·8
Pebble Bed	SiO_2	88·96	73·17		
	Al_2O_3	4·06	5·9		

Barton Sand at Barton and Alum Bay, and the sands in the succession at Whitecliff Bay. These contain more clays and feldspars; and sortings during their deposition would have been relatively less intensive.

12.2.2 Fe_2O_3 and FeO

The dominant iron-oxide is ferric-oxide, comprising between 60% and 98% of the total iron content (Figs. 21a - c). Fe_2O_3 occurs in variable amounts of trace to 16%, with the clayey sediments generally containing substantial amounts that average 5·4% compared with very small amounts (averaging about 1%) in the sands. Correlation between chemical and mineral constituents of the sediments suggests that where Fe_2O_3 is $<$ 6% in the clayey sediments or $<$ 1% in the sands, much of it is associated with the clay minerals, especially illite, illite-smectite and, to a lesser extent, the smectites. In these phases, Fe(III) would be occurring mainly as structural and/or adsorbed iron. In pure states, those clay phases can contain up to 5% structural Fe_2O_3 (Weaver & Pollard, 1973). The only iron-rich clay phase in the succession is glauconitic-mica in parts of the marine Barton Clay (Chapter 6). The glauconitic grains contain about 22·5% structural Fe_2O_3 (Table 12) and would have contributed to the iron recorded for the glauconitic sediments.

Abundances of ferric-oxide in excess of the average values mentioned above occur only in limited horizons and essentially at the sites where jarosite and goethite were recorded as being present. Jarosite and goethite are iron minerals, respectively containing about 48% and 63% structural Fe_2O_3 (Deer et al., 1962). Jarosite was recorded in the basal parts of the Barton Clay at Barton, whilst goethite was in the clays at the top and base of the 'Lower Headon Beds' at Whitecliff Bay. Goethite is also commonly disseminated in most parts of the Barton Sands, particularly on the Isle of Wight.

The jarosites observed are very likely to be alteration products of pyrite in the sediments upon the post-Oligocene regional uplift and coastline developments in southern England (Jones, 1981). The origin of the iron-oxide phases is, however, more difficult to ascertain. They could have been detritally derived although, as argued in Chapter 9, their limited extent would suggest localised sources and/or contemporaneous pedogenesis involving substantial mobilisation of iron. In fact, pedogenous accumulations of goethite were substantial, so as to cause induration of the pebble bed and podzol palaeosols in the succession at Alum Bay. The free iron-oxides would largely account for the yellowish coloration (ferruginous nature) of the Barton Sands. It is, however, noteworthy that many coloured sands in the succession at Barton and the 'Lower Headon Beds' only contain traces of Fe_2O_3. They are not as ferruginous as their petrographic descriptions (Chapter 2; Appendix 1) would suggest. Their coloration, which is sometimes lightly purplish or brownish, might rather be due to disseminated, and coatings of, organic matter and organo-Fe complexes.

FeO occurs in small amounts, up to 2%. The Barton Clay sediments mostly contain $\gtrsim$ 0·8% FeO, whereas clay units in the Barton Sand Formation and 'Lower Headon Beds' usually contain $<$ 0·6% FeO; whilst $<$ 0·4% FeO is common in the sands. When related to the sulphur contents of the sediments, it is seen that virtually all the FeO could be due to pyrite. In addition, correlation data in the clayey sediments suggests the presence of some Fe(II) in the smectite and, to a lesser extent, organic matter. The greater possibility of preserving those materials in marine sediments may account for the relatively higher abundance of ferrous iron in the marine Barton Clay compared to the non-marine 'Lower Headon Beds'. An apparent maintenance of oxidising conditions in the very porous sand sediments has, however, not facilitated extensive formation of diagenetic ferrous iron phases. The significance of this to the development of the diagenetic carbonates in the Upper Eocene succession is highlighted in Chapter 14.

12.2.3 MgO

Magnesia occurs in very small amounts of trace to 2% in the sediments; it nevertheless varies systematically up the succession. In the marine Barton Clay, MgO often occurs in amounts greater than 1%, whereas lesser amounts typify sediments of the Barton Sand and the 'Lower Headon Beds'.

MgO would be largely contained in the clay minerals, especially the smectitic and illitic phases. These dioctahedral clay phases can contain up to 4% structurally bound MgO (Weaver & Pollard, 1973). Glauconitic micas in the Barton Clay contain about 3% MgO (Table 12) and would have contributed to the magnesia contents of the glauconitic sediments. Contributions from the smectitic phases are underlined by significant correlation between smectite and MgO (r = 0·7) (Fig. 30). These would also account for the significant sympathetic relationship observed between the MgO values (Figs. 20a - c), the Mg/Al ratio values (Figs. 21a - c) and the smectite abundances and crystallinity indices (Figs. 23, 24). These relationships may have environmental implications. In the alkaline sea conditions, the smectitic phases would generally be stable (Kittrick, 1971), although smectites that are degraded may also be aggradated by partial adsorption of Mg^{2+} into the interlayer positions (Nicholls & Loring, 1960). There is no convincing evidence, however, that aggradation occurred on a significant scale in the Barton Sea (see Chapter 5 on clay mineralogy). In non-marine environments, especially in coastal-flood plains such as that in which the 'Lower Headon Beds' were believed to have accumulated (Edwards, 1966; Keen, 1977), freshly laid sediments can be brought into the ground-water zones with consequent possible degradation of the clay phases, including loss of magnesium by leaching (Dunoyer de Segonzac, 1970).

12.2.4 CaO

The CaO contents of the sediments vary widely from trace to 11%; the amount in each sediment being more or less dependent on the presence and abundance of biogenic carbonates and/or, in places, gypsum. A plot of $CaO_{(carbonate + gypsum)}$ vs Total CaO (Fig. 31) shows that virtually all the lime is in the carbonate minerals and/or gypsum. In the absence of these two materials, the lime content is generally $<$ 0·3%. This will possibly be structurally held in clay phases; hence the clays are not rich in calcium, and the smectites would not be beidellite (cf. Weaver & Pollard, 1973).

Fossil shells, which are primarily deposited materials, are very abundant in the marine Barton Clays and parts of the Barton Sand at Barton, and many horizons in the 'Lower Headon Beds'. The shells actually contribute up to 11% aragonite and/or calcite to the fossiliferous sediments. Much of the CaO would thus be due to the fossils. However, gypsum occurs in significant amounts in parts of the 'Lower Headon Beds' (i.e. BLH-11 from Hordle Cliff). In such sediments, substantial contributions of lime would come from the gypsum. The problem of dating the gypsum is discussed in Chapter 10. In the absence of evidence for prevalence of arid conditions and evaporitic depositions in the Palaeogene of the Hampshire Basin, the gypsum is very likely to be alteration products of the sulphide phases

Fig.30: Plot of %Smectite vs. %MgO For Clastic Sediments.

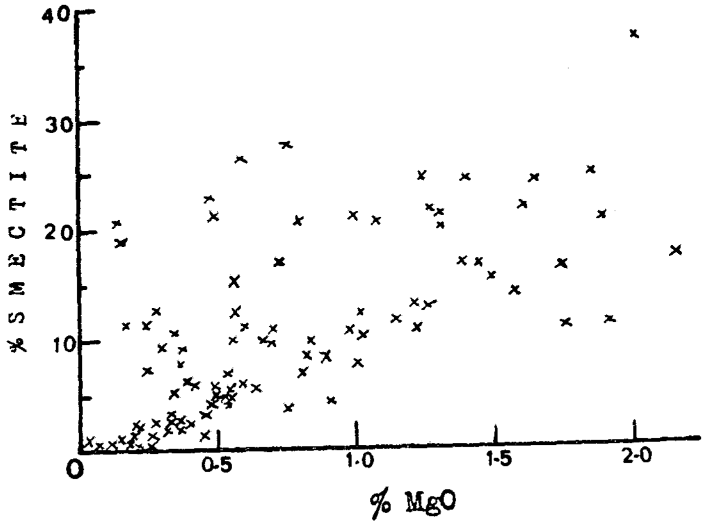


Fig. 31: Plot of CaO(Cal,Arag,Gyp) vs. Total CaO For Clastic Sediments

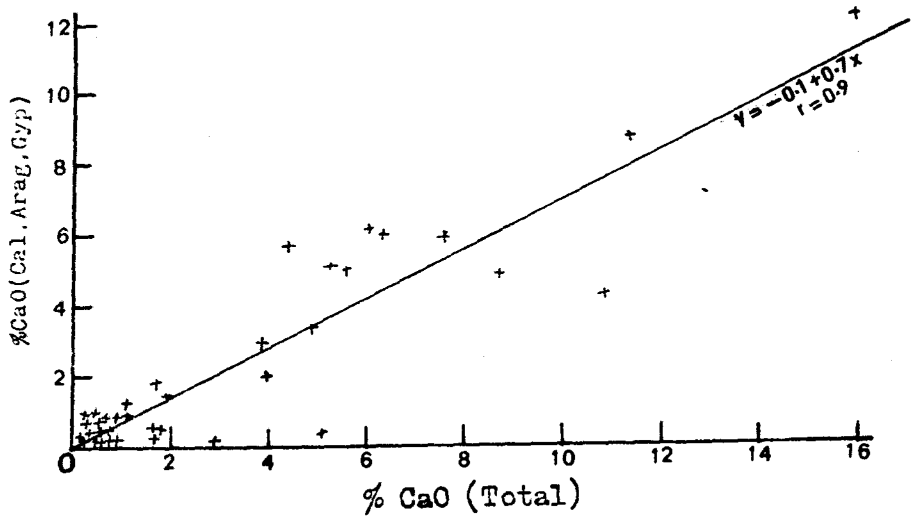
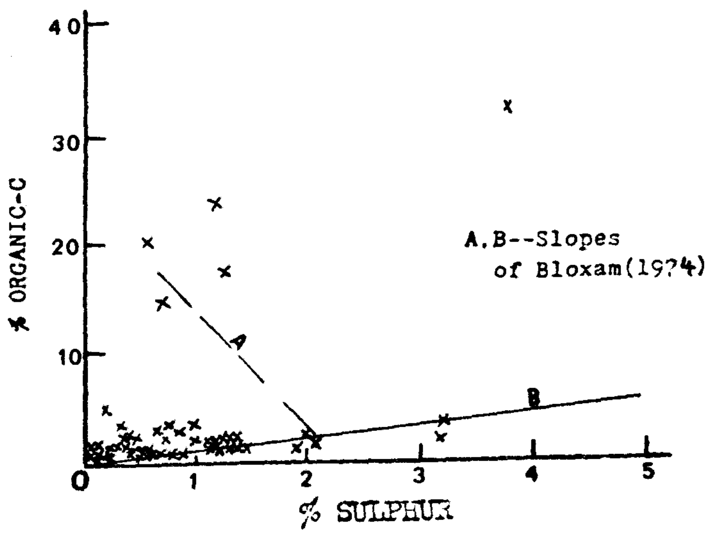


Fig.32: Plot of %Organic C vs %Sulfur For Lignitic and Carbonaceous Clays



such as the pyrite. Although the alteration could occur penecontemporaneously in the non-marine environment of deposition of the 'Lower Headon Beds', it is more likely to result from Recent weatherings.

12.2.5 Na_2O and K_2O

The alkali contents of the sediments are low ($<$ 5%) and dominantly potassic. The soda occurs often in insignificant, $<$ 0·3%, amounts. It would mainly be contained in the sodic feldspars; the very small soda contents appropriately reflect the low abundance of sodic feldspars in the succession. In contrast, the potash contents of the sediments are more substantial, varying from trace to 5·4%; although it averages 2·54 ± 0·8% in the clays and only 0·8 ± 0·4% in the sands.

Potash only significantly correlates with the potassic feldspar ($r = 0{\cdot}7$) and the illitic and smectitic phases ($r = 0{\cdot}6$). The sand sediment generally contains more feldspar (up to 15%) than clay minerals ($\lesssim$ 10%), whilst in the clayey sediments there are more illitic and smectitic phases (20 - 40%) than feldspars ($\lesssim$ 5%). These minerals would thus have contributed differential amounts of potash to the sediments. The glauconitic micas, with about 7% structural K_2O (Table 12), would also be significant in the glauconitic sediments of the Barton Clay. The presence of the 'glauconites', along with exogenous K-rich jarosites in some of the glauconitic sediments at Highcliffe, could account for the relatively high, 4-5% K_2O recorded in those sediments.

Apart from variation of abundance with regard to lithology, the soda and potash contents do not in themselves show any significant systematic variation up the succession (see Figs. 20a - c). The Na_2O/K_2O ratio was thus calculated and this, when plotted stratigraphically (Figs. 21a - c) was seen to show a relative lithological and environmental related variation. The ratios, or relative soda contents, increase into the very sandy clays and the sand sediments. They also increase from the marine to non-marine sediments. The increase of the ratios into sandy sediments would suggest the derivation of the sodic-feldspars as hydrodynamic equivalents of coarse detrital grains, which are dominated by medium sand-sized quartz grains. But the relative lower potash in the non-marine sediments may be due to possible degradation (leaching) of silicates, particularly the illitic and smectitic phases in near-surface conditions (Nicholls & Loring, 1960; Hirst, 1962).

Possible penecontemporaneous leachings have been advanced to account for very poorly crystalline illites, smectites and kaolinites occurring in the 'Lower Headon Beds' (Chapter 5). In contrast, potassic phases would be stable and the fixation of potassium into 2:1 clay phases (Nicholls & Loring, 1960) is more possible in marine environments. Indeed, potassium and iron (Fe III) have, very extensively, been fixed into authigenic glauconies in the early phase of the Barton Sea.

12.2.6 TiO_2

Titania occurs in small amounts, varying from trace to 1%, and averages 0·8 ± 0·3% in the clayey sediments, but 0·44% in the sands. Titanium often occurs in sediments as authigenic or derived anatase, rutile, brookite and ilmenite (Hirst, 1962; Walder, 1964). In the presently studied sediments, TiO_2 only has a significant correlation with the clay minerals ($r = 0{\cdot}5$) and could be occurring as finely-disseminated or adsorbed material in association with the clay minerals. However, a few small needle-like rutiles were observed in grain-mounts of the sand sediments. In fact, rutile is one of the common heavy minerals that Walder (1964) and Blondeau & Pomerol (1968) found in the Palaeogene succession of the Hampshire Basin.

Titania contents of sediments have sometimes been employed for sedimentalogical interpretations (cf. Hirst, 1962; Bhatt, 1974). Hence the Ti/Al and Quartz/Ti ratios of the sediments under study were calculated and plotted stratigraphically in Figures 21a - c. At the type locality, the Ti/Al ratio values are closely similar in the clayey sediments. Their detritus could have been similarly composed and derived. In the sand matrix of the pebble bed and sands of the 'Lower Headon Beds' the Ti/Al ratios are relatively very high, suggesting less clay-related titania but more of the coarser (possibly rutile) grains. This may have been related to differential supplies of coarser detritus and the prevalence of stronger currents during the deposition of these sandy sediments. In the case of the succession on the Isle of Wight, the Ti/Al ratio values are relatively very uniform and similar to those in the marine sediments at Barton. Derivations and depositional conditions would be closely similar for the succession. The pebble bed and Barton Sand at Alum Bay are, however, different from their equivalents on the mainland; they possess much lower Ti/Al ratios. The differences mostly arose from the contemporaneous development of the pebble bed and parts of the Barton Sand at Alum Bay as palaeosols with enriched authigenic goethite and kaolinite (see Chapter 16).

12.2.7 P_2O_5

Phosphorous is a minor constituent of the sediments. The amounts in which it mostly occurs are very low (0·1%) and within the lower detection limit of phosphorous on the β-Probe Spectrometer. Slightly higher P_2O_5 amounts of between 0·3 and 0·7% occur only in some of the very goethite horizons (i.e. ABBB-20, ABHB-3) and diagenetic carbonate horizons (BBB-39, BBB-43 and WBBB-2). These low phosphorous contents reflect the virtual absence of detectable phosphate materials (i.e. faecal pellets) and minerals (apatite) in the sediments. There are, however, sharks' teeth, fish otoliths and animal bones in the Upper Eocene succession (Stinton, 1976-78; Hooker et al., 1980). These may contain phosphorous; but they were not present in the samples analysed.

12.2.8 Sulphur

Sulphur occurs in variable amounts from trace to 5%, averaging 0·8% in the clays, but 0·4% in the sands. Organic matter buried in sediments could be one of the primary sources of sulphur. To verify the relationship, the plot of Organic C vs. % Total S was made (Fig. 32). When compared with a similar plot by Bloxam (1974) for some Palaeozoic sediments in Wales, the plot indicates that organic matter in the succession under study is largely 'denatured'. Sulphur associated with the organics had, with sulphur from depositional waters, apparently been fixed into pyrite in poorly drained surface conditions and in shallow burial diagenesis. Some of the pyrite has also been exogenously altered to gypsum and, in places, jarosite. The pyrites and exogenous minerals show a strong correlation (r = 0·7) with the sulphur contents; those minerals would be the main site of sulphur occurrence in the sediments. The highest amount, 5·17%, recorded in BLH-11 from the base of the 'Chara Bed' in the 'Lower Headon Beds' on Hordle Cliff would thus be due to substantial presence of gypsum in the altered pyritic fossil shells in the horizon. Altered pyritised shells and plant materials would also account for some other horizons with < 1% S; the horizons include BBB-2 and BLH-3.

12.2.9 CO_2

The carbon dioxide contents reflect the abundance of organic matter and carbonate materials in the sediments. CO_2 occurs in amounts of trace to 15%, with amounts $>$ 3% occurring in the fossiliferous and/or carbonaceous horizons. CO_2 occurs in substantially high amounts in the lignites including WBLH-9, BLH-11, ABLH-13, BBB-1 and BBB-3. These lignites contain organic C in excess of 13% and up to 31% in WBLH-9.

12.3 Discussion - Comparison with Sediment Types

The clayey sediments of the Upper Eocene Hampshire Basin possess chemical compositions that compare closely with the average compositions of some clays and shales in the literature (quoted in Table 17). These are the non-marine and continental clays on the Russian Platform (Ronov & Kitchebnikova, 1955) and non-marine Carboniferous Shales in the U.S.A. (Murray, 1954). Exceptions to the above are the less siliceous brown clays close to the top of the Barton Clay Formation at Alum Bay and Barton. They possess compositions similar to those of some Recent near-shore marine brackish water clays (Hirst, 1962) and shales (Murray, 1954). The pipe-clays are closed in composition to the reported non-marine clays of the tropical Russian Platform, except that the pipe-clays contain higher amounts of magnesia and potash.

The sand sediments, when compared with some reported deposits (Table 17), are seen to be dominantly quartz-arenites, whilst a few would be lithic-arenites. Further characterisation was made using the plot of log wt%(Na_2O/K_2O) vs log wt%(SiO_2/Al_2O_3) shown as Figure 32. When compared with a similar plot by Pettijohn _et al_. (1972), the sand sediments under study are seen to fall into the sub-arkose - sub-lithic arenites - quartz arenite sand type field. These sands are generally matured and well-sorted, often with compositions dominated by quartz but low in feldspars.

In general, the clastic sediments are very siliceous. Further indications of their siliceous nature and low alkali contents are provided by the plot of log wt%(SiO_2 + Al_2O_3) vs log wt% $\left[(Na_2O + CaO)/K_2O\right]$ shown as Figure 33. A similar plot by Garrels & Mackenzie (1971) for some modern sediments is shown as an insert in the figure. Comparison of the plots shows the clayey sediments in the succession studied to spread over a wide field including nearshore marine clays, terrigenous clays and also extend into a higher silica, more potassic but low soda and lime

Table 17: Average Compositions of Sedimentary Rocks.

	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	S	CO_2	H_2O
CLAYS & SHALES													
Near-Shore Marine Clays (Hirst,1962)	55·6	0·8	15·5		7·4	2·2	1·0	2·2	2·3	0·1	-	1·4	10·3
Temperate Belt Clays (R&K*)	63·06	0·69	13·53		5·25	1·57	3·16	1·98	3·97	-	0·12	7·08	-
Tropical Belt Clays (R&K*)	53·32	1·21	29·79		2·43	0·54	0·93	0·56	1·24	-	0·09	10·01	
Marine Clays(R&K*)	58·32	0·91	16·60		6·13	2·22	3·76	0·67	3·07	-	0·17	7·97	
Non-marine Shales(M*)	63·8	0·87	15·44		5·4	1·27	0·17	0·55	2·94				
Brackish-Water Shales (M*)	57·8	0·77	17·6		6·9	1·80	1·53	0·64	2·87				
Marine Shales (M*)	57·0	0·75	18·2		5·4	1·82	3·01	0·79	3·24				
Shales (Clarke,1924)	53·38	0·65	15·47		6·77	2·45	3·12	1·31	3·25	0·17			
SANDSTONES													
Quartz Arenite (P*)	95·4	0·2	1·1		0·66	0·1	1·6	0·1	0·2	-	-	-	0·3
Lithic Arenite (P*)	77·1	0·3	8·1		5·36	2·4	6·2	0·9	1·3	0·1			3·6
Arkose (P*)	66·1	0·3	8·7		2·28	0·5	2·7	1·5	2·8	0·1			0·9
LIMESTONES													
Limestones (Wedepohl,1969)	8·2	-	1·7	1·3	0·98	0·97	47·6	0·08	0·57	0·16	1·8	41·0	

R&K* → Russian Platform Sediments (Ronov & Khtebnikova, 1957)
M* → Pennsylvanian-age Sediments (Murray, 1954)
P* → Sandstones (Pettijohn, Potter & Siever, 1972)

Fig.33: Plot of Log(Na_2O/K_2O) vs. Log(SiO_2/Al_2O_3) For Sand Sediments

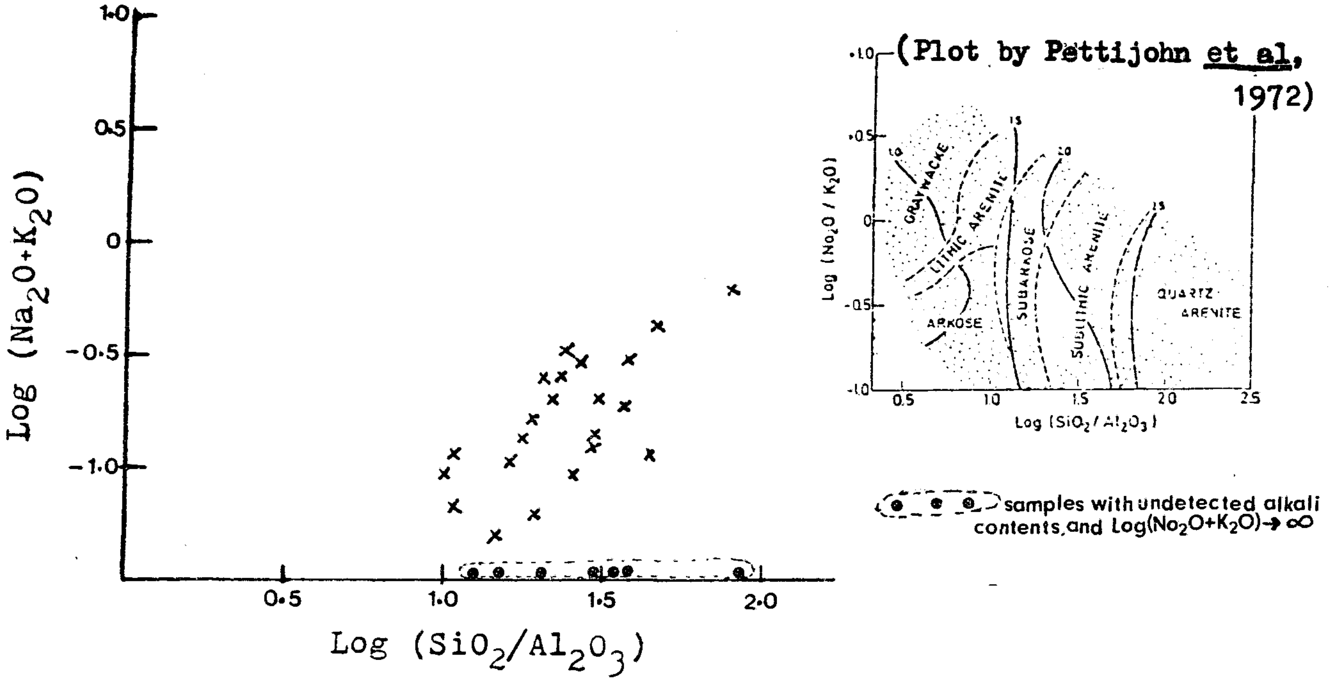
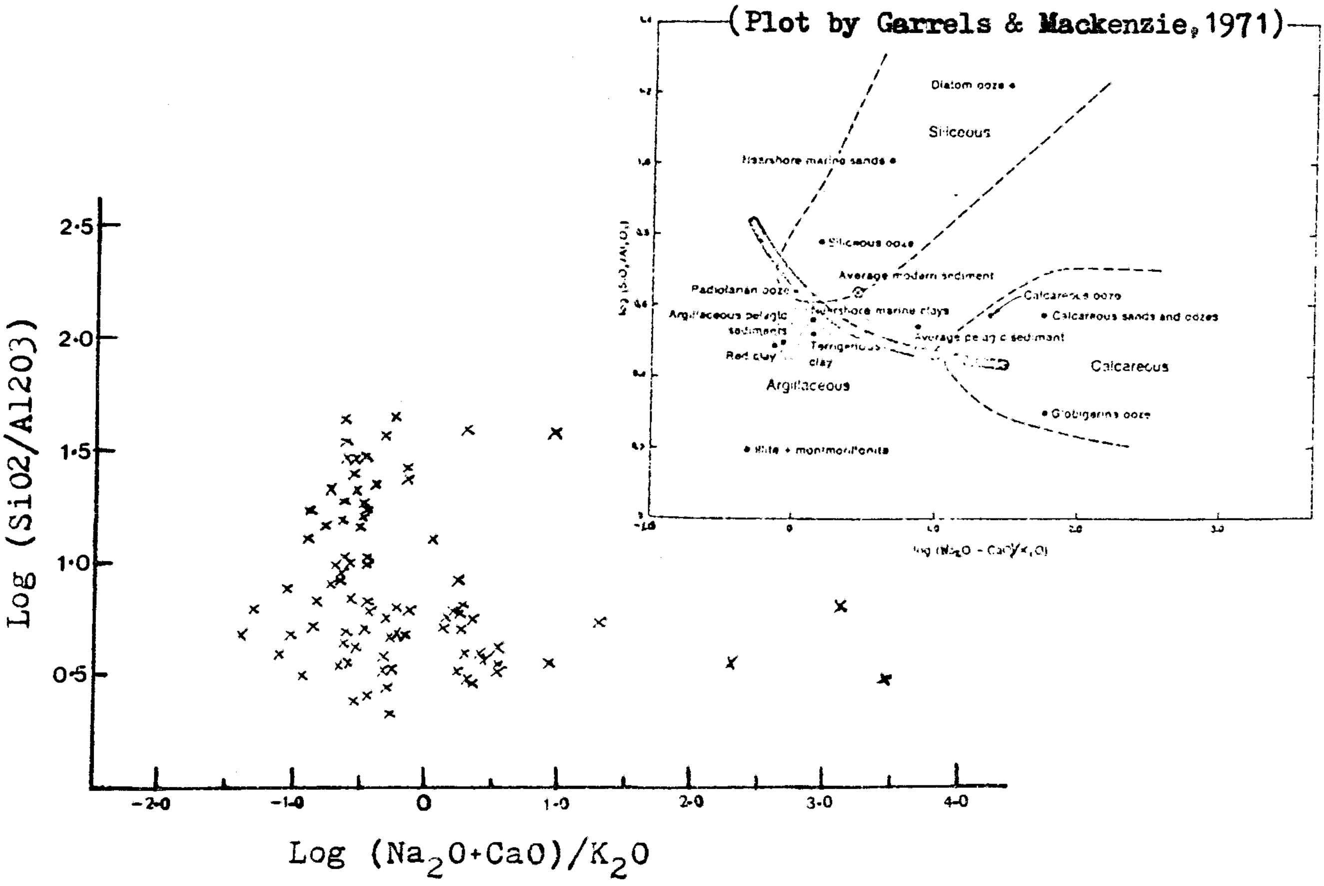


Fig.34: Plot of Log(SiO_2/Al_2O_3) vs. Log(Na_2O+CaO)/K_2O For Limestones and Clastic Sediments.



compositional field. It could also be seen that the sands not only plot in the fields of alkali-poor compositions but also that they are more siliceous than the average modern nearshore marine sands and lithic sandstones.

12.4 Summary

The clastic sediments of the Upper Eocene Hampshire Basin are generally siliceous but poor in alkali and alkaline earths. The composition of the sediments is predominantly silica and alumina; with small ($\lesssim$ 20%) amounts of iron, magnesia and potash, and trace amounts of other chemical components. These reflect the predomination of quartz, feldspars and clay minerals in the sediments; the feldspars being largely potassic, whilst the clay minerals, which are predominantly illitic and smectitic phases, are non-magnesian and not rich in lime.

Virtually all the lime in the sediments is contributed by fossil shells and/or gypsum. The iron content, which is predominantly ferric-iron, mainly occurs in association with the clays; exceptions being where $>$ 6% Fe_2O_3 occurs in the clayey sediments or $>$ 2% Fe_2O_3 occurs in the sands. In those exceptions, the excess iron is due to detectable free iron oxides (i.e. goethite) and/or jarosite. The ferrous iron is small in quantity and mainly bound up in the pyrites, the abundance of which is higher in the marine Barton Clay but significantly absent in the Barton Sands. The pyrites also account for much of the sulphur contents, although surficial alterations of the pyrites in places have led to the sulphur becoming incorporated into gypsum and/or jarosite.

On comparison with clastic sediment compositions in the literature, the clayey sediments resemble some nearshore and non-marine clays, although generally more siliceous than the reported average composition of Recent Clay deposits. The sands, being predominantly ($>$ 80%) silica, compositionally resemble the well-sorted or matured sub-arkose, sub-lithic arenites or quartz-arenites sand types.

CHAPTER 13

THE FRESHWATER LIMESTONES - PETROLOGY, MINERALOGY AND MAJOR ELEMENT COMPOSITIONS

13.1 Introduction

Mud-supported bioclastic limestones constitute parts of the 'Lower Headon Beds' succession in the Hampshire Basin. Several earlier studies have established that they are protected, shallow freshwater limestones (Edwards, 1967); fossiliferous with abundant *Planorbina* and *Galba (Lymnae)* gastropods, freshwater ostracods - *Cypridopsis* ssp and *Candona* ssp (Keen, 1977), and aquatic algae plant - *Charaphytes* (Feist-Castel, 1977). However, in none of the earlier studies has the petrological and compositional studies of the limestones been undertaken. These, in the present study, have been performed for the limestones in the cliff sections exposed and sampled at Heatherwood Point on the Isle of Wight and on Hordle Cliff at Long Mead End on mainland Hampshire (Figs. 5, 6a). In addition to the bulk compositions, the acid insoluble residues were also analysed, and the phase compositions of the carbonate constituents determined. With the exception of the trace element contents considered later in Chapter 15, the petrology and composition of the limestones are presented and discussed in this chapter; with a further view of the limestone occurrences given.

13.2 Brief Review of Freshwater Limestones

Limestones are lithified carbonate sediments which are primarily composed of calcite and/or aragonite, either as grains and/or mud. The grains could consist of shell remains, faecal pellets, ooids and pisolites, and re-worked pre-existing carbonate rocks. Lime-mud, on the other hand, could be granulated carbonate grains of various types and origin, but more often it is biochemical and/or physico-chemical precipitates of calcite and aragonite. Carbonate sediments may also contain primary magnesian calcites and dolomites.

Bathurst (1975) has given comprehensive accounts and reviews of works on limestone and related rocks in his classical book entitled "Carbonate Sediments and their Diagenesis". Prominent among other works on carbonate rocks are those of Pettijohn (1957); Durnham (1962); Cloud (1962a); Chillinger *et al*. (1967); Folk (1969, 1974); Lippman (1973);

Fuchtbauer (1975); Leeder (1980) and Murphy & Wilkinson (1980).

The limestones encountered in the present study are lime-mud supported shelly limestones, so the mechanism of lime-mud precipitation is of interest and briefly reviewed below.

There are two main modes of lime precipitation - biogeochemical and/or physico-chemical. The precipitations are often influenced or controlled by one or more of several factors, which include:
i) the existence of water bodies saturated in Ca^{2+} and $CO_3{}^{2-}$ with respect to calcium carbonate; ii) the physico-chemical constants of H_2O, CO_2, H_2CO_3, and the solubility constant of $CaCO_3$; iii) the chemistry of the water body, especially its Mg content or Mg/Ca concentration ratio; iv) the presence of aquatic plants; and v) the geographical and/or climatic location of the water body.

The saturation of natural water bodies in Ca^{2+} and $CO_3{}^{2-}$ with respect to $CaCO_3$ varies considerably; river waters being less saturated compared to sea-water, by virtue of their greater dissolved components (Garrels & Mackenzie, 1971). Surface non-marine waters mainly acquire saturation compositions on passage over or through carbonate-rich rocks and sediments. This is reflected in the greater number of river waters saturated with $CaCO_3$ occurring in Europe and North America, where limestones and carbonate-rich glacial drift deposits are common compared to Africa with crystalline rocks and argillaceous terrains (Garrels & Mackenzie, op. cit.). It is thus not uncommon, in North America, for some lake waters, particularly the marl lakes (Takashashi et al., 1968; Terlecky, 1974), to be 3- to 10-fold saturated with respect to $CaCO_3$.

Precipitation of lime-mud is essentially the chemistry of $CaCO_3$ precipitation in aqueous systems, and this depends on some constants which are:

(i) the solubility constant for $CaCO_3$:

$$Ks_{CaCO_3} = \left[Ca^{2+}\right] . \left[CO_3{}^{2-}\right]$$

(ii) the ionization constant for water:

$$K_W = \left[H^+\right] . \left[OH^-\right]$$

(iii) the ionization constants for carbonic acids:

$$K_1 = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3]}$$

$$K_2 = \frac{[H^+] \cdot [CO_3^{2-}]}{[HCO_3^-]}$$

and where the Henry's Law constant for CO_2

$$K_{CO_2} = \frac{P_{CO_2}}{[H_2CO_3]}$$

[at 25°C and 1 atm the equilibrium constants $K_1 = 10^{-6.5}$; $K_2 = 10^{-33}$ and $K_{CO_2} = 10^{+}$ - Garrels and Christ, 1965.]

The applications of these temperature and pressure dependent constants to $CaCO_3$ solubility with respect to varying CO_2 conditions have been treated in much detail by many authors. A concise but comprehensive review of the subject made by Chillinger et al. (1967) and Leeder (1980) showed that, in conditions of constancy or absence of CO_2, $CaCO_3$ precipitation from a saturated solution would occur with increasing temperature, decreasing hydrostatic pressure, decrease in soluble salt (i.e. NaCl, Na_2SO_4) content, addition of or presence of unbonded Ca^{2+} ion, and when water bodies evaporate in arid and semi-arid climatic regions.

Further, the effects of decrease or increase in CO_2 on the formation and dissociation of H_2CO_3 in H^+ and HCO_3^- were also considered. Increase in CO_2 is accompanied by increased $CaCO_3$ solubility; but the H^+ released will combine with already present CO_3^{2-} to form the more stable HCO_3^- with a consequent decrease of $CaCO_3$ solubility and hence its precipitation. Such situations could be achieved when the P_{CO_2} of water bodies in equilibrium with atmospheric P_{CO_2} is decreased; CO_2 escapes into the air under reduced pressure; the release of CO_2 with gaseous phase at elevated temperatures;the formation of CO_2 by organic decomposition is reduced or inhibited; and when salinity increases.

Biogeochemical precipitation is often brought about by aquatic plants extracting HCO_3^- from waters to secrete their protective calcite crust. Upon the plants' death, the crust could disintegrate into variously sized plates to be incorporated into accumulating deposits. Important amongst the plants are the green algae such as Charaphytes. They are common in marl lakes (Murphy & Wilkinson, 1980).

In contrast, the physico-chenical precipitation mainly occurs as a result of the loss of CO_2 to the atmosphere when water bodies warm up and, very importantly, in the uptake of CO_2 by aquatic plants for photosynthesis.

The importance of Mg concentration on carbonate precipitation has been documented by Muller et al. (1973). These authors established that when Mg/Ca < 2, low-Mg calcites principally form, whereas increase in the concentration ratios from 2 to 12 progressively favours precipitation of high magnesian calcites, aragonite and even hydrous magnesium. Low (< 2) concentration ratios commonly typify freshwater environments, including streams, lakes and associated bogs, marshes and other shallow, ponded, protected and low-energy water bodies (Folk, 1974). High, Mg/Ca > 2 mainly characterises warm, shallow seas where aragonite is the sole precipitate. This is the situation in the extensive Recent tidal flats' carbonate deposits in the Bahama Banks, Andros Island, Barbados and southern Florida (Cloud , 1962; Bathurst, 1975). High, > 2, Mg/Ca ratios also characterise saline lakes and sabkhas in arid and semi-arid regions. These are common in south-western U.S.A. (Feth, 1964) and the Middle East (Blatt et al., 1972). There is, however, no consensus of opinion as to whether the Mg/Ca ratio of ancient sea-water was much less than the 3:5 value for the present seas and hence greater calcite precipitation (cf. Ronov, 1964; Folk, 1974).

The presence of other dissolved cations and compounds does also have some influence on carbonate precipitations either by becoming incorporated into the minerals' lattice structure (i.e. Fe^{2+}, Sr^{2+}) and/or inhibiting or enhancing precipitation of one or the other phases and $CaCO_3$ polymorphs (e.g. Pb, Ba, SO_4^{2-}) (Lippman, 1973; Folk, 1974).

Calcite in carbonate muds is generally micritic (i.e. < 10 µm - Wachs & Hein, 1974) but could, during diagenesis, be recrystallized into larger-sized (> 10 µm) sparry calcites (Folk, 1974). Folk (1974) has also recognised that rapid growth and lack of Mg ions in freshwater settings do enhance precipitation of sheets of flattened (hexagonal) plates of calcite.

Lithification of freshwater calcareous sediments is very rapid and often immediately follows precipitation (Lippman, 1973). This is in sharp contrast to the marine carbonates that have to await flushing by freshwater, either in the phreatic zone upon emergence, or by submarine upwelling of freshwater (Bathurst, 1971).

Freshwater carbonate sediments, ancient and Recent, are rare in comparison with marine limestones. Some of the reported ones include those of the Eocene lacustrine Green River Formation, U.S.A. (Williamson & Picard, 1974); Lower Eocene lacustrine and alluvial plain carbonates of Languedoc, southern France (Freytet, 1973); and the freshwater, brackish lagoon Upper Eocene and Oligocene limestones in the Hampshire Basin (White, 1921; Edwards, 1967; Daley, 1969). Those of the Recent ages include calcitic chalks in Lake Zurich (Kelts & Hsu, 1978) and the Black Sea (Hsu & Kelts, 1981); and the marl lakes in North America, such as those studied by Terlecky (1974) in Rochester, New York State, and Murphy & Wilkinson (1980) in Littleville Lake, Michigan. Calcites in caliche, travertines or tufa are also examples of precipitation in freshwater flushed environments.

There are very few well-established characteristics of freshwater limestones. Hudson (1977) and Leeder (1980) have shown that by virtue of their surface origins, they are characterised by enriched lighter and more energetic ^{16}O and ^{12}C isotopes; thereby, generally possessing $\delta^{13}C$ values of -4 to -10 and $\delta^{18}O$ values of -3 to -10 (cf. Fig.27.5 of Leeder, 1980). Then, in an attempt to present interpretational criteria for ancient lake carbonate facies, Murphy & Wilkinson (1980) advocated the use of the geometry, lithology and components described for a marl lake in Michigan. The authors presented six units for a complete sequence which, in basinwards and vertical (increasing depth) order, are peat (above surface water level), calcareous peat, pisolitic gravel, sandy-algal micrite, gastropodal micrite and ostracodal micrite. They would be typical of marl lakes in temperate regions, possibly below 1500m altitudes and not beyond latitude 60° (Kindle, 1929). They could also develop in ponded waters where warmer climatic seasons favour calcite precipitation and/or $CaCO_3$-saturated surface waters exist. Most characterising, however, is the presence of shell remains of molluscs, especially the vagrant gastropods Planorbis, Lymnae, Viviparus and Physa, which might, in some cases, have been transported materials or washed in from basin margins. The limestones could also contain detrital clays and quartz in variable amounts depending on influx and load-levels of the local drainages.

13.3 Petrology

The petrographic descriptions of the limestones in the 'Lower Headon Beds' are given in detail in Chapter 2. The limestones are generally $<$ 10 cm thick; only the 'How Ledge Limestone' at Heatherwood Point is about one metre thick. They are mud-supported bioclastic limestones (Folk, 1962) and are variably coloured creamy-yellow, brownish and greyish-white. They are poorly lithified, being generally soft or friable and chalky to hand. The limestone horizons commonly have carbonaceous or lignitic partings at their bases or, as in the case of the How Ledge Limestone, interbedded with it. These are remains of vegetation in the water bodies of lime accumulations. One of the limestone horizons at Heatherwood Point had been sideritised into an ironstone. It still, however, contains patches of unaltered lime-mud, often within fossil shell enclosures.

In thin section (Plates 63, 64), the limestones were observed to be largely composed of micritic matrix-mud with fragmented fossil aragonitic shells, scattered aggregations of silt to find sand-sized quartz grains and aggregations of organic matter. The micritic mud largely consists of undifferentiated microcrystalline calcites. Under the SEM, they were seen to be micritic (5 - 10 µm sizes) fluffy, anhedral calcites (Plate 62a-d), most of which are thin hexagonal plates that were, in places, poorly intergrown or aggregated. They are apparently physico-chemically precipitated calcites that have not undergone substantial recrystallization or cementation. Occasionally, irregular pieces of calcite, of sizes up to 20µm (Plate 62e), were seen. They are likely to be broken-up calcitic crust of aquatic plants that inhabited the water body of lime accumulations.

Similar features characterised the micritic-mud relict in the sideritised limestone (ABLH-5). The crystals are, however, more subhedral and better differentiated (cf.Plates 82c,84d), although they still exhibit the random orientations and poor aggregations.

13.4 Mineralogy and Chemical Composition

The bulk mineralogical and chemical compositions of the limestones are contained in Tables 7a, d and 15a,d respectively. These are also shown in the stratigraphical variation plots - Figures 20a,b and 29a,b. . The compositions of the HCl-insoluble residues are given in Table 18 , whilst the spectrophotometrically obtained (AAS) carbonate phase composition for sample ABLH-3 is given in Table 20. The compositions of the fossil shell contents from ABLH-1 are given in Table 14 and have been discussed in Chapter 11, along with shells from other parts of the Upper Eocene succession.

13.4.1 Carbonate Contents:

The limestones' composition is dominantly ($> 80\%$) $CaCO_3$. This comprises varying (3-25%) amounts of biogenic aragonite and 66-97% amounts of matrix-mud calcites. The ratio of calcites to the aragonite contents is generally between 3 and 10, an exceptional ratio of 32 being in the lower half of the 'How Ledge Limestone (ABLH-3). These high carbonate contents are reflected in the chemistry, which showed the presence of 45-54% CaO and 36-44% CO_2; hence a $CaCO_3$ purity of 80-97% . These are in agreement with the $< 1\%$ to 15% HCl-acid insoluble, non-carbonate contents (Table 18).

X-ray diffraction showed the (104) reflection of the micritic calcites to hardly shift from the 3·03Å d-spacing value for pure calcites. The reflection, on resolution, indicates less than 3 mol% $MgCO_3$ contents. These are characteristics of low-magnesian calcites (Goldsmith et al., 1955). On staining of the thin sections (method of Lindholm & Finkelman, 1972), the micritic calcites possessed a purplish-red hue, which further suggests that they are only slightly ferroan ($< 0{\cdot}5\%$ FeO). Similar deductions are provided by the AAS analyses of the leachate of the most pure and least aragonite-containing sample ABLH-3, which gave a matrix calcite phase composition of $(Ca_{0.98}Fe_{0.01}Mn_{0.009}Mg_{0.005})CO_3$ (Table 20, Fig. 36). Staining and analyses of shell materials (from ABLH-1) also showed that these are non-ferroan, wholly aragonitic (gastropodal) shell materials.

The nature of the carbonate contents of the limestones is further deduced from the re-calculation of dissolved iron, magnesium and calcium contents obtained by the subtraction of the acid insoluble residues composition (re-calculated to 100%) from the bulk chemical composition. Virtually all the lime (45·54% CaO) in the bulk sampls is acid soluble and, in addition, 0·21 to 0·49% FeO and 0·64 to 1·1% MgO. These amounts to about 100% of the CaO, 54-97% of the FeO and 87-100% of the MgO in

Table **18** Composition of Acid Insoluble Residues of Upper Eocene Freshwater Limestones, Hampshire Basin.

Samples	BLH 19	ABLH 1	ABLH 2	ABLH 3	ABLH 4	ABLH 6	ABLH 7
% Insoluble Residue	14.09	1.02	5.31	0.80	53.06	2.70	13.0
Mineralogy:							
Quartz	53.1	3.4	24.1	9.0		21.8	53.4
Total Clay	34.8	19.2	45.3	33.3		38.6	42.0
Potassic Feldspar	8.7		1.7			4.0	2.9
Sodic Feldspar	3.4						1.1
Pyrite		10.6		5.8		2.6	0.6
Goethite		50.7	11.8	27.3		15.5	
Organic-C	1.2	16.1	17.1	18.0		17.6	2.4
Partial Chemical Composition :							
SiO_2	65.36	10.04	38.19	30.18	79.89	41.67	76.83
TiO_2	0.93	0.23	0.57	0.46	1.00	0.60	1.00
Al_2O_3	18.81	4.37	12.85	8.37	10.22	10.07	13.32
FeO	1.38	3.23	2.59	1.44	0.20	0.43	1.36
Fe_2O_3	2.56	40.91	5.84	18.74	3.46	10.14	2.55
MgO	0.97	-	-	-	0.65	-	0.75
CaO	0.25	0.20	0.06	0.09	0.03	0.18	0.12
Na_2O	1.13	-	0.07	0.03	0.18	0.02	1.05
K_2O	2.47	0.43	0.97	1.02	1.43	1.26	1.86
P_2O_5	0.03	1.85	0.32	0.75	0.04	0.13	0.03
S	0.07	3.90	1.16	2.38	0.13	2.34	0.31
CO_2	4.54	58.55	62.38	66.63	2.57	64.10	8.80

the samples can be attributed to the carbonate phases. Re-calculation thus shows $CaCO_3$ phases with $<$ 3 mol% $MgCO_3$ and $<$ 1 mol% $FeCO_3$, compositions that agree with the low magnesian and very slightly ferroan $CaCO_3$ phases obtained from other, earlier mentioned methods.

13.4.2 Non-Carbonate Contents

The non-carbonate components of the limestones are only poorly detected on the X-ray diffraction of the bulk samples. This was largely due to their small abundances and the masking effect of the high carbonate contents. The HCl-acid insoluble residues were therefore used instead. These indicated the presence of quartz, clay minerals, feldspars, pyrite, goethite and organic-C. The relative amounts of these (Table 18) showed that the non-carbonate contents are largely clayey and also either goethitic and/or rich in organic matter. The acid insoluble residues compositional variations allow differentiation of the limestones into two or three types. These are:

i) Limestones with very high ($>$ 95%) $CaCO_3$ contents and, non-carbonate contents characterised by very high (10-51%) goethite, high ($\sim$ 17%) organic-C, trace to 25% quartz, trace to 50% clays, and 0-10% pyrite. All the limestone horizons at Heatherwood Point, except ABLH-7, belong to this group. Their compositions indicate accumulation of lime in water bodies with substantial organic (plant) matter but which were receiving very little detritus. The considerable iron contents may be related to the abundant organic matter, although the Fe^{3+} phase could have been derived as adsorbed or suspended colloidal material.

ii) Limestones (BLH-19) on Hordle Cliff, and ABLH-7, the lowest limestone horizon at Heatherwood Point, both characterised by higher ($\sim$ 14%) non-carbonate contents dominated by quartz ($\sim$ 53%), clays ($\sim$ 35-42%) and feldspars ($\sim$ 4-12%) - a composition that is closely similar to those of normal clayey sediments in the 'Lower Headon Bed' succession (see Chapter 4). These limestones differ from the first type by being less pure (or $CaCO_3$-rich) and possibly have accumulated in more open water bodies with detritus-laden stream outlets.

13.4.3 Comparison to Limestones

Finally, the bulk chemical compositions of the limestones studied are seen to compare closely with reported average limestones composition, shown in Table 17. Also, the values of $\log(SiO_2/Al_2O_3)$ and $\log\left[(Na_2O + CaO)/K_2O\right]$ for the limestones plot well within the compositional field of calcareous sediments in Figure 34.

13.5 Mode of Deposition

The limestones occurring in the 'Lower Headon Beds' succession of the Hampshire Basin are lime-mud supported bioclastic deposits. Their freshwater origin established by earlier workers from lithological (Edwards, 1967) and palaeontological (Edwards, 1967; Keen, 1977) criteria is in agreement with the petrological and compositional data obtained from the present study. In essence, the study has provided information on the amounts and nature of the lime-mud matrix and biogenic contents; and, in addition, the composition of the non-carbonate contents.

The matrix lime-mud dominantly comprises fluffy anhedral calcites. These are the typical calcite of freshwater calcareous muds and lake marls (Terlecky, 1974). Even the calcites' platy hexagonal and sheet stacking morphology has similarly been found characterising freshwater creek calcites by Folk (1974), who regarded the features as indicative of fast crystallization. Fast $CaCO_3$ nucleation, in less than 500 hours, was experimentally attained by Pytkowicz (1965) in situations of high loss of CO_2. Fast nucleation in natural waters would be enhanced in warm water bodies with abundant aquatic micro-flora and possibly low scale, localised turbulent mixing up of the waters (Newell et al., 1960; Cloud, 1962; Brunshill, 1968). Perhaps such fast nucleation was also aided in the Lower Headon environment by the presence of carbonate grain nuclei, such as broken pieces of shells and/or encrusting calcites on algae. The nuclei might also have induced the aggregation of the crystals. In fact the broken-up calcitic crust of algae could account for the occasional irregular, relatively larger-sized ($\sim$ 20 μm) calcites observed in the limestones. Similar broken-up algal plates were observed by Terlecky (1974).

The low-magnesian nature of the calcite is consistent with the calcite types forming in fresh-waters with very low ($<$ 2) Mg/Ca concentration ratios (Folk, 1974; Müller et al., 1973). However, being slightly ferroan, it could be thought that recrystallization of an earlier non-ferroan calcite had taken place (i.e. Irwin & Hurst, 1982). But there is no petrographic evidence for any recrystallization. Thus it would appear that the calcite primarily precipitated as low-ferroan; therefore implying precipitation in waters with some amount of dissolved Fe^{2+}. The presence of Fe^{2+} could have been aided by the ponded nature of the water bodies coupled with the accumulation of plant matter; and, in fact, could have been reduced from derived goethite phases common in the How Ledge Limestone.

The essential low Mg/Ca waters with their saturation with respect to $CaCO_3$ could have been derived as drainages from the carbonate rich Upper Cretaceous Chalk and/or the 'Upper Greensands' exposed in the regions surrounding the Hampshire Basin. Judging from the 200-320 ppm $CaCO_3$ of Chalk stream waters in present-day southern England and groundwater aquifers in the Chalk in Dorset, similarly characterised by 210-300 ppm $CaCO_3$ content and pH 7·1 to 7·5 (Sperling et al., 1977; Jones, 1981), it would have been possible for ponded Palaeogene surface waters to be saturated with respect to $CaCO_3$.

The physiography of the basin, and details of the vertical variations of the lime accumulation could not be well established in the present study because of cliff slumps and slump terraces that limited the deposits' exposure. So comparison with the facies variations established by Murphy & Wilkinson (1980) for lake carbonates was difficult. However, it would appear that the lime lake had its margins and points of stream detritus-discharge located to the west of Heatherwood Point. This would account for the discovery by Edwards (1967) that the How Ledge Limestone grades into sandier facies westwards of Heatherwood Point. The basin apparently varied considerably from early shallow water phases, with substantial supply and incorporation of detrital materials, to later relatively deeper waters with less detrital materials, but substantially high goethite and vegetation (peat?) debris. An intervening period of high influx of sandy detritus probably led to the accumulation of the marl unit, whose exposure was only partial beneath the How Ledge Limestone. The marl analyses showed a composition of about 50% calcite-mud, 3% aragonitic bioclasts; 30% quartz, 14% clays and 3% feldspars.

13.6 Summary

Primary calcite precipitations in freshwater low-energy ponded waters had led to the accumulation of mud-supported bioclastic limestones in the late half of the Upper Eocene times in the Hampshire Basin. The micritic calcites are low-magnesian and slightly ferroan variety. These have not undergone noticeable, extensive re-crystallization, nor have the predominantly gastropodal fossil shells, which still remain wholly aragonitic. Variations in the amounts and composition of the incorporated non-carbonate (detrital) materials allowed differentiation of the limestones into main groups. These are represented by the Low Ledge Limestone with very high ($>$ 95%) $CaCO_3$ content and insoluble residues very rich in goethite and organic matter; the Lymnae Limestone with lower ($\sim$85%) $CaCO_3$ content but quartz and clay-rich insoluble residue. The former are believed to have accumulated in larger, well-established water bodies with little detrital supplies, whilst the latter possibly accumulated close to basin margins and stream outlets.

CHAPTER 14

CALCAREOUS AND SIDERITIC DIAGENETIC CARBONATES

14.1 Introduction

Burial diagenesis in the Upper Eocene succession of the Hampshire Basin is most obvious in the development of calcareous concretions in the marine Barton Clay Formation, and sideritic clay ironstones in both the marine and non-marine sequences. With the exception of chemical analyses of some of the calcareous concretions obtained by Knight (1974), these diagenetic carbonates have been little studied. Of particular interest are the phase compositions of the siderites and calcites. These have been investigated by X-ray diffraction and chemical analysis of acid leachates. The present study provides a greater understanding of the carbonates, especially with respect to their modes of formation. However, some aspects of the formation of the siderite phases remain enigmatic. In order to facilitate the interpretation of the data, a brief review of diagenetic calcitic and sideritic carbonates is given below.

14.2 Review of Diagenetic Carbonates

14.2.1 Historical Concept

The establishment of the mode of formation of diagenetic carbonates, particularly calcareous concretions, has followed several paths. Hall (1843, quoted in Twenhofel, 1961) thought they were pre-consolidated and pre-compacted spheres deposited in insufficient amounts to form strata. Lang (1914) considered them to be rhythmically deposited calcareous ooze. Then Twenhofel (1950) suggested three modes involving organic (algal) growths, physical rounding and enlarging of mud-balls, and chemical precipitation during and after host sediment depositions. In the following two decades, Lippman (1955) and Berner (1968), amongst many others, established the currently held view that concretionary growth commenced after the deposition of the host sediments. In other words, they are diagenetic phenomena; essentially resulting from diagenetic processes within buried sediments. The environment of deposition and rates of sedimentation have considerable influence on the diagenesis. Other factors of importance to their growth include the nature of the sediment concerned (lithology, porosity and permeability), and the distribution of organic remains. These are considered as follows.

14.2.2 Diagenetic Conditions and Processes

Diagenesis principally concerns physical and chemical processes within sediments, often in oxygen-depleted conditions below sediment-water interfaces. The processes involved are numerous but interrelated, and grossly variable with depth of burial. These have been recognised and established into depth-related reaction zones that can be applied to almost all sediment types. Many authors, including Berner (1971, 1980), Curtis (1977, 1980), Irwin et al. (1977), have presented and discussed the diagenetic zones from different points of view, whilst concise outlines of diagenesis in clastic sediments and primary carbonate deposits have also been given by many authors, e.g. Leeder (1980).

The precipitation of carbonate minerals, and indeed most other diagenetic phases, occurs in two main diagenetic zones. These are the 'sulphate reduction zone' within very shallow (few cms) to ~ 10m burial depths, and the 'fermentation zone' in relatively deeper, ~10m to ~1000m, burial depths (Curtis, 1977). Anaerobic oxidation or biological decomposition of organic matter, along with bacterial reduction of sulphates, are the dominant reactions within the sulphate reduction zone. The reactions may be summarized and represented as:

$$\underset{\text{organic matter}}{[CH_2O]_{\alpha C}}\quad \underset{\text{organic-N \& protein-N}}{[NH_3]_{\alpha N}}\quad \underset{\text{organic phosphate}}{[H_3PO_4]_{\alpha P}} \quad + \quad \tfrac{1}{2}\alpha S\ SO_4^{2-} \longrightarrow$$

$$\alpha_C\ HCO_3^- + \alpha_N\ NH_3 + \alpha_P\ H_3PO_4 + \tfrac{1}{2}\alpha_S\ H_2S \qquad (1)$$

with the stoichiometric coefficient often being in the order

$\alpha C >>>> \alpha N > \alpha S \simeq \alpha P$ (cf. Lerman, 1979; Delwiche & Likens, 1977; Redfield et al., 1963)

Also, detrital hydrated iron-oxides can also be subjected to inorganic and bacterial reduction, represented by:

$$CH_2O + 4FeOOH + H_2O \longrightarrow HCO_3^- + 4\ Fe^{2+} + 7OH^- \qquad (2)$$

Much of the HCO_3^- and NH_4^+ may be lost by upward diffusion into the depositional waters (Curtis, 1977). However, localised conditions could favour their concentrations with consequent substantial rise in alkalinity to between pH 7 and 8·5 (Berner, 1971). These conducive conditions mainly occur in the vicinity of decaying organic materials and sites of bacterial decomposition of proteins and their constituent amino-acids. With Ca^{2+} from dissolved shells, trapped sea water and expelled compaction waters, a high degree of supersaturation with respect to $CaCO_3$ may be established. Hence precipitation of calcite in the presence of abundant Mg^{2+}, dolomite can occur. These carbonates are often poor in iron because dissolved Fe^{2+} in thessystem has mostly been preferentially fixed with HS^- into iron-suphide phases (see Chapter 8 on pyrites). In fact, the high sulphur activity in the sulphate reduction zone is unfavourable to the stability of siderite. Hence siderite is relatively uncommon in this diagenetic zone. Also in the sulphate reduction zone, where energentically lighter ^{12}C of organic matter is mainly involved in the reactions, the carbonates precipitated are characterised by enriched ^{12}C and often possess $\delta^{13}C \rightarrow -25‰$(Irwin et al., 1977).

In the absence of reducible sulphate ions and particularly in the fermentation zone, organic material present can be subjected to microbial degradation; the fermentation being represented by the reaction:

$$2CH_2O \longrightarrow CH_4 + CO_2 \qquad (3)$$

This is characterised by marked carbon isotope fractionation with the methane being very light with $\delta^{13}C \rightarrow -80‰$ and the CO_2 being heavy with $\delta^{13}C \rightarrow 15‰$ (Irwin et al., 1977). The utilisation of the carbon-dioxide inevitably leads to precipitation of isotopically-heavy carbonates, which are generally richer in iron. This is because, in the absence of HS^-, ferrous ions become more abundant in the interstitial fluids. The carbonates percipitated generally range from ferroan calcite to ankerite $[Ca(Mg,Fe)(CO_3)_2]$and siderite, which forms when the pore fluid composition shows Ca/Fe < 20:1 (Berner, 1971).

With increasing depth of burial and hence higher intra-formational temperatures, biogenic decarboxylation processes can set in. The abiotic reaction is represented by:

$$RCO_2H \longrightarrow RH + CO_2 \qquad (4)$$

The carbon dioxide is isotopically light and leads to light ($\delta^{13}C \rightarrow -10$ to $-25‰$) carbonates which are often dominantly siderite (Curtis, 1977). Also, because of the elevated temperatures, isotopically light ^{16}O is more active in the reactions. Hence this becomes more enriched in carbonates precipitated at greater depths (Irwin et al., 1977).

14.2.3 Environments and Rates of Sedimentation

The depths at which diagenetic zones occur and the scale or nature of the diagenetic reactions are strongly influenced by the environment of deposition and the rate of sedimentation. A particularly important aspect is the nature of the depositional waters, particularly in mud-rocks. Not only do surface waters generally become trapped in sediments as pore fluids, but, with the establishment of concentration gradients, diffusion of ionic and molecular species can occur with respect to the sediments and the pore fluids. Sea-waters generally make a greater effective contribution to diagenesis because, relative to freshwaters, they are enriched 26X in Ca, 318X in Mg and 2,500X in SO_4^{2-}, but are about 35X poorer with respect to Fe (see Table 4.2 of Carrell & Mackenzie, 1971). Hence in freshwater sediments, the surface reduction zone processes will generally be limited to much shallower depths. Consequently, calcite precipitation is infrequent, whilst bacterial fermentation with attendant siderite precipitation may occur close to the surface. This is usually the situation in Recent lakes (Anthony, 1978); bogs, peats and marshes (Postma, 1977, 1981; Ho & Coleman, 1969; Pye, 1981) and soils (Fitzpatrick, 1971). In contrast, the sulphate reduction zone is usually well developed in marine environments with consequent pyrite formation commonly commencing at shallow burial depths. As would be expected, the fermentation zone is found at relatively greater depths. Classical examples of diagenetic carbonate precipitation, with respect to the environment and depth of burial, have been documented for the Palaeogene coal measures in Japan (Matsumoto, 1978b; Matsumoto & Iijima, 1981).

The rate of sediment accumulation is important in controlling the length of time sediments stay in the various diagenetic zones. Sedimentation rates, which often reflect the extent of detritus influx, vary considerably. They are generally lowest (few mm/1000 yr) in pelagic environments, but very high (few cm - tens of cm/1000 yr) in shelf environments and many freshwater lakes (Fuchtbauer, 1974; Lerman, 1979). The relationship between the rate of sedimentation and diagenetic processes has been described at many localities and has been extensively mathematically modelled. These relationships are presented and discussed by many authors, including Lerman (1979) and Berner (1980), and Gautier (1982).

In conditions of slow sedimentation and burial, only small amounts of organic matter should become incorporated in sediments. This is because most of the organic matter will be lost by aerobic oxidation during long residence at the sediment-water interface, or within a very few millimetres below the interface. Also, downward diffusion of SO_4^{2-} into the sediment will continue for a longer period, probably aided by bioturbational irrigation (Berner, 1980). These may be attended by greater losses of HCO_3^-, HPO_4^- and NH_4^+ diagenetic products by upward fluxes into depositional waters. In consequence, fermentation diagenetic precipitation may be impaired at shallow depths. For example, siderites would mainly be expected to occur at deep depths of burial. But in conditions of rapid sedimentation, high amounts of metabolisable organic matter may be accumulated. Also, with less time available for diffusion, SO_4^{2-} may decrease rapidly with depth, becoming depleted at relatively shallow depths. This would make the sulphate reduction zone very limited, with the fermentation zone occurring at much shallower depths.

14.2.4 Growth Influencing Factors

Diagenetic carbonates occur either as disseminated material or, more often, as banded, nodular or concretionary bodies. Their formation and growth is mainly influenced by the porosity and permeability of the host sediment and the distribution of organic matter, although other factors may be important.

The porosity of the sediment is dependent on lithology and depth of burial. Porosity values are highest at shallow depths, especially in newly-laid sediments; whilst overburden compactional strains cause the porosities of sediments to decrease with depth. Recent fine-grained sediments often retain a large volume of water, and are generally characterised by high (60-90%) porosity values at the sediment-water interface down to about 100m depth (Matter, 1974; Tucholke et al., 1974). Their abundant clay mineral contents allow them to pack very densely on compaction. This allows the initial high porosities to decrease to between 45% and 60% at depths of about 500m, and to $<$ 40% at greater depths. In sand sediments, the dominating coarse grains have a more open packing on compaction. Hence, the common porosities of 30-50% sands at shallow ($<$ 100m) depths; although cementing materials often contribute to greater porosity decrease (Fuchtbauer, 1974).

The significance of porosity is that, in favourable circumstances, it is possible to infer the relative time and depth of the formation of concretions. Assuming that all pore spaces (actual and potential) are filled, the quantities of interstitial minerals precipitated will be a good indicator of the 'initial porosity' at which growth took place. Thus growth in fine-grained sediments at shallow ($<$ 100m) depths would be characterised by very high quantities of carbonate, whilst lower carbonate contents would indicate deeper depths. This has been described by Raiswell (1971, 1976) for calcareous concretions in Liassic and Cambrian sediments from South Wales, Britain. The early growth phases were typified by $\gtrsim$ 70% initial porosities. Their growth in uncompacted hosts is indicated by the presence of uncrushed shells and the absence of bedding relicts in the concretions. The resistance of the concretion to later compaction is reflected in the deformation of bedding planes in the host sediment around the concretions. The opposite situation typifies late growth phases, which show initial porosities of between 30 and 40%.

Permeability is important in determining the growth of concretions, since it dictates the movement of pore fluids which are essential concretion growths. Fluid flows and ionic diffusion are greater in coarse-grained horizons or sediments such as sands compared with fine-grained, clayey sediments (Pettijohn, 1975). Hence the often observed limitations of occurrences of concretions to certain horizons has led to suggestions that grain size inhomogeneity within the sediment host may be responsible (Pearson, 1979). It is believed that pore fluid, under pressure gradients, is channelled along coarser-grained and hence more permeable horizons. There will be sand or silt horizons in clay deposits (Shuruber, 1967; Raiswell, 1971; Pearson, 1979). But often the fluid-channelling is along stratigraphical breaks, especially bedding planes between sediments of similar or different lithologies.

The distribution of metabolisable organic matter within sediments has also been recognised (i.e. Dickson & Barber, 1976; Berner, 1980) as having a strong influence on concretion growth. This is because, in the initial phase of diagenesis, super-saturation with respect to mineral phases would often occur in the vicinity of the organic matter being decomposed or degraded, leading to the initial precipitations. But this would be attended by under-saturation within the pore fluid. Hence a chemical gradient would be established whereby ions mobilised from surrounding sediments are brought to, and subsequently precipitated around the initial organic matter. The developed differential pH and the migration of ions would thus maintain the growth of the concretions. This mode of formation would explain the numerous reports of concretion with organic nucleii (i.e. Weeks, 1953; Clifton, 1957; Gad et al., 1969). However, many concretions lack organic nuclei and many even contain no apparent organic relicts. Such concretions could still have had an organic origin. Dickson & Barber (1976), in trying to explain regularly-spaced concretions, suggested that, in addition to large carcases, tiny carcases and microscopic organic detritus could also bring about the development of concretion. In fact, Berner (1980) has shown that $CaCO_3$ could owe its derivation to a natural fat substance, adipocire. The author, using fish adipocire, obtained $CaCO_3$ from sea-water in the laboratory (Berner, 1968a). The process was summarised as:

$$\text{Protein N} \rightarrow NH_3 \tag{5}$$

$$\text{Fats} \rightarrow \text{Fatty acids (RCOOH), where R is hydrocarbon chain} \tag{6}$$

$$NH_3 + RCOOH \rightarrow NH_4^+ + RCOO^- \tag{7}$$

$$Ca^{2+} + 2RCOO^- \rightarrow Ca(RCOO)_2 \tag{8}$$

However, the calcium soap is thermodynamically unstable, and, with time, breaks up into $CaCO_3$ and hydrocarbons.

The growth of concretions has also been mathematically modelled by Berner (1968b). The author derived expressions giving the time of growth for concretions from both static and flowing pore fluids. Time of growth in rapid flow conditions does not differ greatly from that of static water, which is:

$$t = R^2/2VD\ (C_\infty - Cr) \tag{9}$$

where t = growth time in years

R = radius in cm

V = molar volume of cementing material = 35 cm^3/mole

D = diffusion coefficient = 10^{-5} cm^2/sec

$C_\infty - Cr$ = degree of super-saturation ($\sim$10 ppm) $\cong 10^{-7}$ moles/cm^3.

Using this equation, the time for growth of calcite concretions could be about 500 years for concretions of 1 cm radius; about 12000 years for those with 5 cm radius; and about 100,000 years for large concretions of 15 cm radius.

14.2.5 Compositional Aspects of Concretions

Concretionary carbonates are very variable in terms of the type, quantities and isotopic composition of the mineral phases present. This is essentially a reflection of the chemistry of the pore fluids and/or depth of growth. Concretions can either be monomineralic or polymineralic. In the latter case, the minerals can be homogeneously distributed throughout the concretion or graded or zoned from core to rim. Homogeneously-composed concretions often form within a particular depth of burial, and apparently from pore fluids of similar chemistry. Such concretions are probably the most common, examples being the concretions of Liassic age from Dorset described by Raiswell (1971). Many concretions possess variable composition. Often they are monomineralic, but the quantity of the mineral phase decreases from core to rim. This probably occurs as a consequence of growth over a range of depths, with porosity and hence mineral precipitation decreasing as depth increases. Raiswell (op.cit.) has described this type of concretionary growth in the Upper Cambrian sediments in South Wales. In some sediments, concretions are characterised by different minerals zoned from core to rim. These often involve calcite-pyrite (Raiswell, 1971), pyrite-siderite (Curry et al., 1968) or calcite-siderite (Girin, 1967). Other characteristics of poly-phase concretions include changes in the phase compaction of the same mineral type and/or isotopic compositional changes. Matsumoto & Iijima (1975) have observed zoned sideritic concretions with a pure, ~ 100% $FeCO_3$, core and outer layers of Ca-Mg siderite. Examples of isotopic changes are the concretions described by Curtis et al. (1975) from the Westphalian of Yorkshire, England. These are characterised by Mn-rich siderite core enriched in $\delta^{13}C$, and an outer part with Mg-siderite (pistomesite) enriched in $\delta^{12}C$. The inner early phase probably has a fermented-organic origin, whilst the latter was formed at deeper depths as a result of thermal decarboxylation of organic matter.

Ionic substitutions are another important aspect of carbonate mineral contents of concretions. These reflect the nature of the pore fluids from which precipitation occurred. By their similar ionic sizes,

Fe^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+} can substitute for the main cations in calcite and siderite. Hence calcites can be either low-magnesian ($\lesssim$ 5 mol% $MgCO_3$) or high magnesian ($>$ 5 mol% $MgCO_3$) varieties (Goldsmith et al., 1955; Graf, 1960), and non-ferroan ($<$ 2% FeO or $\leq$ 1 mol% $FeCO_3$) or ferroan ($<$ 2-10% FeO or $\sim$ 1·5-4 mol% $FeCO_3$) (Lindholm, 1975). Siderites also can be either stoichiometric $FeCO_3$ or Ca-, Mg-, Mn-substituted. Structural factors limit substitution of the large (0·99Å) Ca^{2+} to a maximum of about 10% (Zaritskii, 1964; Pearson, 1974a); whereas the smaller sized Mg^{2+}(0·66Å) can substitute to much higher amounts; as much as 35% $MgCO_3$ has been recorded in magnesian siderites (pistomesite) (Girin, 1967; Pearson, 1974b). Mn^{2+} substitution in siderite is commonly $<$ 5%, although amounts of up to 17% have been recorded in some siderites from Japan by Matsumoto (1978b). Matsumoto (1978a,b) and Matsumoto & Iijima (1975, 1981) have related siderite phase composition to depth of formation. They showed that pure and low Ca-Mg substituted siderites ($<$ 10 mol% $(Ca+Mg)CO_3$) are typical of shallow ($<$ 100m) burial diagenesis, whilst more highly substituted magnesian siderites form at deeper depths.

Finally, mention should be made of the variations in compositions of concretions with respect to their different environments of formation as observed by Weber & William (1965). These two authors, working on some Carboniferous ironstones in the U.S.A., found that the ironstones are characterised by a decrease in CaO/Ba, Al_2O_3/MgO and SiO_2/MgO from freshwater through brackish into the marine environment. The possession of those compositions would be due to the preservation of host sediment materials without any apparent alteration,as incorporated during the concretion's development.

14.2.6 Reported Occurrences

As previously described, diagenetic carbonate minerals are common in sediments as cement materials; as disseminated forms and concentrated into concretions, nodules and bands. Nodules and concretions are either spherical, ovoidal or elliptical bodies. They exhibit variable sizes which can be as much as 100 cm along the major axis, which is usually aligned parallel to the bedding of the host sediment. Siderite is more commonly found in the disseminated form, particularly characterising sideron horizons in peat soils (histosols) (Fitzpatrick, 1971).

A few examples of numerous reported occurrences of calcareous concretions include those in the Upper Cambrian of South Wales, Britain

(Raiswell, 1971); the Carboniferous in Ohio, U.S.A. (Clifton, 1959), in the Isle of Man (Dickson & Barber, 1976); Jurassic in Britain (Raiswell, 1971; Gad et al., 1969; Hallam, 1962, 1967) and Russia (Girin, 1967); the Palaeogene in Japan (Matsumoto & Iijima, 1975, 1981); and the Eocene Bracklesham Group (Potter, 1977) and London Clay Formation (Hewitt, 1982 in the London Basin of south-east England. In the Palaeogene Hampshire Basin of southern England, calcareous concretions also occur in the Bracklesham Group (King & Kemp, 1982; Curry, Hodson and West, 1968; Curry et al., 1977) and in the Barton Clay Formation (Burton, 1933; Knight, 1974).

Siderite occurrences in ancient sediments include those reported as:

a) spathic sideritic ore in the Jurassic limestones and dolomites in southern Bavaria, Germany (Pfeufer, 1974);

b) disseminated siderite crystals in the Carboniferous Hepworth sediments, England (Pearson, 1979); the Jurassic Dogger and Cornbrash Limestones, England (Dean, 1934); the Tertiary Llanbedr (Mochras) Borehole sediments, South Wales (Wood & Woodland, 1971); and the Eocene Bracklesham Group, southern England (Curry et al., 1968).

c) siderite cements in concretions, clays, sands and limestones in the Carboniferous Coal Measures in Britain (Curtis, 1967; Pearson, 1974; Curtis et al., 1975) and in New Zealand (Hodgson, 1968); Jurassic (Liassic) Whitbian sediments, Yorkshire (Gad et al., 1969; Hallam, 1967); Marlstone and Nerinae Beds, Yorkshire (Greensmith, 1971); Palaeogene coal measures in Japan (Matsumoto & Iijima, 1975, 1981; Matsumoto, 1978b); the Eocene Bracklesham Beds, England (Potter, 1977); and the Holocene Black Sea sediments (Hsu & Kelt, 1981).

Occurrences in Recent sediments and environments include those reported from bogs, peats and marshes (Postma, 1977, 1981; Ho & Coleman, 1969; Fitzpatrick, 1971; and Pye, 1981); lakes (Anthony, 1978; Greensmith, 1971); estuaries (Bray et al., 1973); deltas (Moore, 1966); and near-shore shelves (Bricker & Troupe, 1975; Calvert, 1976; Ristvet, 1978).

Outcrop exposures of sideritic ironstones are, however often characterised by weathered rims or envelopes composed of haematite or goethite and limonite. Examples are common in Japan (Matsumoto, 1975) and England (Gad et al., 1969; Hallam, 1967). Extreme oxygenous outer alterations and internal dissolutions often lead to the formation of hollowed centres, in addition to the iron-oxide crusts on the ironstones (Todd, 1903; Bates, 1938; Taylor, 1949; Childs et al., 1972).

14.3 Diagenetic Carbonates in the Upper Eocene of Hampshire Basin

14.3.1 Occurrence

Detailed descriptions of diagenetic carbonate-bearing horizons occurring in the Upper Eocene succession studied have been given in Chapter 2. The carbonates occur principally as thinly bedded nodular bands, concretionary calcareous bodies and clay ironstones (Plates 2-4, 11, 13, 33, 34). The bands are thin; usually < 10 cm thick. The nodular bodies are small, with < 10 cm long axis diameters, whilst the concretions are larger with diameters between 30 and 100 cm. In addition, the calcareous concretions are usually glauconitic, and often show yellowish, milky-white septarian calcite (Plates 4 and 5). The calcareous and sideritic carbonates usually occur separately and at different horizons, with the exception of two horizons in the Barton Clay Formation section at Barton. These horizons are near the tops of the Highcliffe and Naish Members respectively. Here, soft friable sideritic clay-ironstone bands occur enclosing more compact calcareous concretions or bands, their interface being sharp. They represent distinctly different growth phases, with the calcareous concretions being the earlier.

In both the calcareous and sideritic concretions, fossil shells and carbonised plant material commonly occur. The fossils are largely undeformed and, reflecting the manner of their distribution in the host sediments, they often occur scattered within the concretions. They do not appear to be the focal (nucleii) sites of precipitation and hence growth of the diagenetic carbonates. Thus they differ from concretions described by many authors, including Weeks (1953), Clifton (1957) and Gad et al.(1969), as having grown about a nucleus of organic remains.

Some of the calcareous concretions are further characterised by thin encrustations of pelecypodal and gastropodal fossil shells. The shells often enclose masses of pyrite (Plate 6). These encrustations suggest penecontemporaneous exposure of the concretions and periods of reduced sedimentation in the Barton Sea. Similar observations apply to the preserved trace fossils and bioturbational features observed in the

Shell Band ('Bed G') at the base of the Barton Sand at Barton. The features (Plates 8,9) consist of escape burrows and impressions of Chondrites, Thallasnid and Lithodomus (P.Shelford, pers.comm.). The escape burrows are very similar to the mining-type burrows such as those described by Cluff (1980) from the Palaeozoic New Albany Shale Group in Illinois, U.S.A. The burrows vary from hairline to a few millimetres in thickness. They probably indicate low energy aerobic - dysaerobic shelf ($\lesssim$ 100m) conditions. Preserved burrows are not common in diagenetic carbonates. They have been described by Sellwood (1971) from the Liassic sideritic shales in Yorkshire, England. Since the burrows are contemporaneous with deposition, Sellwood employed the biological features in deducing periods of non- and/or slow-sedimentation. The maintenance of differential physico-chemical conditions at shallow burial depths (pre-compaction) would account for the preservation of the burrows compared with the sideritised bulk of the sediment. Similar conditions also apply to the ironstone ABLH-5 in the 'Lower Headon Beds' at Heatherwood Point. The ironstone is a sideritised shelly, micritic limestone (Plate 22), within which patches of the primary lime-mud remain preserved unsideritised.

- Two other important observations are provided by the field occurrences of the diagenetic carbonates. Firstly, the host sediments' bedding planes show compactional deformational flow around the carbonate bodies. This indicates a pre-compaction time of formation for all the nodules and concretions. Secondly, the application of the growth rate equations of Berner (1968b) (Equation 9, p.272) suggest that the nodular bodies with $\lesssim$ 5 cm radius have probably developed over a period of 2000-11,000 years; whilst the concretions, with much larger sizes, have probably taken between 50,000 and 300,000 years to develop. However, on a geochemical time-scale, these would both be 'instantaneous growth phenomena'.

14.3.2 Petrology, Abundance and Composition of the Carbonate Phases

The diagenetic carbonate bodies are similarly fine-textured and each is also uniformly composed. Preliminary sampling from core to edge (cf. Raiswell, 1971) showed no significant compositional variation, so the analytical results recorded should be regarded as representative. Details of the mineralogy of the bulk samples are given in Tables 7a-h, and their relationship in the stratigraphy is shown in Figures 20a-c.

The compositions of the HCl-acid insoluble residues (matrix materials) are given in Tables 23 and 24.

14.3.2A Calcareous Concretions

The calcareous bodies are predominantly composed of calcite. This occurs in amounts of 65% - 82%, averaging 74%. Less than 2% of this is due to incorporated fossil shells.

In thin section, the diagenetic calcites are largely microcrystalline with the exception of septarian calcites, whose sizes vary widely from micrite (< 10 μm) to about 2 mm (Plates 66-70). Under S.E.M., the predominating < 2 μm-sized anhedral calcite crystals are seen to be densely inter-grown and admixed with similarly sized clays; silt- and sand-sized quartz and glaucony grains; and pyrite masses and framboids often enclosed in calcitic and aragonitic fossil shells (Plate 7). The fineness of the calcite probably indicates rapid crystallization from pore fluids highly super-saturated with respect to calcite. It may also be reflecting the limiting sizes of pores in the silty- and sandy-clay host sediments. The fossil shells and non-carbonate materials have been incorporated with no apparent indication of having suffered diagenetic dissolution, alteration or, in the case of the aragonite, transformation.

Thin section staining showed the calcites to be ferroan, with ~4·5% FeO. This agrees with the ~ 3 mol% $(Fe+Mn+Mg)CO_3$ obtained by the X.R.D. and A.A.S.analyses (Tables 18-20, and Fig.36). They are ferroan but low magnesian calcite varieties.

The septarian calcites, where present, constitute less than 3% of the calcareous concretions. Microscopically, they comprise two or sometimes three calcite generations; none of which correspond to any of the four pore-filling calcite models given by Lindholm (1974).

The calcites are dominated by equant crystals (length/width ratio of 1·5 to 4) with flat rhombohedral terminations (Plates 69-71a-c, 73). Interspersed between these are a few bladed (l/w ratio of > 4) forms, with steep terminations and, in addition, occasional prismatic forms. These calcites are roughly aligned with their crystallographic c-axis perpendicular to the fissure walls. They are all length-fast.

The first generation calcite is ferroan (1·5 to > 3·5% FeO), < 10 um in size, and mainly occupies the basal 50-200 μm part of the fissures.

Fig.35: Types of Septarian Calcite within Calcareous Concretions

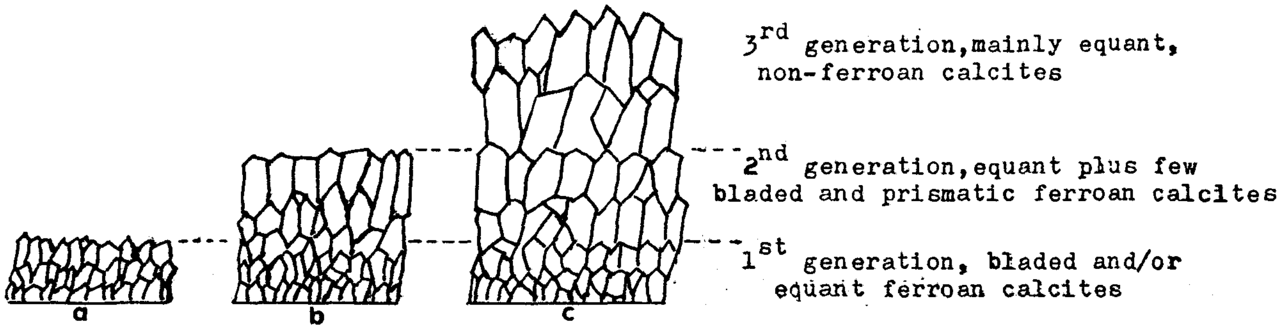
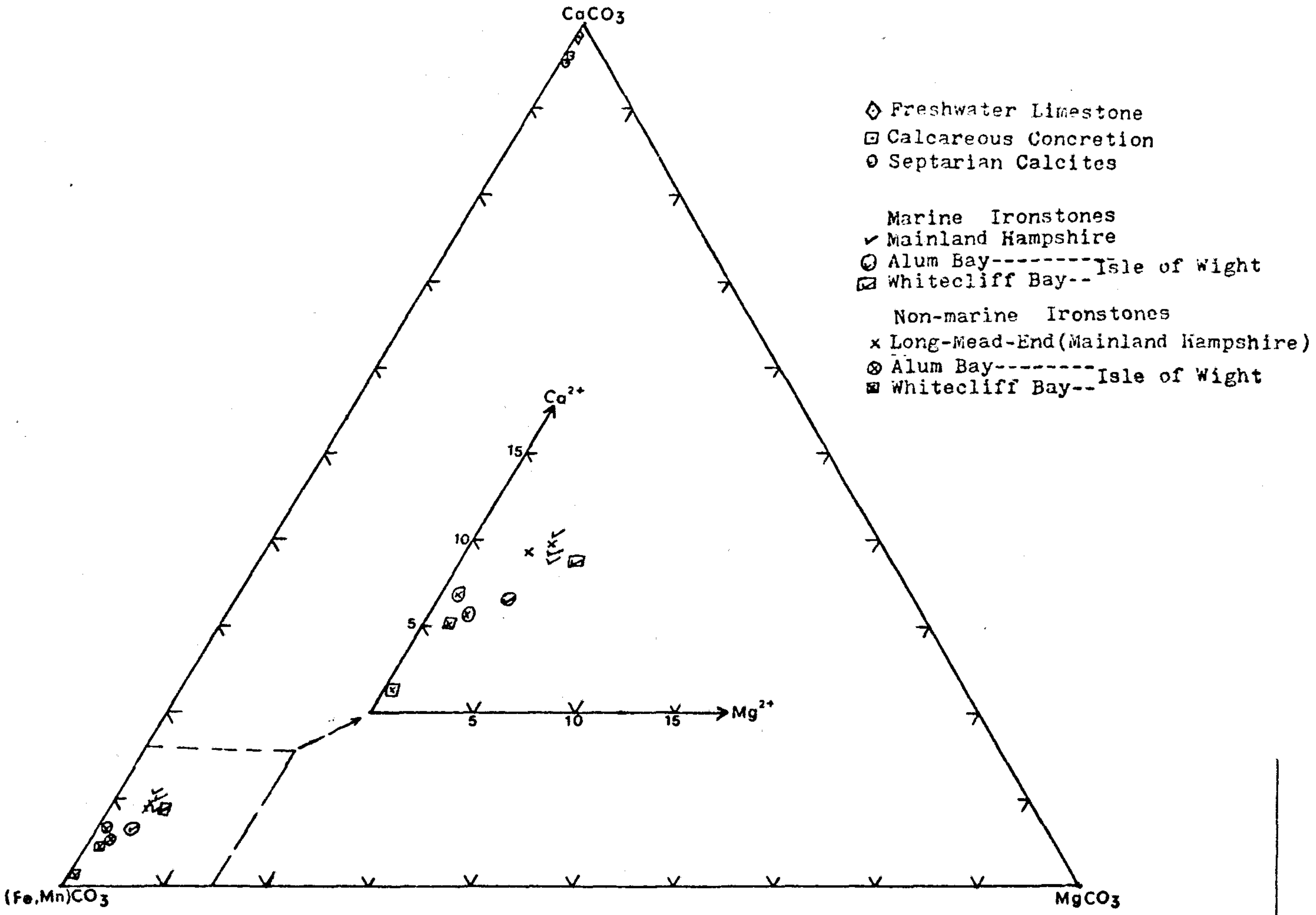


Fig.36: Triangular Plot of $CaCO_3$-$MgCO_3$-$(Fe,Mn)CO_3$ For Carbonates



Hence all fissures of less than 500 μm width are completely filled by first generation calcites (Fig.35a). The forms assumed vary; in some fissures they are mainly bladed, whilst in others they are mixtures of equant and bladed forms. These calcites were also observed filling expansion cracks in the non-ferroan fossil shells (i.e. Plates 68-70, 73), and glaucony grains.

The second generation calcite is also ferroan (1·5 to 3·5% FeO), but is dominated by equant crystals whose sizes increase from about 10 μm to over 200 μm at the fissure centres. Sizes of 1 mm to 2 mm or more are attained by most of the crystals in fissures near the core of the concretions (i.e. Plates 5, 69, 70; Fig.36b). In some veins, non- or slightly ferroan (0 - 1·5% FeO) equant, 20-250 μm-sized calcite occurs at the fissure centres (i.e. Plate 69; Fig.35c). These constitute the third calcite generation. Contacts between the calcite generations are sharp but often sinuous.

A partial major element analysis of separated pieces of the septarian calcites from Sample BBB-36 is given in Table 15c. These contain 94·6% $CaCO_3$, 1% MgO and 4·5% FeO. Ti, Al, Fe^{3+} and P impurities, possibly incorporated from matrix materials, only amount to an insignificant 0·13%. The chemistry closely agrees with the ~4 mol% $(Fe+Mn+Mg)CO_3$ content obtained by X.R.D. and A.A.S. methods (Table 20). The calcites are thus low-magnesian but ferroan, and are similar to those comprising the bulk of the concretions. This compositional similarity of the calcites thus indicates no significant changes having occurred in the nature of the pore fluids in which the growth of the concretions was initiated and maintained. The pore fluids concerned would have had very low Mg/Ca ratios of < 2, and a Fe/Ca ratio of < 20 (cf. Berner, 1971; Muller et al., 1973; Folk, 1974; Richter & Füchtbauer, 1978). These are considered later. It is, however, significant noting that the shallow formation of ferroan calcites, rather than Mg-rich carbonate phases, is a very unusual early fermentation diagenesis. The probable causative factors are discussed later.

14.3.2B Sideritic Ironstones

The siderite contents of the ironstones are very variable, ranging from about 10% to 96%. The variation allows differentiation of the ironstones into three groups:

i) ironstones with very high, >70%, siderite content. This includes WBLH-10, ABLH-5, ABLH-8 and ABBB-13 on the Isle of Wight, and BLH-36 and BBB-11 on the mainland;

ii) ironstones with moderate, 40-60%, siderite contents. They are WBLH-6, WBBB-2, BLH-33, BBB-23, BBB-26 and BBB-43;

iii) ironstones with low, ~10%, siderite contents. Only two ironstones, BLH-22 and BBB-50, both on the mainland, belong to this group.

This variation in abundance is partially related to the lithology and facies of the host sediments. This is illustrated in Figure 42, the plot of quartz(+feldspar)/quartz+feldspar+clays ratios of the ironstone matrix (non-carbonate contents) against the absolute siderite contents. The ironstones matrices are predominantly clayey with Q+F/Q+F+Cl ratios of 0·3 - 0·6 (cf. Fig.22). Ironstone WBBB-2 possesses a very sandy-clay matrix with a ratio value of 0·7, whilst WBLH-6 and BLH-33 are sandy with a ratio value of ~ 0·9.

Considered together, the nature of the matrix and the siderite abundance, which may also be taken as the host sediment's porosity at times of concretionary growth, show that sideritisation conditions were uniform in the marine succession compared with the non-marine sediments. The non-marine ironstones were developed in both the sands and clayey hosts. Nevertheless, the 30-50% and 70-96% siderite contents of the sandy-ironstones and clay-ironstones respectively indicate that growths were within very shallow depths when the host sediments still possessed the utmost porosities possible. In the case of the marine ironstones, whilst they are all clayey, their siderite abundance, however, varies from 30-70%. This cannot, however, be interpreted as differential porosities or depth growths because the ironstones, particularly those from the succession on mainland Hampshire, remain texturally soft or friable. Siderite precipitations for these ironstones had certainly not been to the utmost porosities of the host clayey sediments. Unfortunately, an alternative porosity estimation method involving mineral grains/pore spaces counting in thin section (i.e. Mellon, 1964) could not be employed because of the very fine-grained texture of the ironstones and the intimate admixing of the carbonates and clayey matrix materials.

The siderite morphology is closely similar in all the ironstones. It mainly occurs as spherulitic aggregates of rhombohedral crystals where sizes mostly range from about 2 µm to 5 µm (i.e. Plates 77a,b; 86) in thin sections. Some spherules in ABLH-5, where siderite has replaced lime-muds, are up to 20 µm in size; whilst larger, 100-150 µm, spherules predominate in ABLH-8 from the section at Heatherwood Point. Those large spherules (Plates 78a,b) are also rimmed or separated from each other by cryptocrystalline siderite. Virtually all the fossil shells in ABLH-8, and many in ABLH-5, have been replaced by undifferentiated cryptocrystalline siderite (Plates 78, 83c). In places, the siderite has pseudomorphed on the primary aragonitic structure.

Under the S.E.M., the spherules comprise 2-10 µm-sized siderite rhombs (Plates 79, 80, 81, 85), the smaller ($<$ 5 µm) crystals being most common in ironstones from the succession at Barton and Whitecliff Bay. Growth from solution is indicated in Samples ABLH-5, ABLH-8 and WBLH-10 by the presence of sparry equant crystals within channels (Plates 80d, 85b). The crystals concerned are not only arranged with their c-axis perpendicular to the 'channel' walls, but also show slight variations in size towards the 'channel' centre. In many samples, a radial arrangement of the siderite crystals at contacts with detrital grains is also exhibited.

The biogenic and detrital contents of the ironstones include aragonitic and/or calcitic fossil shells, quartz, feldspar, glauconies, clays and pyrite. These, as in the calcareous concretions, are generally intimately admixed with the precipitated siderite contents (i.e. Plates 82,83). Two ironstones, BBB-23 and ABLH-5, however, possess additional features. The escape burrows in BBB-23 (Plates 8,9,77) contrast strikingly with the bulk of the ironstone by containing no siderite, but are mainly filled by clays, fine silt-sized quartz, pyrite and coccoliths. Identification of the coccoliths, some of which are shown in Appendix 3, is beyond the scope of the present work. They resemble, however, some of the forms characterising the Chalk; if identified as re-worked Chalk material, then the importance of that deposit as a source of detritus to the Upper Eocene Hampshire Basin could be ascertained further. It also significantly supports suggestions made in Chapter 5 that the Chalk probably did not suffer very intense acidic weathering, since smectite-rich detritus was being deposited in the Palaeogene Hampshire Basin. If, however, found to be contemporaneous, then the coccoliths will be chrono- and biostratigraphically important for the Palaeogene succession of southern England.

In the case of the sideritided limestone, the relict lime-mud is observed to be separated from the bulk of the ironstone by unaltered prismatic and/or fibrous aragonitic shell material (Plates 84a-e). The preserved lime-mud and shells occur mostly in the thin, very shelly horizons around the base and top of that ironstone band (see Plate 22). Almost certainly, the unsideritised burrows and lime-muds represent mini-environments of thermodynamic instability of siderite. In the burrows, this could be due to SO_4^{2-} from trapped sea-water or derived as organic-sulphur upon the death of the organisms that made, or infilled the burrows. Differential Ca^{2+} concentrations of the pore fluids would, however, better account for the lime-mud preservation. Siderite precipitation would only be ensured when Ca/Fe $<$ 20:1 (Berner, 1971); otherwise calcite will be favoured to precipitate or stabilise.

The siderites are predominantly substituted siderites. They mostly possess asymmetrical diffraction peaks that have been resolved (cf. Pearson, 1974b) into two phases: ϕ_1 and ϕ_2(Figs.18,19). ϕ_1 is the more substituted and more abundant phase (Table 18). It accounts for between 75 and 91% of most of the siderites, and possesses cell dimensions of a_o= 4·7062 - 4·7209Å and C_o = 15·4778 - 15·6031Å, with corresponding amounts of 6-10 mol% $CaCO_3$ substitution. The purer phase, ϕ_2, has cell dimensions of a_o= 4·6747 - 4·7182Å and C_o = 15·4338 - 15·4959Å with about 1-4 mol% $CaCO_3$. Attempts at identifying each of the phases and their distribution by spot analysis of randomly selected crystals with EDAX attachment to a scan electron microscope proved inconclusive. The phases appear to be intimately mixed, giving the composite phase compositions. This raises stability questions; one of the phase must be in disequilibrium state, but which one it is is difficult to establish. Further future investigations employing electron microprobe may shed more light on this.

Not all the ironstones possess asymmetrical peaks however. The ironstones concerned are BBB-11 and WBLH-10 respectively from 'Bed J' of the Barton Sand Formation at Becton Bunny and the 'Lower Headon Beds' at Whitecliff Bay. WBLH-10, investigated more in detail, was found to possess cell dimensions of a_o = 4·7182Å and C_o = 15 5398Å equivalent to

TABLE 19: **Phase Composition of Carbonate Phases determined by X-Ray Diffraction**

Sideritic Ironstones		d-spacing Å	Relative Intensity %	Equivalent mol % $CaCO_3$	d-spacing Å	Relative Intensity %	Equivalent mol % $CaCO_3$	Cell-Dimension a_o(Å)	c_o(Å)	Equivalent mol % $CaCO_3$	Relative Intensity %	Composite Phase Composition *	Calcite $10\bar{1}4$
BLH-22	φ	2·8159	100	10·5	3·6165	100	9·8	4·7178	15·5454	10·1	100	$Fe_{89\cdot9}$ $Ca_{10\cdot1}$	3·026Å $Ca_{96\cdot5}$
BLH-33	φ2	2·8008	9	4·5	3·6014	9	3·8	4·702	15·4338	4·2	9	$Fe_{90\cdot6}$ $Ca_{9\cdot4}$	3·033Å Ca_{99}
	φ1	2·8200	91	12	3·6165	91	10	4·7178	15·6031	11	91		
BLH-36	φ2	2·7992	21	4	3·5971	16	2·8	4·6943	15·4397	3·5	18	$Fe_{90\cdot3}$ $Ca_{9\cdot7}$	3·03Å $Ca_{97\cdot8}$
	φ1	2·8191	79	11·8	3·6199	84	11 3	4·713	15·5678	11·5	82		
ABLH-5	φ2	2·796	18	2·3	3·5897	4	0	4·6773	15·4959	0·7	11	$Fe_{94\cdot3}$ $Ca_{5\cdot7}$	3·034Å Ca_{100}
	φ1	2·8067	82	7	3·6072	96	6·2	4·7079	15·4778	6·3	89		
ABLH-8	φ2	2·7953	27	29	3·5862	17	1·0	4·6747	15·4569	1·6	22	$Fe_{93\cdot2}$ $Ca_{6\cdot8}$	
	φ1	2·8125	73	9	3·6102	83	7·7	4·7079	15·5388	8·3	78		
WBLH-6	φ2	2·7417	29	0·5	3·6027	100	4·6	4·6989	15·4965	5·4		$Fe_{94\cdot7}$ $Ca_{5\cdot3}$	
	φ1	2·8059	71	6·5									
WBLH-10	φ	2·7951	100	1·8	3·5924	100	1	4·7182	15·5398	1·4	100	$Fe_{98\cdot6}$ $Ca_{1\cdot4}$	
BBB-23	φ2	2·7958	21	2·4	3·5906	21	0·5	4·6839	15·4350	1·5	21	$Fe_{90\cdot9}$ $Ca_{9\cdot1}$	3·031Å $Ca_{98\cdot5}$
	φ1	2·8188	79	11·5	3·6185	79	10 7	4·7195	15·5709	11·1	79		
BBB-26	φ2	2·803	20	4	3·5967	13	2·5	4·6868	15·5023	3·4	17	$Fe_{89\cdot9}$ $Ca_{10\cdot1}$	3·034Å Ca_{99}
	φ1	2·8212	80	12·7	3·6207	87	11·2	4·7209	15·592	11·9	83		
BBB-43	φ2	2·7915	16	0·4								$Fe_{91\cdot2}$ $Ca_{8\cdot8}$	
	φ1	2·816	84	10·4									
BBB-50	φ2	2·7903	31	0	3·5945	100	1·8					$Fe_{97\cdot5}$ $Ca_{2\cdot5}$	
	φ1	2 8058	69	6·2									
ABBB-13	φ2	2·7966	44	2·6	3·5908	26	0·2	4·6834	15·4449	1·8	35	$Fe_{93\cdot6}$ $Ca_{6\cdot4}$	
	φ1	2·8099	56	7·6	3·6081	74	6·8	4·7062	15·5162	7·2	65		
WBBB-2	φ2	2·8019	27	5	3·5963	29	2·5	4·6894	15·4828	3·9	24	$Fe_{91\cdot3}$ $Ca_{8\cdot7}$	
	φ1	2·8155	73	10·4	3·6165	79	10	4·7182	15·5398	10·2	76		

Septarian Calcite (BBB 36) 3.02 Å Ca_{95}

Calcareous Concretion (") 3.025Å Ca_{97}

* Fe = mol % (Fe, Mg, Mn) CO_3

Ca = mol % $CaCO_3$

Table 20: Acid Leachate Contents of Carbonates by A.A.S.

	WT% WHOLE ROCK					CORRECTED WT% WHOLE ROCK				EQUIVALENT	Mol% *			
	Fe	Mn	Ca	Mg	Al	Fe	Mn	Ca	Mg	CO_2	$FeCO_3$	$MnCO_3$	$CaCO_3$	$MgCO_3$
Sideritic Ironstones														
WBBB-2	22·25	1·02	1·15	0·76	0·35	21·67	1·00	0·88	0·62	19·84	86·1	4·1	4·9	5·0
ABBB-13	38·25	0·33	1·10	0·72	0·23	37·87	0·32	0·92	0·63	32·19	92·5	0·8	3·1	3·6
BBB- 23	23·20	0·22	1·82	0·54	0·13	22·99	0·21	1·72	0·49	21·03	85·9	0·8	9	4·3
26	16·5	0·10	2·82	0·40	0·16	16·20	0·09	2·70	0·34	16·42	77·7	0·4	18·1	3·8
43	14·4	0·08	1·11	0·35	0·09	14·25	0·08	1·04	0·31	13·0	86·4	0·5	8·8	4·3
50	5·21	0·02	0·27	0·20	0·03	5·17	0·02	0·25	0·19	4·53	89·9	0·5	6·5	3·7
WBLH-6	20·3	0·78	0·5	0·21	0·21	19·95	0·77	0·34	0·12	16·93	92·9	3·7	2·2	1·3
10	41·2	0·52	0·38	0·06	0·03	41·15	0·52	0·35	0·05	33·32	97·4	1·2	1·2	0·2
ABLH-5	35·5	0·51	2·31	0·39	0·19	35·19	0·50	2·06	0·31	31·06	91·2	1·2	4·8	1·8
8	36·05	0·49	1·03	0·14	-	36·05	0·49	1·03	0·14	29·75	94·1	1·3	3·8	0·8
BLH- 36	31·27	0·63	3·49	0·79	0·39	30·63	0·61	2·86	0·63	28·90	83·5	1·7	10·8	3·7
33	12·2	0·17	1·98	0·25	0·16	11·94	0·16	1·86	0·18	11·91	79·0	1·1	17·1	2·7
22	3·51	0·05	2·48	0·15	0·12	3·31	0·04	2·39	0·10	5·45	47·9	0·6	48·3	3·3
Calcareous Concretion														
BBB- 36	1·8	0·23	14·20	0·17	0·07	1·69	0·23	14·15	0·14	17·31	7·7	1·0	89·8	1·4
Septarian Calcite														
BBB- 36	2·8	0·15	19·8	0·17	0·09	2·65	0·15	19·73	0·13	24·12	8·7	0·5	89·8	1
Freshwater Limestone														
ABLH- 3	0·46	0·26	22·10	0·10	0·09	0·31	0·26	21·93	0·06	24·64	1·0	0·9	97·7	0·5
Non-carbonate Sediments														
BLH-34 and ABLH-9	0·28	0·01	0·13	0·07	0·17									

*Biogenic $CaCO_3$ uncorrected for

Table 21: Phase Compositions of Carbonate Phases from Combined X.R.D and A.A.S. Analyses

	(Fe+Mn+Mg)CO_3 ≡	mol% (Fe + Mn + Mg) CO_3			mol% $CaCO_3$
	[X.R.D. obtained]	($FeCO_3$	$MnCO_3$	$MgCO_3$	[X.R.D.obtained]
		X.R.D. estimates proportioned on the relative wt% acid leached elements content by A.A.S.			
Sideritic Ironstones					
BLH-22	(89·9)* ≡	83·1*	1·0*	5·8*	10·1*
33	(90·6)	86·4	1·2	3·0	9·4
36	(90·3)	84·6	1·7	4	9·7
ABLH-5	(94·3)	91·1	1·3	1·8	5·7
8	(93·2)	91·1	1·1	0·7	6·8
ABLH-6	(94·7)	89·3	3·5	1·3	5·3
10	(98·6)	97·1	1·3	0·3	1·4
BBB-23	(90·9)	85·9	0·8	4·2	9·1
26	(89·9)	85·4	0·5	3·8	10·1
43	(91·2)	86·4	0·5	4·4	8·8
50	(97·5)*	93·3*	0·4*	3·8*	2·5*
ABLH-13	(93·6)	89·4	0·8	3·4	6·4
WBBB-2	(91·3) ≡	85·3	4·1	5·6	8·7
Calcareous Concretions					
BBB-36	(3) ≡	2·3	0·3	0·4	97
Septarian Calcites					
BBB-36	(5)	4·3	0·3	0·5	95
Freshwater Limestone					
ABLH-3	(1)	0·4	0·4	0·2	99

(* Data unreliable because of low, <10%, siderite abundance) a low, ~ 1 mol% $CaCO_3$ substitution.

The Mg^{2+} and Mn^{2+} substitutions in the siderites vary from trace to ~ 5 mol% (Table 20) respectively. This shows the siderites to be low-magnesian, low-manganese varieties. The Mg^{2+} and Mn^{2+} substitution in the siderites shows facies-related variations; with siderites from the marine ironstones mostly possessing the higher (3-5 mol%) Mg^{2+} substitution, but lower $<$ 1 mol% Mn^{2+} substitution. These and the other compositional variations of the siderites are given below.

i) The resolved siderite phases, on the basis of their relative abundances (Table 19) and plotting against the absolute siderite abundance (Fig.37), show that substitution decreases with increasing siderite abundance, and from the mainland ironstones to those on the Isle of Wight. This could be a function of the differential abundance of iron available for diagenesis, much higher detrital-iron having been supplied to the area of the Isle of Wight.

ii) The Ca^{2+}-, Mg^{2+}- and Mn^{2+}-substitutions are individually independent of the absolute siderite abundance (Fig.38a,b,c); and whilst the Mg^{2+} and Mn^{2+} show facies-related variations, the Ca^{2+} variation appears to be lateral.

Three levels of Ca^{2+}-substitution characterise the ironstones:

a) a high, 9-10 mol%, Ca^{2+} in siderites constituting ironstones from the succession on mainland Hampshire, and ironstone WBBB-2 from the top of the Barton Clay at Whitecliff Bay. This amount of Ca^{2+} substitution is the maximum possible in siderite lattice (cf. Zaritskii, 1964; Pearson, 1974b).

b) a moderate, ~ 6 mol% Ca^{2+} in siderites of ironstones ABLH-5, ABLH-8 and ABBB-13 from the succession at Alum Bay - Heatherwood Point, and ironstone WBLH-6 from Whitecliff Bay.

c) a low, ~ 1 mol%, Ca^{2+}-substituted siderite of ironstone BBB-11 from the Barton Sand on the mainland and WBLH-10 from the 'Lower Headon Beds' section at Whitecliff Bay.

The Mg^{2+} substitution (Figs. 36, 35b) differentiates the ironstones into two:

a) siderites from the freshwater 'Lower Headon Beds' on the Isle of

Fig.37: Plot of Relative Abundance of Siderite Phases vs. Absolute % Siderite

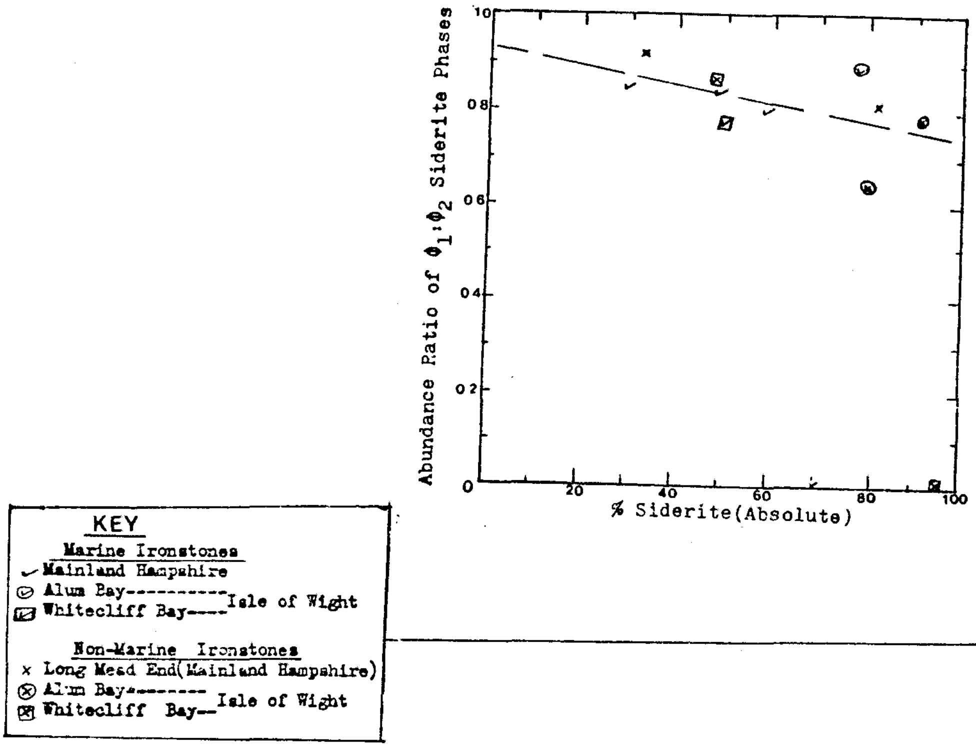
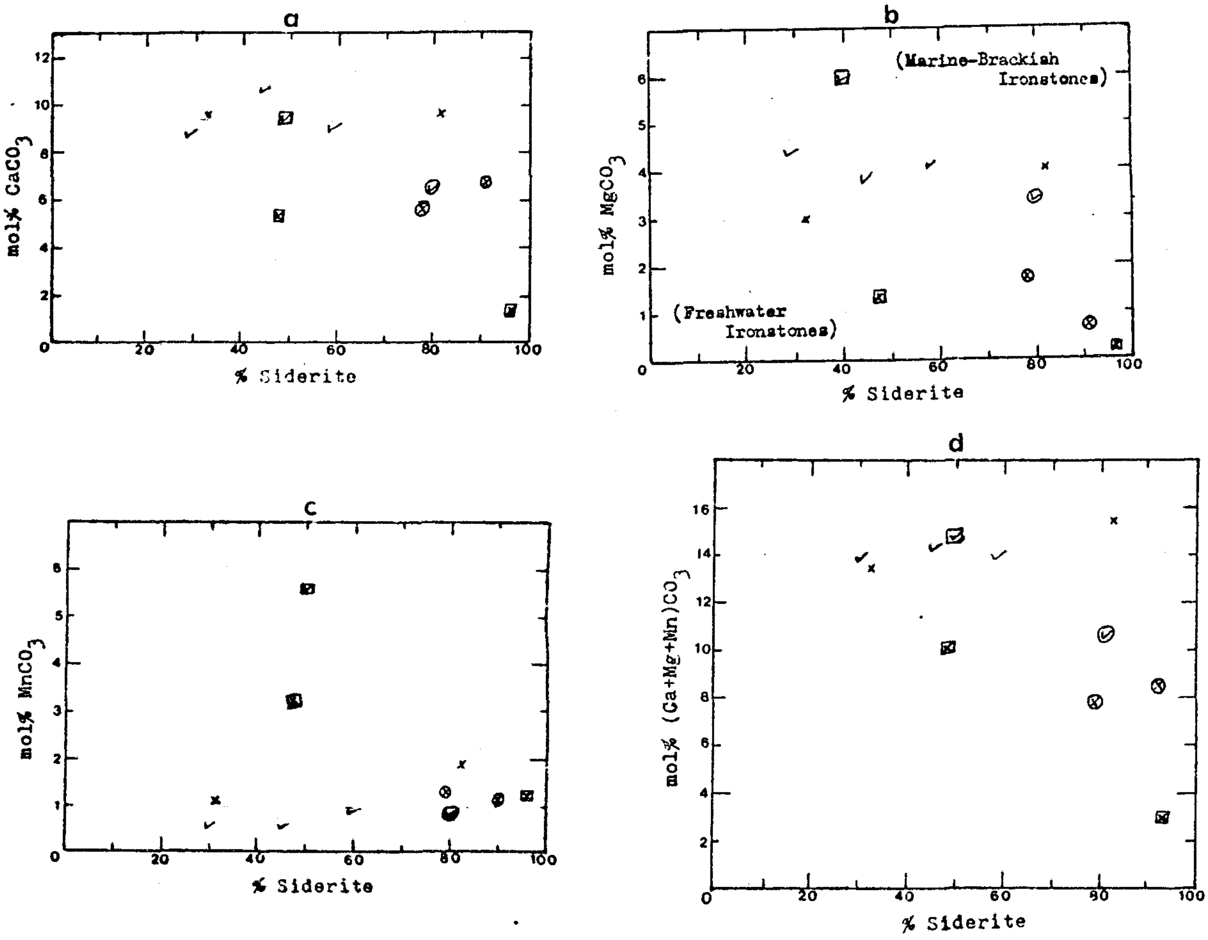


Fig.38: Phase Compositions of Siderite--Plots of
a)mol%$CaCO_3$ vs. %Siderite
b)mol%$MgCO_3$ vs. %Siderite
c)mol%$MnCO_3$ vs..%Siderite
d)mol%$(Ca,Mg,Mn)CO_3$ vs. %Siderite



Wight characterised by $<$ 2 mol% $MgCO_3$ contents; traces being recorded for WBLH-10.

b) siderites from the marine Barton Clay sediments at all the localities studied, and the brackish 'Lower Headon Beds' possessing 3-5 mol% $MgCO_3$ contents.

The Mn substitution is $<$2 mol%, with siderites from marine ironstones possessing $<$ 1 mol% $MnCO_3$ contents (see Fig.6, plot of mol% $MnCO_3$ vs.% siderite). Exceptionally high, 3·5 and 4·1 mol% $MnCO_3$ respectively occur in WBLH-6 and WBBB-2. Relatively higher but localised Mn-accumulation with iron-oxides may account for these.

Together, the Ca^{2+}, Mg^{2+} and Mn^{2+} substitutions amount to about 14 mol% in the marine ironstones, the exception being the 10·6 mol% for ABB-13. BBB-11, although not analysed in detail, is also little substituted. The same amounts, ~14 mol%, of substitution also typify siderites from the 'Lower Headon Beds' on the mainland; whilst 8-10 mol% substitutions occur in the 'Lower Headon Beds' on the Isle of Wight. WBLH-10 is almost pure, only having ~ 3 mol% substitution. In relative elemental proportions, the substitution may be summarized into two groups:

i) the Ca $\gg$ Mg $\gg$ Mn or $Ca^{2+}_{x} + Mg^{2+}_{x/2} + Mn^{2+}_{x/8}$ substitutions; where x = 8-10 mol%. This characterises siderites from the succession on the mainland; and

ii) the Ca $>$ Mg $\simeq$ Mn or $Ca^{2+}_{x} + Mg^{2+}_{x/2 \text{ to } x/6} + Mn^{2+}_{x/2 \text{ to } x/6}$ substitution where x varies widely from ~ 1 to ~ 9 mol%. This typifies siderites from the succession on the Isle of Wight.

Differential pore fluid compositions are thus more apparent laterally (i.e. from the mainland in the west to the Isle of Wight to the east - see Fig.1); whilst facie-influence is only apparent on the Isle of Wight. These are further discussed later.

14.3.3 Chemical Composition

The calcareous concretions have similar compositions dominated by lime and carbon dioxide, as expected. Their CaO contents vary from 33% to 43%, averaging 40%, whilst the CO_2 content is between 26% and 35%, with an average value of 32%. These are equivalent to 60-78% $CaCO_3$ and closely agree with the X.R.D. estimates. Re-calculation of the compositions of the acid insoluble residues show that virtually all the lime in the bulk samples of the concretions is acid-soluble and, hence, contained within calcite.

In addition to the high Ca abundance, the calcareous concretions are enriched in magnesia and ferrous iron when compared with the host clastic sediments. The concentrations of magnesia and ferrous iron vary very little from one calcareous concretion to another; their average contents being 2·05% FeO and 1·18% MgO. About 83% of the FeO ($\sim$ 1·7% absolute amounts) and 66% of the MgO ($\sim$ 0·8% absolute amounts) in the concretions are in the acid soluble carbonate phases. Combined, these elemental abundances give calcite phase compositions of 3-5 mol% $FeCO_3$, $\lesssim$ 3 mol% $MgCO_3$ and $\sim$94 mol% $CaCO_3$. These closely agree with the low magnesian but ferroan nature of the calcites earlier deduced by other methods. Furthermore, the amount of ferrous iron incorporated in the calcites ($FeO_{calcite}$, Table **22**) is found to be about five times that bounded in the sulphide (FeO pyrite). This reflects an apparent insignificant scale of sulphide diagenesis taking place during the growth of the concretions. This is very important with respect to the ferroan nature of the calcites and their very shallow depths of formation. Depletion of reducible sulphur and sulphate ions, and the establishment of a fermentation diagenetic zone apparently occur at very shallow burial depths of the Barton Clay sediments. This is even more significant with respect to the development of ironstones.

In contrast to the calcareous concretions, the ironstones possess a wide range of compositions in sympathy with their siderite-dominated carbonate contents, and the clayey or sandy nature of their non-carbonate matrices. They contain highly variable amounts of FeO, Fe_2O_3, CaO, CO_2, SiO_2 and Al_2O_3, and small amounts ($<$ 3%) of MgO and K_2O. All other constituents are generally less than 1%. In order to discuss the iron contents of the ironstones, these have been re-cast as Total iron (Fe_2O_3T), Carbonate iron (FeO_{sid}), Sulphide iron (FeO_{py} - using sulphur contents of bulk samples, Total diagenetic iron (Fe_2O_3 D) and Residual or Non-diagenetic iron (Fe_2O_{3R}). These are given in Table 22. Iron contents, re-cast as such, have been employed by Curtis (1967) and Pearson (1979) in their studies of sideritic and pyritic Carboniferous sediments of Yorkshire, England. They showed that iron contents expressed in such re-cast

Table 22: 'Recast' Iron Contents of Diagenetic Carbonates.

	SAMPLES	Total Fe ($\%Fe_2O_3$)	$FeO_{sulphide}$	$FeO_{siderite}$	Diagenetic Fe($\%Fe_2O_3$)	Residual Fe($\%Fe_2O_3$)
	BLH 22	11·19	0·05	3·27	3·69	7·5
	33	21·48	0·18	13·7	15·43	6·05
	36	48·38	0·11	37·56	41·86	6·62
Sideritic Ironstones	ABLH 5	49·09	0·29	42·07	47·03	2·06
	8	52·95	0·18	42·83	47·8	5·15
	WBLH 6	37·27	0·52	23·42	26·61	10·66
	10	65·61	0·16	49·55	55·24	10·37
	BBB 23	37·4	0·36	28·35	31·91	5·49
	26	22·74	0·63	17·96	20·66	2·08
	43	22·16	0·64	17·35	9·99	2·17
	50	21·71	0·63	3·07	4·11	17·6
	ABBB 13	49·55	0·36	41·55	46·58	2·97
	WBBB 2	32·12	0·35	23·82	26·86	5·26
				FeO (calcite)		
Calcareous Concretions	BBB 25	4·9	0·82	2·38	3·45	1·45
	31	3·98	0·24	1·64	2·09	1·89
	36	4·34	0·46	1·50	2·18	2·16
	39	4·25	0·37	1·56	2·15	2·1
	42	5·28	0·42	2·1	2·80	2·48
	ABBB 5	3·33	0·43	1·41	2·05	1·28

Fig.39: Plot of FeO(Siderite) vs. Total FeO For Sideritic Ironstones.

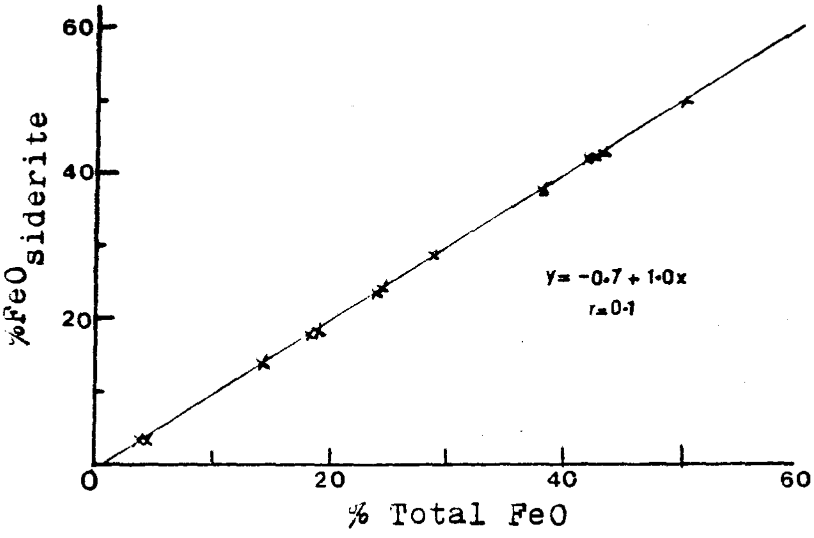


Fig.40: Plot of Fe_2O_3(Diagenetic) vs. Total Fe_2O_3 For Sideritic Ironstones

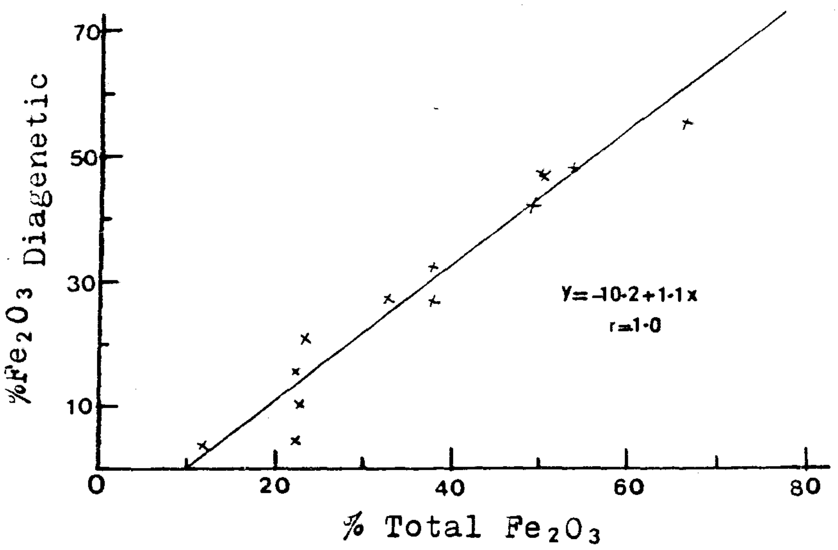
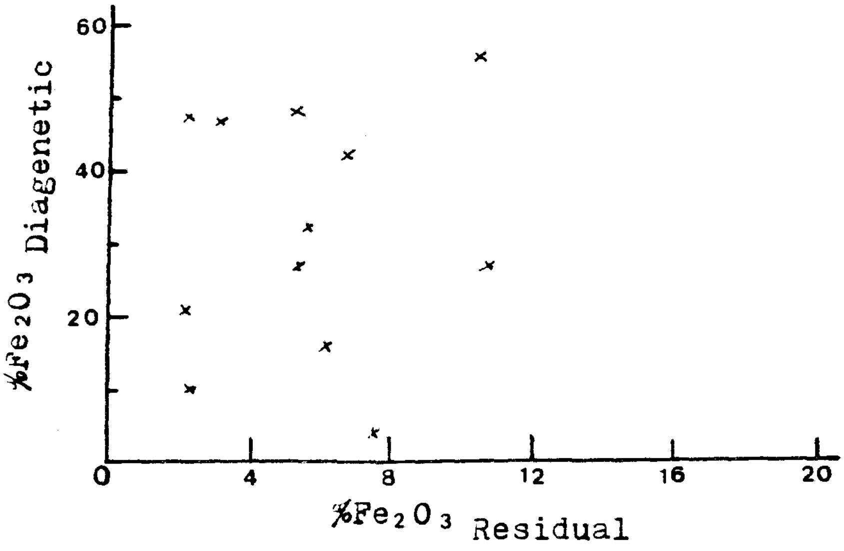


Fig.41: Plot of Fe_2O_3(Diagenetic) vs. Fe_2O_3(Residual) For Sideritic Ironstones.



forms are useful in the study of ironstones and related diagenetic material.

The ironstone samples contain between 3 and 50% ferrous iron, whilst the ferric iron ranges between 2 and 17%. The abundance of FeO_{sid} over FeO_{py}, and also the distribution of the samples in the plot of FeO_{sid} vs. FeO_T (Fig.39) show that virtually all the ferrous iron is contained in the acid-soluble siderite phases. FeO due to pyrite is very small, averaging 0·34%, and is only of significance (about 0·6%) in the marine ironstones on mainland Hampshire. Therefore ferrous iron can be considered as directly related to the siderite abundance in the ironstones. A small amount ($\sim$ 5%) of FeO is present in ironstones BLH-22 and BBB-50 as reflections of their low, $\sim$ 10%, siderite contents. The highest, 49·6% FeO, is in WBLH-10, the almost pure sideritic ironstone in the 'Lower Headon Beds' at Whitecliff Bay.

The magnesia content of the bulk ironstone samples varies from trace to 2·3%. It was largely undetected in ironstones from the 'Lower Headon Beds' on the Isle of Wight; whilst $<$ 0·6% MgO contents typify other ironstones in the 'Lower Headon Beds' on the mainland, and those of the Barton Clay on the Isle of Wight. Only the ironstones in the marine succession at Barton contain relatively higher, 1-2% MgO, most being in BBB-23 and BBB-26.

Re-calculation of the insoluble residue compositions shows that between 70% and 100% of the MgO content is acid soluble and, hence, in the siderites. However, the small absolute amounts ($<$ 1-6%) involved confirm the low-magnesian nature of the siderites.

The lime contents of the ironstones vary from trace to 6%, with 3-6% CaO occurring in ironstones with unaltered fossil shells constituents, whereas $<$ 3% CaO typifies ironstones with sideritised shells or without shells.

14.3.4 Non-carbonate Contents

The calcareous concretions contain between 15% and 36% acid insoluble residues. These possess similar compositions (Table 22) which, mineralogically, are dominated by quartz, clays and potassic feldspars. Sodic feldspars, pyrite and organic-carbon occur in minor ($<$ 5) amounts. The chemical composition is, as expected, dominated by silica and alumina.

Table 23 Compositions of Acid Insoluble Residues of Calcareous Concretions in the Upper Eocene Barton Clay, Hampshire Basin.

Samples	BBB 25	BBB 31	BBB 36	BBB 39	BBB 42	ABBB 5
% Insoluble Residue	24.22	14.80	23.90	26.70	35.47	26.22
Mineralogy :						
Quartz	27.6	37.3	41.8	51.0	40.3	44.9
Total Clay	62.2	57.4	48.5	42.0	49.8	40.1
Potassic Feldspar	7.5	4.7	5.5	3.7	6.2	11.2
Sodic Feldspar			1.8	1.3		1.8
Pyrite	2.1	0.6	2.4	2.1	3.7	2.1
Organic-C	1.3	1.3	1.1	1.2	1.2	1.2
Partial Chemical Compositions :						
SiO_2	58.71	59.25	67.20	69.28	65.16	68.66
TiO_2	1.04	1.12	0.95	0.92	1.30	0.89
Al_2O_3	19.37	16.17	11.41	11.01	14.96	11.28
FeO	1.48	2.30	1.54	1.12	0.70	0.99
Fe_2O_3	5.37	5.78	6.48	4.82	4.58	4.22
MgO	1.81	1.99	1.59	1.42	1.54	1.30
CaO	0.52	0.36	0.25	0.16	0.12	0.31
Na_2O	-	0.25	0.24	0.22	0.24	1.05
K_2O	3.13	3.02	2.74	2.60	2.50	2.82
P_2O_5	0.12	0.07	0.07	0.05	0.09	0.03
S	0.99	1.61	1.30	1.39	0.93	1.27
CO_2	4.69	4.85	4.01	4.45	4.47	4.42

Table **24** Compositions of Acid Insoluble Residues of Sideritic Ironstones, Upper Eocene, Hampshire Basin.

	BLH			ABLH		WBLH		BBB				ABBB	WBBB
Samples	22	33	36	5	8	6	10	23	26	43	50	13	2
% Insoluble Residue	75.65	61.54	14.43	15.96	17.52	48.84	7.59	31.11	47.28	64.63	77.55	22.48	47.0
Mineralogy :													
Quartz	86.1	88.2	22.3	51.8	48.3	79.1	20.7	25.8	32.2	38.5	42.10	31.0	68.7
Total Clay	7.7	6.8	59.3	43.3	43.0	11.2	33.9	66.3	54.3	53.7	41.0	61.7	20.8
Potassic Feldspar	4.8	5.0	2.6	3.5	7.9	7.0	2.2	4.5	12.4	4.0	3.0	4.5	7.6
Sodic Feldspar Feldspar	1.5		1.9	1.5		1.5	1.2	1.9		2.5	0.9	1.1	1.9
Pyrite					0.8	1.2		1.6	1.2	1.2		1.8	1.0
Goethite			14.1				42.0				13.0		
Organic-C	0.3	0.3	0.9	0.7	0.8	0.4	0.9	1.6	1.4	1.0	0.8	1.0	0.5
Partial Chemical Composition :													
SiO_2	87.44	87.46	56.26	73.04	73.26	87.58	50.53	60.65	58.38	64.31	62.76	66.02	80.33
TiO_2	0.78	0.65	1.27	1.26	1.13	0.77	0.98	1.28	0.97	1.20	0.79	1.27	0.65
Al_2O_3	4.04	4.32	22.91	13.73	12.76	4.80	11.12	19.00	18.81	18.22	11.66	18.51	9.37
FeO	0.17	0.20	0.95	0.56	0.07	0.33	0.82	0.45	1.44	0.92	1.75	0.66	0.40
Fe_2O_3	0.54	0.13	5.04	2.61	4.39	1.30	26.24	5.03	6.32	4.35	12.59	3.72	1.83
MgO	0.18	0.17	1.13	0.74	0.70	0.33	-	1.82	1.78	1.47	1.63	1.32	0.80
CaO	-	-	0.10	0.12	0.12	0.11	0.10	-	0.17	-	-	-	-
Na_2O	0.10	0.12	1.20	1.09	0.68	0.99	0.11	0.21	0.11	0.27	0.16	0.28	0.29
K_2O	0.15	0.35	3.53	2.13	2.03	0.89	1.90	3.36	3.08	3.12	3.62	2.92	1.93
P_2O_5	0.03	0.03	0.05	0.03	0.03	0.01	0.24	0.06	0.07	0.07	0.12	0.05	0.04
S	0.04	0.08	0.51	0.20	0.26	0.38	-	0.48	0.82	0.70	0.29	0.99	0.37
CO_2	0.99	1.43	3.21	2.41	2.81	1.61	3.32	6.01	5.09	3.59	3.08	3.66	1.83

The residual Fe_2O_3 is between 4% and 6·5%, whilst the K_2O is ~ 2·5, MgO is ~ 1·5%, and S is ~ 1%. The other constituents amount to < 1%.

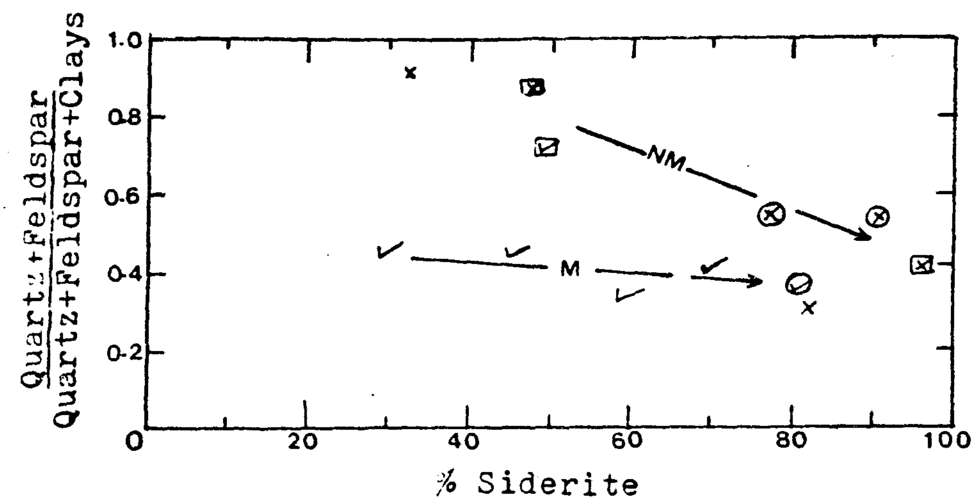
The matrices of the calcareous concretions possess a (Q+F)/(Q+F+Cl) ratio of 0·36 to 0·59. These compare closely with those of the host clastic sediments; they are similarly sandy-clay (cf. Fig.22). Hence, it seems unlikely that the concretionary horizons are 'sandier' than their hosts. Particle size analysis, which might clarify any uncertainty, could not be performed during the present study. However, if, as apparent, the concretionary horizons are not significantly coarser-grained or more porous than the host sediments, then other factors such as distribution of organic matter and channelling of pore fluids along or close to bedding planes, could have had greater influence on the development of the diagenetic carbonates (cf. Dickson & Barber, 1976; Shurubor, 1967; Pearson, 1979).

One constituent not present in every concretion is glaucony. Its distribution is reflected in the residual iron, magnesia and alumina contents. The plot of residual Fe/Mg and Mg/Al ratios for calcareous concretions is shown in Figure 43. The large concretions, which are glauconitic, are relatively more rich in iron and magnesia. They plot together and away from the non-glauconitic small nodules and the banded BBB-25.

The low lime contents (< 0·5%) of the matrix material further confirm the previous observation in Chapter 12 that the clays and feldspars in the Upper Eocene sediments are not Ca-rich. Apatite is also present, but in insignificant amounts.

The composition of the acid insoluble residues of the ironstones (Table 23) is more variable compared with that of the calcareous bodies discussed above. Their mineralogy consists of 22-88% quartz, 7-66% 'total clays' and 2-12% potassic feldspars. Sodic feldspars, pyrite and organic carbon are also commonly present, but in amounts of < 2%. In addition, goethite occurs in considerable amounts, 13-42%, in the matrix of samples BBB-50, BLH-36 and WBLH-10. The goethite is composed of oxidised material found along incipient fractures in the apparently fresh, unweathered samples collected in the field, or as secondary material formed during storage of the powdered samples prior to analysis. Oxidation of previous minerals at outcrops and in the laboratory is a major problem in geological studies, as has recently been highlighted by Gallois & Horton (1981). However, the presence of oxidised material does not seem to have

Fig.42: Plot of(Quartz+Feldspars)/(Quartz+Feldspars+Clays) vs. %Siderite For Sideritic Ironstones.

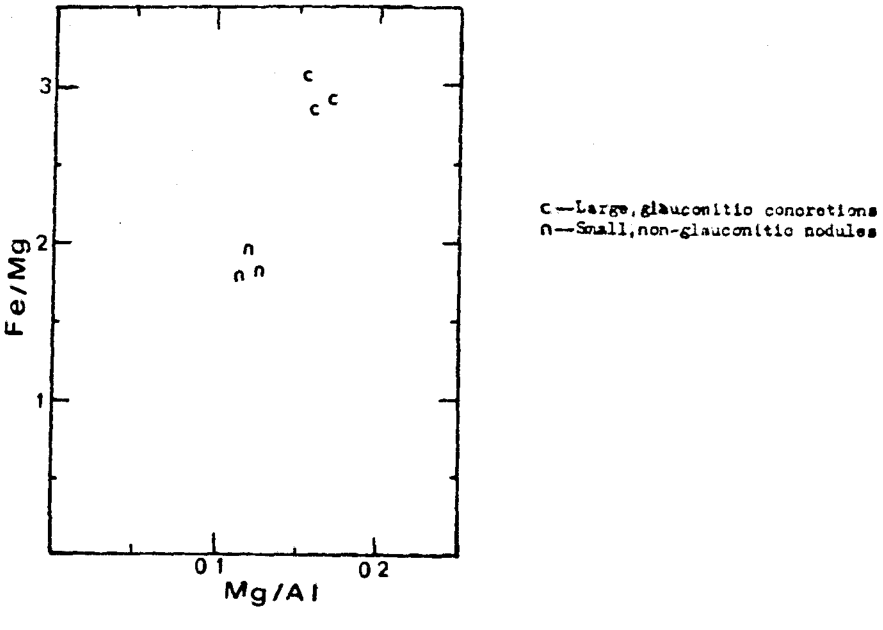


NM → Compositional trend of non-marine ironstones

M → ,, , ,, marine ironstones

(see Fig.37. for key to symbols)

Fig.43: Plot of Fe/Mg vs. Mg/Al For Calcareous Concretions.



significantly affected the present study.

The chemical composition of the ironstone matrix is also very variable and agrees with the mineralogy. The wide compositional variation is a result of the clay to sand lithology of the host clastic sediment. The Q+F/Q+F+Cl ratios of the matrix vary from 0·3 to 0·9. The lithological variation is, as previously discussed, reflected in the abundance of siderite, particularly in the non-marine ironstones. Up to 96% siderite was precipitated in the clayey host compared to between 33% and 50% in the sands (see Fig.42). These are within the utmost porosities of uncompacted sediments (cf. Fuchtbauer, 1974; Tuckholke et al., 1974). Ionic substitution within the siderite is, however, independent of the lithology (cf. Figs. 37 and 42).

An important aspect of the ironstone compositions is the absence of a relationship between the residual iron, which averages about 6·5% (i.e. Fig.40), and the total diagenetic iron (Fig.41). Correcting for the few occurrences of free iron-oxide (goethite) does not improve the disparity. This would suggest some external derivation of iron for the diagenesis. Had the system been a closed one, there could have been an antipathetic relationship between the diagenetic and residual iron. Such a relationship in support of substantial local derivation of iron has been described from some pyritic and sideritic English Carboniferous sediments studied by Curtis (1967) and Pearson (1979). Chlorite was one important local iron phase.

14.4 Discussion - Mode of Formation

Precipitation of ferroan calcites and dominantly-Ca substituted siderites has resulted from fermentation diagenesis of the Upper Eocene sediments under study. These diagenetic carbonates raise a number of important questions concerning their distribution, compositional variations, pre-compaction ages and apparent formation close to the sediments/water interface. Although some discussion has been given in the preceding sections, the probable formational processes are considered below with respect to the derivation of the reactants, constraints of physico-chemical conditions and pore fluid chemistry, and facies and sedimentological controls.

14.4.1 Derivation of the Carbonate Constituents

The derivation of the Fe^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+} and $CO_3^{=}$ essential for the carbonates' formation was most likely from altered deposited materials and/or incorporated depositional waters. Significant contribution was also very likely from Ca-rich surface and sub-surface drainage waters from the Chalk; whereas the opposite was possibly true of the compactional fluids, given the very shallow depths of formation of the carbonates and the poor lithification state of the underlying older Tertiary sediments. Hydrothermal sources, occasionally reported in the literature (i.e. Cooley & Davies, 1969), are unimportant in the present study.

a) Iron

Diagenetic iron is generally believed to be derived from detrital iron-oxide and organo-Fe complexes discretely flocculated out of suspension or deposited as adsorbed coatings on clay particles, quartz and other clastic materials (i.e. Carroll,1958). Less important sources are structurally-held iron from clay phases, particularly chlorite (i.e. Pearson, 1979), and incorporated depositional waters and compactional fluids (i.e. Matsumoto & Iijima, 1981).

Influxes of pedogenous iron-oxide were the dominant iron sources in the present study. These resulted from the goethite weatherings of warm, humid climatic conditions prevailing in the Hampshire Basin and adjoining region. Supportive evidence is provided by the presence of goethitic palaeosols and substantial amounts of disseminated goethite within parts of the succession (see Chapters 9 and 16); the iron-oxides remaining preserved mainly in coarse sediments where oxidising conditions probably prevailed after deposition. This iron-influx inference is similar to the correlation of siderite formation with high iron influx from regions undergoing humid tropical weatherings established for the Japanese Palaeogene (Matsumoto, 1978), the Upper Carboniferous of Yorkshire, north England (Pearson, 1979), and the late Neogene of the Black Sea (Hsu & Kelts, 1982).

Contribution from clay minerals was improbable; unlike the Upper Carboniferous of north England, the Upper Eocene succession under study is characterised by a clay mineralogy with trace abundance of chlorite (see Chapter 5; cf. Curtis et al., 1975; Pearson 1979). Glauconies are the other high iron containing phase, occurring in the Barton Clay. These, however, do not appear to have been involved in the diagenesis; they possess no dissolution or alteration features, not even where incorporated into the diagenetic carbonate bodies (see Ch.6, Plates 65,82) Dissolved Fe-content of surface waters is negligible ($<$ 1 ppm - see Table 4.2 of Garrell & Mackenzie, 1971) and would make an insignificant contribution to the diagenetic carbonates.

Manganese often scavenges on detrital iron-oxides (i.e. Katchenkov, 1967) and would thus be made available for diagenesis with the reduced iron.

b) Calcium and Magnesium

Dissolution of skeletal materials, particularly aragonitic and magnesian-calcite forms, is the commonly suggested source of diagenetic-Ca and Mg (i.e. Saas & Kolodny, 1972). Other sources include exchangeable or sometimes structural cations in clay phases (Oldshaw & Scoffin, 1967; Drever, 1971; Ristvet, 1978); plant matter (i.e. chlorophyll) and calcic plagioclases (Irwin, 1980); and incorporated depositional waters (i.e. Matsumoto & Iijima, 1981).

In the present study, derivation from calcic feldspars and clays is unlikely, whilst derivation from skeletal material seems limited. Calcic plagioclases have not been observed to be present in the succession; the feldspar content predominantly consisting of potash feldspar plus small amounts of sodic feldspars (see Chapter 4). The clay minerals do not contain substantial amounts of Ca- or Mg-rich phases (see Chapter 12); whilst the similarity between the MgO contents and Mg/Al ratios of the clastic matrix (acid insoluble) material of the diagenetic carbonates and the host sediments suggest no involvement of clay phases in the carbonate diagenesis.

Evidence of derivation from skeletal material is found only in some of the non-marine ironstone (i.e. ABLH-5, ABLH-8) where fossil shells replaced by siderite occur. This contrasts with the greater part of the succession where fossil shells remain wholly calcitic or aragonitic without dissolution or alteration features (see Chapter 11). Calcareous microfossils such as the Nummulites, however, could have made some contribution. Such sources are unlikely to have been sufficient to account for the diagenetic carbonates, particularly the calcareous concretions.

It would thus appear that dissolution of incorporated clastic and shell materials was insignificant and cannot sufficiently account for the volume of the precipitated carbonates. The derivation of Ca and Mg would hence be from external sources, essentially comprising of depositional waters and/or compactional fluids. The latter is unlikely to have made significant contributions because the underlying, $\lesssim$ 400m-thick, older Tertiary sediments are poorly compacted, unlithified and could not have expelled any appreciable volume of interstitial fluids into the sediments during the time of concretionary growth. Secondly, the older Tertiary sediments themselves contain diagenetic calcareous concretions and clay ironstones (see Curry et al., 1968; Potter, 1977; West, 1980) which would be expected to remove ions from interstitial fluids. Thirdly, no compactional fluids could have come from the Upper Cretaceous Chalk; the Chalk was largely compacted contemporaneously (i.e. Hancock, 1975), whilst it was largely over sub-aerial or submarine erosional surfaces of the Chalk that the Tertiary sediments were deposited in southern England (i.e. Curry, 1965; Jones, 1981).

Depositional waters would thus appear to be the most probable source of the Ca^{2+} and Mg^{2+}. The relative elemental contributions would be expected to vary according to the water compositions, which are essentially facies-related. Freshwaters contain, on average, $\sim$ 20 ppm Ca and $\sim$ 4 ppm Mg, whilst normal sea-waters contain $\sim$ 400 ppm Ca and 1,310 ppm Mg (i.e. Garrell & Mackenzie, 1971 - Table 4.2). If these waters were trapped in uncompacted highly porous freshly deposited sediments, they would account for less than 0·1% of the diagenetic-Mg (i.e. $<$ 5 mol% Mg in 2% diagenetic carbonate) in the succession; and less than 0·05% of the diagenetic-Ca of the non-marine ironstones. They alone cannot, however, account for the $\sim$ 1% diagenetic-Ca of the marine calcareous concretions and clay ironstones; the essential Ca^{2+} concentrations of the pore fluids concerned would have to be $\sim 10^8$ times that of normal sea-waters.

That amount of Ca^{2+} suggests additional Ca^{2+} derivation. One possibility is derivation by diffusional contact with sea-water. This seems unlikely because of the relatively low pyrite observed, whereas reducible SO_4^{2-} would be expected to accompany Ca^{2+} diffusion from sea-water and preferential fixation of available Fe^{2+} with $S^{=}$ would form pyrite (cf. Berner, 1980; Hallam, 1980).

Diffusional derivation could, however, occur along chemical gradients that might have existed between the developing diagenetic carbonates and Ca-rich materials in sediments, locally or distantly located. But, apart from the fact that no sufficient Ca-rich sources can be established in the depositional area, the concretionary growth periods indicated using Berner's equation (Eqn.9, p.272) appear to be rather too long. In the case of the four major calcareous concretion horizons in the succession, the growth periods would add up to $\sim 10^6$ years (p. 277). However, the microcrystalline nature of the calcites, constituting the bulk of the concretions, suggests very rapid crystallization (cf. Pytkowicz, 1965). Berner's equation assumes a 10 ppm degree of super-saturation; this could, in fact, have been much lower than that actually present in the Upper Eocene sediments. Higher super-saturation levels have ensured shorter growth times.

One possible external source of super-saturated Ca^{2+} could be sub-surface Ca-rich waters from the Chalk; the Chalk exposure was extensive and predominates the moderate relief (400-700m) uplands areas of the region bordering the Hampshire Basin (i.e. Jones, 1981). The Chalk is porous, permeable to water seepage and cavernous with underground streams and aquifers. The waters would be rich in dissolved-$CaCO_3$, possibly containing up to $\sim$250 ppm $CaCO_3$ like waters on the Chalk in present day southern England (i.e. Sperlin et al., 1977). Plint (1983) has suggested the discharge of hard Chalk waters into the Hampshire Basin. The ponding of such waters had been responsible for the accumulation of marl lake-like limestones in the basin (Plint, 1983; this study - Ch.13). Sub-surface discharge of these hard waters would thus boost the Ca-saturation of the interstitial fluids and enhance the likelihood of precipitation of Ca-rich phases in the sediments. Subterranean drainage has been shown to be common in limestone terrains; for example the Yucatan Peninsula in Mexico studied by Hanshaw & Back (1980).

Further evidence for this mode of Ca-derivation should be sought in other diagenetic carbonates occurring in the Tertiary sediments of the Hampshire Basin.

c) CO_3^{2-}

Carbonate ions can be derived from a variety of sources. One such source would be microbial degradation of organic tissues associated with plants and animal remains which were buried with the sediments. The absence of fossil nuclei in the diagenetic carbonates suggests that the organic matter involved was in a finely disseminated form. This would be concentrated along particular stratigraphic horizons, and hence act as points of super-saturation of CO_3^{2-} (cf. Dickson & Barber, 1976).

In addition, considerable quantities of HCO_3^- ions could have been introduced along with the dissolved-Ca in influxed Chalk waters. Isotopic analysis would help to ascertain the origin of the carbonate ions (i.e. Irwin, 1980), but this was not performed during the course of the present study.

14.4.2 Facies and Sedimentological Factors

The Upper Eocene diagenetic carbonates formed at very shallow depths. This, with their compositional variations, suggests that local sedimentological factors and facies variations were probably important. These are considered below.

14.4.2A Phase Distribution and Composition

Calcareous concretions with ferroan calcites predominantly developed within glauconitic sediments of the Barton Clay. The ironstones developed throughout the succession, but are composed of siderites with ionic substitution varying from $\sim$ 15 mol% (Ca $\gg$ Mg $\gg$ Mn) in the marine and brackish sediments to $\leq$ 10 mol% (Ca $\geq$ Mg $\simeq$ Mn) in the freshwater sediments.

Factors that might help to explain these variations are:

i) the abundant supply of detrital iron oxide and dissolved Ca^{2+} ions;

ii) the effect of glauconitisation processes on pore fluid compositions;

iii) the facies-controlled initial pore fluid composition.

The iron- and Ca-influx would generate interstitial fluids rich in Fe^{2+} and saturated with Ca^{2+}. Ca influx would lower the Mg/Ca ratios of pore fluids in the Barton Clay below the 3 to 5 values expected for marine sediments at shallow depths (cf. Manheim et al., 1974). The consequence would be the generation of pore fluids with compositions essentially favourable to precipitation of siderites (i.e. with Fe/Ca > 20 - Berner, 1971) with low Mg^{2+} but high Ca^{2+} substitution.

Within glauconitic sediments, however, calcareous concretions rather than sideritic ironstones were much more common. This suggests that glauconitisation processes may have been modifying the pore fluids compositions in such a way as to favour calcite precipitation. The glauconies, whose formation is restricted to parts of the Barton Clay, have been described in Chapter 5. They are of the glauconitic-mica variety and had formed at sediment/water interface, most likely by the 'verdissement mode' of Odin & Matter (1981). This involves diffusion of necessary ions, including Fe^{3+} and Mg^{2+} into a substrate comprising foraminiferal tests. The ions would come from detritally-derived materials and/or sea-water. If colloidal iron-oxides were mobilised for glauconitisation, then less iron would subsequently be buried with the sediments. In turn, less iron would be available for subsequent diagenesis. This reduction in the amount of 'available' iron in the glauconitic sediments could lead to interstitial fluids with Fe/Ca < 20, and hence favourable to calcite precipitation.

The extent and nature of ionic substitutions found in the siderites and calcites are related to the relative abundances of subordinate cations in the pore fluids. Mg^{2+} is similar in ionic size and charge, and these are able to substitute easily for each other. Their carbonate phases, magnesite and siderite, form a solid solution series. Hence the extent of Mg^{2+} substitution for Fe^{2+} in siderite will depend directly on its concentrations in the pore fluids. Hence the low Mg substitution for Fe in the siderites in this study suggests a low $a_{Mg^{2+}}$ in the pore fluids. If, as suggested earlier, the diagenetic Mg has mainly been derived from depositional waters, contributions from Mg^{2+} would expectedly decrease from marine to fresh-waters. This is, in fact, observed with the Mg-substitution of the siderites decreasing from 3-5 mol% in the marine and brackish ironstones to < 2 mol% in the freshwater ironstones (see Fig.38b).

The 2-4 mol% Fe^{2+} and ~ 0·5 mol% Mg^{2+} substitutions in the ferroan calcites of the calcareous concretions are further reflection of the earlier discussed relatively very high $a_{Fe^{2+}}$: low $a_{Mg^{2+}}$ of the pore fluids; the iron and magnesium having to compete for limited, ~ 5%, substitution sites possible in the calcite lattice.

In contrast, the ionic radius of Ca^{2+} is greater than that of Fe^{2+}, and its incorporation in siderite is structurally limited to ~ 10% (i.e. Zaritskii, 1964). The extent of Ca^{2+} substitution in siderite would be expected to increase with Ca^{2+} concentration up to a certain value, beyond which the structure could accept no more. However, the Ca/Fe ratio at which this occurs is not known. Ca^{2+} substitution in the siderites under study is of three types: the ~ 1 mol%; the ~ 6 mol%; and ~ 9-10 mol% (see Fig.38a). Their variation, however, is apparently geographical rather than facies-related. The siderites present in the succession on mainland Hampshire contain substitution of 9-10% Ca, with the exception of the siderite constituting ironstone BBB-11 from the Barton Sand, which contains only ~ 2 mol% Ca. The siderites of the Isle of Wight show substitution of around 6 mol% Ca; with the exception of samples WBBB-2, with ~ 9 mol% Ca, and WBLH-10, with ~1 mol% Ca from Whitecliff Bay. This somewhat lateral variation is unlikely to be due to the nature of the water sources, since these would be expected to contain similar contents of dissolved Ca^{2+} ions. Although the situation is extremely complex, one possibility might be due to variations in iron abundance affecting the Ca/Fe ratio.

Relative geomorphological differences in the region resulting from tectonic-induced (?) eustatic fall and/or silting-up of the Barton Sea, have led to the development of acid goethitic and kaolinite-rich palaeosols on the Isle of Wight, as has been demonstrated at Heatherwood Point - Alum Bay. Detailed aspects of these are given in Chapters 7, 9 and 16. The consequence of these soils is that relatively more iron is present in the sediments deposited on the Isle of Wight compared with the mainland (Hampshire). Hence the pore fluids would be expected to have higher Fe/Ca ratios on the Isle of Wight than the mainland. They would result in the formation of low Ca-substituted siderites. One of the exceptions from the general trend, WBLH-10, is found within lignitic clays. It is probably of bog or marsh origin, and would be expected to be Ca-poor. The other, BBB-11, is associated with ferruginous sands, which may have increased the iron content.

14.4.2B Shallow Depths of Formation

The diagenetic carbonates under discussion are certainly early diagenetic phenomena; primarily formed within very shallow depths of uncompacted clastic sediments and, in one case, a freshwater limestone. Their shallow formation raises a number of questions as to how or why they formed, particularly in view of the fact that ferroan calcites reported in the literature are predominantly late, deep burial ($\geq$ 500m) diagenetic products (i.e. Lindholm, 1974; Curtis, 1980; Matsumoto & Iijima, 1981), and very rarely early diagenetic products (i.e. Cooley & Davies, 1969). Furthermore, early dominantly Ca-substituted siderites have only been reported from freshwater successions (i.e. Matsumoto, 1978; Matsumoto & Iijima, 1975, 1981). Although shallow marine siderites have been reported (i.e. Sellwood, 1971; Gautier, 1982), their compositions have not been given.

Two main reasons that might be accountable for the formation of early Ca-rich siderites and ferroan calcites in the presently studied Upper Eocene sediments are:

i) high influx of iron-oxide and dissolved Ca, and

ii) rapid depletion of SO_4^{2-} due to differential slow-fast sedimentation of successive lithologies in the Barton Clay Formation.

The iron and Ca^{2+} influx are perhaps the most important causes of the direction of diagenesis in the Upper Eocene succession, as has previously been discussed. Whilst iron influx is widely known to cause authigenic and diagenetic formation of iron-rich minerals (i.e. Shutov et al., 1970b; Pearson, 1979; Hsu & Kelts, 1982), the influence of Ca^{2+}-rich drainage discharge is less well established, and only appreciated by very few authors. Runnells (1969) highlighted the compositions of several possible drainage waters and interstitial fluids, along with their various interaction products. Possible products include iron- and calcium-carbonate precipitations from hard waters and iron-rich fluids.

Although several reported occurrences of diagenetic iron-bearing carbonates have been reported, the most significant feature differentiating this Hampshire Basin is probably the high Ca^{2+} influx from a hinterland of extensive Chalk and older calcareous rocks. In the case of the Japanese Palaeogene, where the diagenetic carbonate compositions and depths of formation are well documented (see Matsumoto & Iijima, op.cit.), the concretions are generally more magnesian. Further comparison, however, would require investigations of other diagenetic carbonates occurring within the English Palaeogene. This was beyond the scope of the present study.

The absence of reducible SO_4^{2-} is one essential pre-requisite for the establishment and sustenance of fermentation diagenesis in which siderite and ferroan calcites may form (i.e. Hallam, 1980; Curtis, 1980). The sulphate content of sediments is largely derived from depositional waters, either by incorporation or by diffusion. Average freshwaters contain ~ 11 ppm SO_4^{2-} compared with ~ 2,650 ppm SO_4^{2-} of normal sea-water. Depletion of SO_4^{2-}, as a result of sulphate reduction, would thus occur very close to the sediment surface in non-marine environments. Recent examples of such depletion within depths of 1m, and subsequent siderite formation, include the Atchafalaya Swamps in the Mississippi Delta, U.S.A. (Ho & Coleman, 1969); peat bogs in Denmark (Postma, 1977) and coastal marshes in Norfolk, eastern England (Pye, 1981). Similar conditions might apply to the non-marine ironstones in this study; in particular, those from the freshwater 'Lower Headon Beds' on the Isle of Wight. Their siderites, as expected, are low ($<$ 10 mol%) - substituted phases and were precipitated in abundance within the expected maximum porosity range of their clastic hosts. In fact, ironstone WBLH-10 from Whitecliff Bay, with its very lignitic and carbonaceous clay hosts (see Plates 24, 25), may be equivalent to siderites from recent marshes or bogs, although no vivianite or iron-monosulphides, which are described in some Recent examples by Postma (1977) and Pye (1981), were observed.

In marine sediments, depletion of incorporated SO_4^{2-} and the cessation of the diffusional contribution generally occur within burial depths of ~ 10m (i.e. Curtis, 1980). But sediments' compaction should be perceivable at depths of ~ 10m. No compactional features were observed in the diagenetic carbonates under study, not even on the delicate trace fossil impressions preserved in them (i.e. Plates 8,9). The depths at which they developed, therefore, were probably shallower than 10m.

Near surface depletion of SO_4^{2-} in the marine environments is only normally feasible in areas with rapid sediment accumulation, often in the order of 10's and 100's cm/1000 years (i.e. Lerman, 1979). Such conditions, with attendant early siderite formation, have been described from the Gammon Member of the Pierre Shale, U.S.A. by Gautier (1982). The overall sedimentation rate is, however, low in the Hampshire Basin. Odin et al. (1978) obtained a rate of 2·5 cm/1000 years for the Palaeogene succession under study. This slow sedimentation was one of the major factors previously considered as facilitating the widespread glauconitisation in the 'early' shelf Barton Sea (see Chapter 6). However, the overall sedimentation rate is an average value for the succession over a long, ~ 5 my, period of accumulation. Sedimentation, like many other geological processes, would most likely have proceeded at different rates for the different lithologies and units comprising the succession, and would be punctuated by periods of non-deposition. The rates for individual units cannot be determined because glaucony is the only authigenic constituent whose radiometric ages are employable. This is limited in occurrence to parts of the marine facies. Nevertheless, differential sedimentation rates would be expected for the different lithologies within the succession, and those would have profound consequences for the direction of diagenesis.

Some justification for the above suggestion comes from the fact that each of the marine diagenetic carbonate horizons occurs within a clayey host, and these are, in turn, immediately or at a few metres ($<$ 5m) higher up, succeeded by very sandy clays or sand sediments (see Chapter 2). It is probable that the accumulation of the sandy sediments not only occurred within much shallower water columns and stronger energy conditions (see Chapters 4 & 12), but also at much faster rates than the clayey sediments. This resulted in alternating slowly (sandy-clays) and rapidly (very sandy-clays and sands) sedimented units. There would be a high probability of clayey sediments being 'sealed' at very shallow depths, from diffusional contact with the sea-water. Cessation of diffusional replenishment would facilitate rapid exhaustion of trapped sea-water SO_4^{2-} by pyrite formation, and hence the establishment of fermentation conditions would occur at quite shallow depths.

A notable example of the establishment of early fermentation conditions, believed to be due to differential rates of deposition, has been described by Sellwood (1971) from the Lias in Yorkshire, England. This succession comprises alternating bioturbated mudstones and fossiliferous shales. The shales sealed off the mudstone units, which then became sideritised early so as to preserve their bioturbational features. Similar trace fossil preservation is found in the present study, notably in the ironstone BBB-23 from the base of the Barton Sand at Barton-on-Sea (Plates 8,9).

Another explanation of the early SO_4^{2-} depletion, although difficult to ascertain, concerns the earlier suggested possibility of sub-surface inflow of Ca-rich waters. These would have a non-marine, non-sulphate-rich origin. When discharged in considerable quantities, perhaps through the sandy horizons, such water would cause dilution and removal of SO_4^{2-} introduced from sea-waters. Once this lowered the sulphate below a critical $pS^2 < 10^{-10}$ (i.e. Curtis & Spear, 1968), fermentation conditions would ensue.

14.4.3 The Sideritised Limestone

Ironstone ABLH-5, from the 'Lower Headon Beds' at Heatherwood Point, is a sideritised limestone whose development was somewhat different from the other ironstones, all of which are within clastic sediments. This ironstone has developed by siderite replacement of primary lime-mud calcites which have previously been described in Chapter 13. The reactions involved may be represented as:

a) attack of microbially-produced carbonic acids on lime-mud:

$$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^-; \text{ and}$$

b) reaction of reduced iron with the bicarbonate ions:

$$Fe^{2+} + 2HCO_3^- \longrightarrow FeCO_3\downarrow + H_2CO_3$$

The essential Fe/Ca > 20 necessary for siderite precipitation might have been achieved by the mobilisation of iron incorporated within the sediments and/or loss of Ca^{2+} from the horizon, which still remained very porous (see Plate 83).

Sideritised limestones are not uncommon. Notable examples include Jurassic Dogger and Cornbrash Limestones and the Liassic 'Nerinaea Beds' in Yorkshire, England (Greensmith, 1971). These are also characterised by spherulitic siderites and fossil shells wholly or partially replaced by siderites.

14.5 Summary

Early diagenetic calcareous concretions composed of ferroan calcites and ironstones consisting of dominantly Ca-substituted siderites were formed within very shallow depths of the Upper Eocene sediments.

This unusual diagenesis was most likely brought about by a high influx of detrital iron-oxide and dissolved Ca from a hinterland with extensive Chalk exposure and undergoing goethitic weatherings. The influxed materials allowed the generation of pore fluids rich in iron and saturated with Ca^{2+}. The influence of Mg^{2+} was much reduced.

Some aspects of the diagenetic carbonates could not be resolved in the present study. These include the distribution of the substituted siderite phases, and the derivation of $CO_3^=$ and Ca^{2+} ions. These require further research into the carbon and oxygen isotopic compositions and electron microprobe microanalysis. Furthermore, detailed compositional investigation of other concretions in the Palaeogene of southern England is necessary towards establishing what diagenetic trends prevailed.

CHAPTER 15

TRACE ELEMENTS GEOCHEMISTRY

The concentrations of trace elements in the Upper Eocene sediments of the Hampshire Basin are contained in Tables 24a - g, whilst their stratigraphic variations are shown in Figures 44a - f. Detailed consideration of each of the elements is as follows:

15.1 Abundance and Distribution

15.1.1 Vanadium, V

Reported Abundances

Shales (Nicholls & Loring, 1962)	162 ppm
Nearshore Shales (Tourtelet, 1964)	158 ppm
Offshore Shales (" ")	243 ppm
Sandstones (Rösler & Lange, 1972)	20 ppm
Carbonates (Goldschmidt, 1954)	10 ppm
Calcareous Concretions (Gad *et al*., 1969)	28 ppm
Sideritic Concretions (" ")	59 ppm

Abundances in the Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	55 - 182	105
" " Barton Clay & Barton Sand Fms.	64 - 172	119
Lignitic & Carbonaceous Clays	78 - 309	130
Sands, 'Lower Headon Beds'	trace - 84	37
" Barton Sand Fm.	trace - 184	33
Red-Yellow Podzol Palaeosols	11 - 200	65
Freshwater Limestones	trace - 28	7
Calcareous Concretions	24 - 71	40
Sideritic Ironstones	24 - 112	59

Vanadium occurs in nature as compounds of its V^{2+}, V^{3+}, V^{4+} and V^{5+} ions. During weathering vanadium may be taken into solution to migrate as $(VO_4)^{3-}$ (Fersman, 1939) and deposited later with clays. Vanadium could also be biogeochemically concentrated in organic matter (Keith & Degens, 1959) and be precipitated with sulphides and sulpho-salts (Day, 1963). Organically-concentrated vanadium may, in addition, be made available for incorporation into clay mineral lattices.

Table 25a: Trace Element Composition of the 'Lower Headon Beds', Mainland Hampshire.

	TRACE ELEMENT COMPOSITION (ppm)																			
BLH	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
1	52	83	77	18	-	26	16	-	40	15	6130	62	39	927	14	-	640	34	-	79	25
2	98	99	219	52	-	28	27	43	72	33	6713	125	126	440	18	-	693	46	5	69	15
3	142	101	223	80	6	15	28	48	77	28	5631	94	112	287	16	5	681	40	23	88	53
4	62	75	363	37	5	10	15	54	47	31	5668	65	167	367	14	-	850	43	27	101	40
5	72	65	1778	32	-	7	20	-	45	17	4258	67	105	282	10	-	476	27	-	47	41
6	29	73	88	7	-	8	13	-	27	14	4353	15	20	828	10	-	213	29	-	48	14
7	109	100	496	59	5	14	31	8	98	32	4233	100	377	232	22	-	571	46	10	64	42
8	83	102	50	25	-	11	25	44	36	12	6811	142	95	515	20	-	842	36		91	57
9	30	50	16	3	-	-	11	10	23	14	3256	25	21	459	10	-	407	17	-	51	25
10	92	100	57	30	5	13	23	52	35	24	8104	127	72	334	23	-	838	37	-	84	52
11	55	105	268	125	-	12	7	8	157	18	2443	46	58	207	-	-	304	29	-	57	68
12	14	15	1161	13	-	-	5	11	19	-	1278	-	16	143	-	-	157	7	-	20	25
14	92	96	65	33	5	15	27	-	55	25	7306	96	86	322	22	-	602	46	5	53	56
15	78	131	38	62	13	26	35	-	165	40	4623	93	58	423	14	-	624	46	-	77	38
16	34	68	38	11	7	-	15	-	36	130	5463	126	64	358	19	-	751	36	-	79	10
18	97	101	100	48	-	15	22	6	75	30	3511	32	57	314	10	-	663	27	-	60	36
19	28	42	2853	17	6	-	28	-	119	8	817	28	511	75	7	-	183	49	113	44	57
20	108	128	204	60	-	17	50	-	197	65	5341	149	120	279	16	-	714	46	-	65	20
21	82	92	83	37	-	12	19	-	66	24	5489	121	60	377	17	-	739	36	9	75	23
22	44	49	761	18	-	10	13	-	30	10	3491	32	55	304	13	-	365	24	9	52	31
24	21	65	34	5	-	9	10	-	25	12	4864	21	24	549	11	-	558	24	17	58	14
25	119	112	568	73	9	13	26	17	81	29	5296	167	247	265	17	-	615	44	9	60	33
26	12	30	31	-	-	-	-	-	20	10	1313	8	18	149	-	-	236	5	-	17	14
27	116	104	369	48	8	10	25	9	86	26	4479	157	232	204	13	-	691	46	9	78	37
28	148	104	54	84	5	13	34	109	109	24	8539	163	100	239	21	9	1086	43	-	119	54
29	26	37	14	-	-	-	11	10	24	13	2527	21	17	127	-	-	286	10	-	42	33
30	28	47	20	-	-	-	9	9	22	16	3207	18	17	306	7	-	404	14	-	40	36
31	47	66	30	19	-	18	14	25	34	16	7213	45	35	520	16	-	660	41	-	85	23
32	138	115	99	53	-	20	36	8	108	33	7142	175	84	276	16	-	878	45	-	110	77
33	40	41	1740	23	-	4	9	-	25	10	2751	29	46	226	5	-	368	29	-	37	57
34	37	63	48	15	-	9	14	-	37	22	4232	42	34	336	12	-	441	20	6	49	50
35	26	68	80	9	-	8	12	-	27	12	3490	19	93	626	8	-	481	65	-	70	45
36	55	29	6652	49	-	-	11	-	8	-	1620	23	63	27	-	-	195	13	6	16	16
37	97	101	172	30	5	47	22	-	64	22	6606	130	85	393	14	-	861	40	-	89	62
39	112	105	80	48	6	16	29	11	70	25	6918	151	91	359	18	-	854	47	-	103	52

Table **25b** Trace Element Composition of the Barton Sand Formation, Barton-on-Sea

	TRACE ELEMENT COMPOSITION (ppm)																			
Samples	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
BBB																					
1	108	229	26	72	25	19	92	50	44	139	3510	111	74	220	-	5	431	19	-	320	231
2	80	94	290	32	12	35	23	14	38	12	7279	109	58	344	18	-	840	32	-	87	23
3	154	164	55	36	7	25	31	45	56	38	5441	147	85	293	7	-	638	17	-	88	50
4	22	37	23	-	9	27	7	-	26	14	1353	30	19	99	-	-	216	-	-	22	5
5	69	76	112	21	12	35	18	11	46	14	4044	117	40	252	7	-	565	17	-	63	24
6	22	33	23	-	6	12	13	-	27	9	1459	27	19	114	-	-	234	6	-	4	10
8	14	27	10	-	7	13	10	-	15	11	1016	27	34	97	-	-	212	5	-	21	11
9	33	54	30	5	7	15	13	-	21	12	2687	42	31	339	-	-	412	14	-	33	24
10	72	87	83	30	-	8	20	11	73	13	4866	93	45	478	14	-	544	31	-	74	42
12	108	102	157	43	-	11	26	16	76	17	5342	126	82	319	10	-	589	29	-	77	48
13	112	104	147	43	-	14	32	16	78	17	5617	128	80	317	16	-	724	38	-	92	40
14	38	38	36	11	10	4	11	-	37	11	1625	46	29	82	-	-	280	7	-	23	13
16	15	28	15	-	11	-	9	-	22	8	769	24	25	79	-	-	202	6	-	12	14
18	22	28	20	5	11	-	14	-	18	7	939	40	36	98	-	-	272	5	-	21	-
20	29	44	49	11	-	4	12	6	29	10	1499	39	35	208	-	-	294	9	-	40	-
22	68	84	140	24	-	8	19	11	54	13	3424	61	57	343	8	-	450	30	7	53	18
23	94	62	2718	45	-	6	11	-	29	-	3260	25	89	68	11	-	299	35	-	52	27

Table 25c: Trace Element Composition of the Barton Clay Formation, Mainland Hampshire.

	TRACE ELEMENT COMPOSITION (ppm)																				
Samples	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
BBB																					
24	158	130	557	61	-	13	28	10	89	22	5979	148	142	186	20	-	735	43	-	103	45
25	51	54	2155	33	11	5	12	-	37	6	1410	47	108	66	7	-	196	16	23	-	-
26	94	76	1100	53	-	7	16	6	51	7	4051	78	127	103	-	-	450	24	-	54	51
27	157	130	431	61	-	-	29	15	92	17	5994	165	192	219	16	-	764	40	-	98	64
30	145	124	294	65	-	-	28	19	39	17	5839	159	191	189	13	-	644	40	5	77	51
31	39	40	3367	25	-	-	9	-	24	-	842	33	94	54	-	8	138	14	10	-	-
32	141	115	209	57	-	-	25	20	72	13	5831	145	170	324	16	-	733	42	5	92	58
34	107	105	128	50	-	14	21	17	71	13	5674	176	114	495	16	-	596	37	-	84	44
35	127	112	154	51	-	12	26	15	72	13	5641	130	77	636	15	-	776	42	7	92	56
36	36	47	3511	23	-	5	7	-	27	-	886	57	85	179	-	-	143	12	13	-	31
37	118	107	130	48	-	11	22	17	76	15	7969	144	94	458	29	-	580	32	-	73	34
39	35	39	3766	26	-	-	5	-	26	-	1153	39	83	185	18	6	147	23	21	-	5
40	110	103	98	46	-	12	21	14	73	7	8639	146	87	469	11	-	536	45	-	90	57
41	114	101	194	43	-	10	23	17	61	15	6858	122	70	445	19	-	765	47	-	88	50
42	71	56	2384	39	-	5	12	8	39	9	2272	71	100	111	6	6	288	37	8	4	12
43	100	84	938	53	-	9	14	9	54	8	4275	98	65	140	7	-	475	36	-	49	47
44	172	132	194	61	-	15	27	19	89	13	4742	201	114	240	8	-	380	36	6	108	61
45	147	120	114	48	-	12	30	17	59	10	5899	193	97	289	15	-	797	50	4	93	59
46	169	158	116	39	-	9	23	21	69	7	5657	190	71	325	8	-	274	32	-	117	52
47	148	118	138	49	5	9	21	30	73	10	4425	185	62	272	18	-	572	38	5	79	41
48	145	128	114	33	-	10	25	19	73	10	5286	173	55	268	4	-	373	31	6	109	54
49	130	105	97	31	-	6	22	27	60	-	4087	173	43	290	-	-	268	20	-	82	41
50	112	86	707	56	-	9	15	20	86	6	4180	128	38	205	-	-	480	37	-	85	52
BHC																					
1	118	83	102	40	-	9	22	46	58	7	3038	192	31	263	8	-	406	33	-	107	65
2	100	141	91	22	-	7	21	19	50	-	3972	147	33	878	9	-	523	26	-	76	69
BPB																					
1	48	206	133	16	-	12	16	29	29	14	5790	41	22	2110	13	-	597	29	-	98	76

Table **25d** Trace Element Composition of the 'Lower Headon Beds', Alum Bay.

									TRACE ELEMENT COMPOSITION (ppm)											
Samples	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
ABLH																					
1	-	82	1151	-	-	-	-	12	25	-	11	-	314	-	-	-	22	7	181	-	-
2	7	12	270	31	16	-	5	28	34	22	130	-	418	-	-	5	43	4	73	-	-
3	-	8	426	-	-	-	-	13	19	-	22	-	377	-	-	6	25	6	86	-	-
4	43	120	272	17	4	8	13	11	36	10	2551	65	392	161	6	-	293	17	-	16	-
5	44	9	4613	43	-	-	5	15	-	-	1619	16	56	27	-	-	167	5	-	7	-
6	4	9	771	8	8	-	7	12	63	14	70	-	400	-	-	4	24	31	74	-	-
7	9	105	331	16	-	-	8	23	40	-	710	21	461	49	-	7	105	8	149	-	-
8	38	15	4701	46	-	-	7	6	-	-	1799	30	15	52	-	-	151	33	4	31	31
9	85	77	49	34	6	13	27	13	81	43	5513	109	54	512	12	-	662	34	-	79	32
10	66	128	46	14	5	14	21	-	124	20	6993	110	42	616	18	-	686	38	-	78	29
11	309	267	187	216	51	31	65	154	53	320	3964	103	56	308	5	9	598	123	7	302	244
12	40	30	24	-	-	-	14	-	34	11	1918	89	34	77	-	-	353	6	-	35	-
13	112	143	31	29	25	14	22	133	17	49	3191	68	32	195	-	-	307	45	4	193	185
14	4	30	15	-	-	-	7	-	7	18	668	14	16	39	-	-	123	5	-	7	-
16	182	105	73	40	-	11	22	6	75	8	6638	221	66	295	14	4	811	42	-	132	-

Table **25e** Trace Element Composition of the Barton Sand Formation and Paleosol, Alum Bay.

	TRACE ELEMENT COMPOSITION (ppm)																				
Samples	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
ABBB/FS																					
1a	38	36	33	13	-	7	16	-	21	6	3007	58	31	73	-	-	199	14	-	44	14
2a	82	85	31	20	-	6	14	6	28	13	5002	111	47	190	-	-	239	19	-	61	39
3a	200	80	42	29	6	-	28	92	89	-	624	-	-	30	-	10	71	19	-	22	-
4a	11	55	89	-	-	-	10	5	26	-	266	-	6	10	-	-	69	-	-	10	-
1b	73	83	28	16	-	7	16	-	34	7	3438	55	30	167	-	-	152	12	-	37	22
2b	68	72	30	11	-	7	14	6	11	6	4031	64	33	193	-	-	198	16	-	48	34
3b	43	53	60	14	5	8	14	-	20	6	2585	45	31	119	-	-	149	10	-	38	36
4b	32	38	44	23	5	-	15	6	28	-	1125	25	17	58	-	-	146	5	5	82	-
6b	93	59	44	24	-	-	16	32	34	36	1057	24	12	38	-	-	98	5	-	5	15
7b	47	50	41	20	-	-	10	12	31	31	845	19	9	39	-	-	116	-	-	11	160
8b	35	54	21	7	-	-	-	6	13	25	2350	24	18	-	-	-	94	12	-	15	23
ABBB																					
19	3	6	5	-	-	-	5	-	21	10	209	-	-	16	-	-	73	-	-	8	-
18	6	11	8	-	-	-	8	-	18	6	346	7	10	11	-	-	104	-	-	27	36
17	168	438	115	45	-	13	49	9	74	18	7020	197	106	234	16	-	367	44	-	149	101
16	12	14	12	-	-	-	6	-	21	11	804	18	19	72	-	-	169	6	-	25	6
15	29	63	31	5	-	5	8	-	21	11	3797	79	41	330	-	-	324	20	6	64	49

Table **25f** Trace Element Composition of the Barton Clay Formation, Alum Bay.

	TRACE ELEMENT COMPOSITION (ppm)																			
Samples	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
ABBB																					
14	126	103	114	44	-	11	26	18	130	12	5875	129	64	349	11	-	627	37	-	68	49
13	58	74	3186	47	-	-	9	6	5	-	2499	23	19	34	-	5	198	19	-	35	5
12	142	131	117	39	-	12	28	13	87	11	6915	171	70	336	14	-	328	29	10	96	63
11	149	112	206	54	-	11	25	19	105	13	6085	157	72	245	15	-	789	40	7	141	57
10	115	158	411	31	-	9	23	13	79	12	5045	126	193	286	13	6	578	33	10	57	25
9	64	81	123	14	-	6	14	12	43	-	5185	70	41	750	9	-	553	35	5	72	-
8	24	**50**	2092	15	-	-	11	-	6	-	898	24	66	174	-	9	53	11	30	-	19
7	90	149	112	32	-	11	15	15	52	9	4698	108	68	1042	5	-	231	31	-	113	39
6	147	131	90	34	5	15	26	12	62	15	7147	148	92	292	13	-	360	33	8	97	64
5	26	29	2473	5	-	5	6	-	26	-	860	36	65	131	-	5	158	10	55	34	-
4	41	40	1569	61	-	-	-	-	72	-	1304	48	70	90	-	-	73	34	13	15	47
3	91	81	61	12	5	9	19	16	51	11	6034	107	55	500	14	-	622	33	4	60	20
2	106	148	219	32	-	13	22	16	71	9	5588	127	153	333	12	4	723	32	4	75	55
1	105	88	131	28	-	10	20	18	74	-	4189	143	116	465	5	-	489	27	5	74	48
ABHC																					
1	80	109	81	18	-	10	17	15	72	7	4726	118	51	975	6	-	567	23	-	73	65
2	72	144	61	15	5	11	15	16	35	8	4927	75	32	798	-	-	524	33	-	92	23
ABPB																					
1	41	55	183	10	-	-	5	61	87	-	541	-	7	43	-	-	228	7	-	20	-

Table 25g: Trace Element Composition of the Upper Eocene Succession, Whitecliff Bay.

	TRACE ELEMENT COMPOSITION (ppm)																			
	V	Cr	Mn	Ni	U	Th	Pb	As	Zn	Cu	Ti	Rb	Sr	Zr	Nb	Mo	Ba	Y	I	Ce	La
WBLH																					
1	132	103	185	42	-	14	25	-	74	15	5716	162	114	228	12	-	635	24	-	80	48
2	126	95	354	45	6	13	25	8	100	28	5448	178	137	194	11	5	726	31	-	88	28
3	108	94	106	34	-	13	28	10	84	26	5660	112	43	365	10	6	655	36	4	78	48
4	84	73	44	15	-	11	21	9	45	15	6475	69	53	519	15	-	691	36	11	65	39
5	60	62	48	10	-	8	14	17	46	16	5334	57	41	508	12	-	570	32	-	64	33
6	28	22	8083	23	-	-	10	7	9	-	3083	20	19	195	-	-	293	12	-	17	33
7	148	177	85	38	-	20	52	11	83	73	6136	217	104	260	9	-	837	32	-	103	11
8	99	95	104	32	-	9	24	-	66	17	5158	140	65	432	-	-	642	28	-	59	10
9	86	80	42	38	17	7	28	121	49	92	3704	55	57	298	-	15	254	23	4	34	41
10	24	-	5494	47	-	-	5	-	84	-	803	-	8	-	-	-	84	13	7	23	-
11	96	157	106	40	-	14	24	6	100	19	7063	122	66	362	8	-	748	70	27	116	64
12	162	118	191	66	5	11	24	33	101	28	6149	212	98	183	10	6	735	80	-	147	103
13	133	162	205	35	-	11	17	12	77	5	5755	222	70	188	-	4	715	33	5	78	26
WBBB																					
9	184	126	43	7	-	8	8	78	40	-	1604	71	29	141	-	-	259	12	8	29	-
8	27	82	33	-	-	-	11	6	21	8	1516	62	64	117	-	-	290	8	4	33	-
7	32	38	36	-	-	5	11	5	31	12	1657	43	32	167	-	-	307	10	-	33	-
6	32	86	34	-	-	-	15	-	25	17	1828	52	32	196	-	-	337	9	6	31	-
5	36	45	45	-	-	5	14	-	33	10	2342	76	61	214	-	-	317	12	-	24	-
4	79	81	323	29	-	7	19	17	68	-	3689	98	49	338	-	-	472	22	4	53	5
3	72	128	978	11	5	7	20	10	81	-	4288	104	55	339	-	-	600	22	3	60	-
2	37	76	9774	68	-	4	7	5	37	-	2404	35	35	90	-	-	249	58	5	159	90
1	120	98	131	28	-	9	18	11	75	-	3869	145	190	210	9	-	613	26	4	80	20

Fig.44a :Stratigraphical Variation of the Trace Element Composition; Highcliffe-Milford-on-Sea, Mainland Hampshire (1).

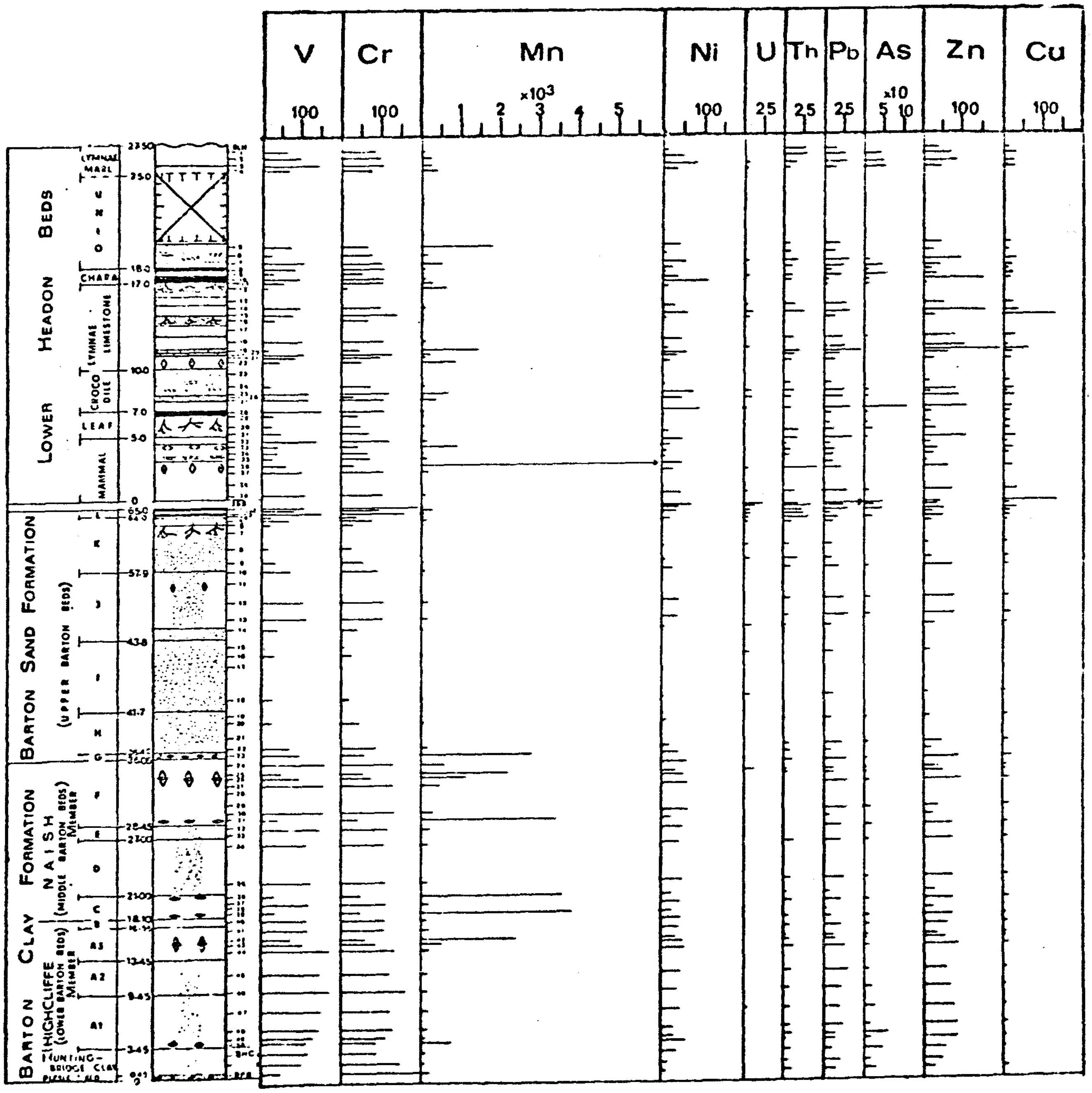


Fig.44a :Stratigraphical Variation of the Trace Element Composition; Highcliffe-Milford-on-Sea, Mainland Hampshire (2).

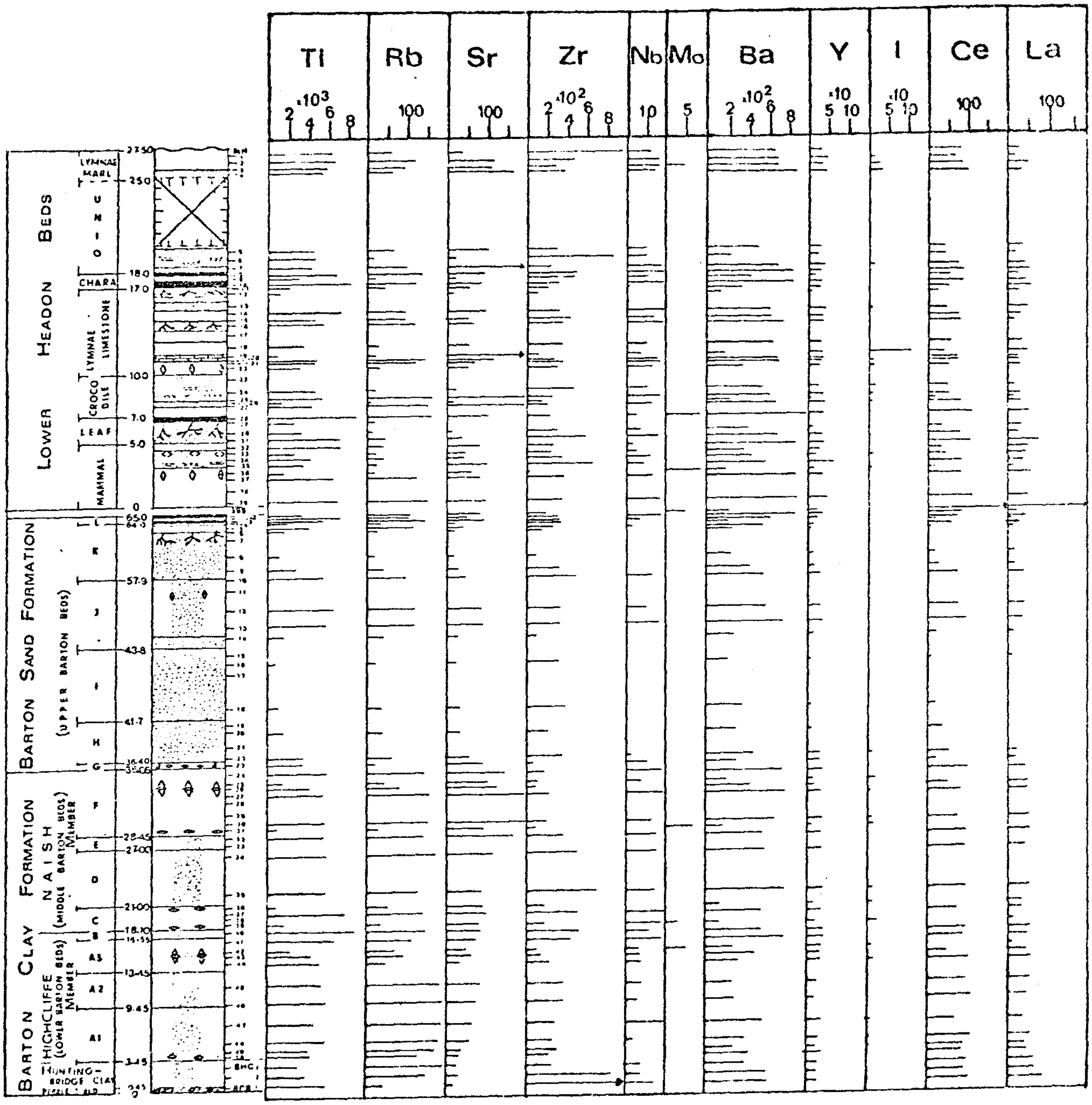


Fig.44b :Stratigraphical Variation of the Trace Element Composition; Alum Bay-Heatherwood Point,Isle of Wight (1).

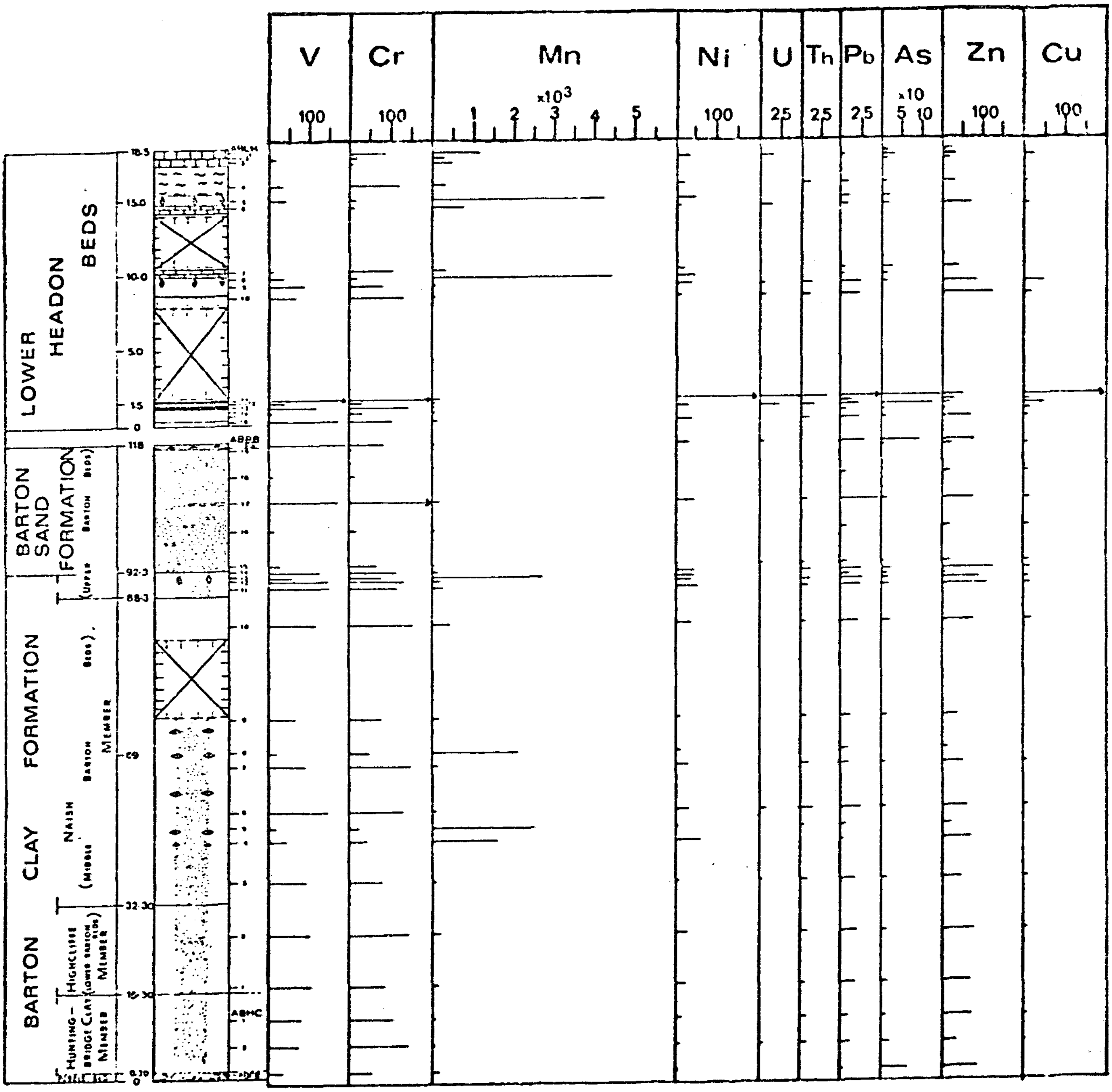


Fig.44b :Stratigraphical Variation of the Trace Element Composition; Alum Bay-Heatherwood Point,Isle of Wight (2)

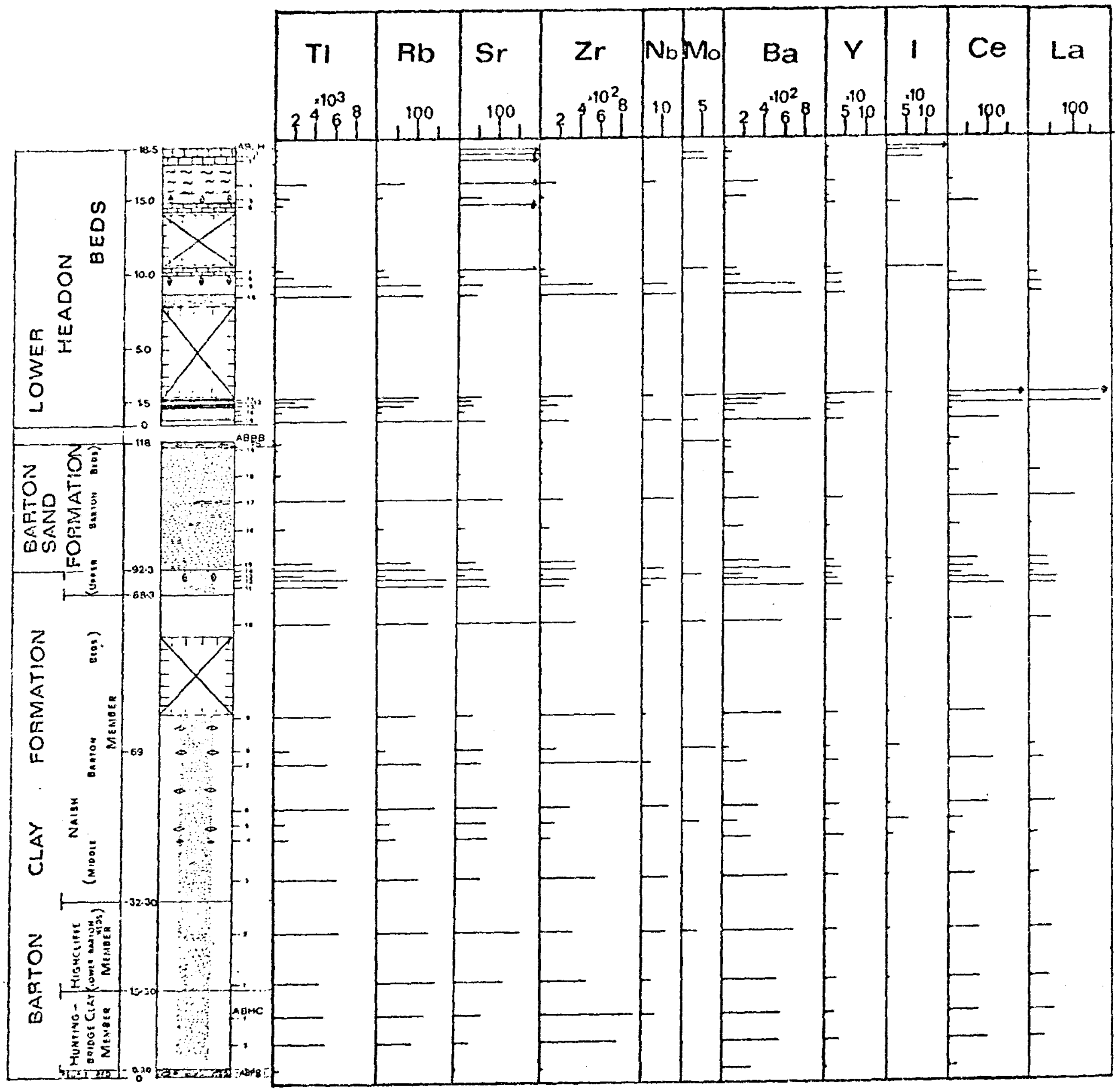


Fig.44c :Stratigraphical Variation of the Trace Element Composition; Whitecliff Bay,Isle of Wight (1).

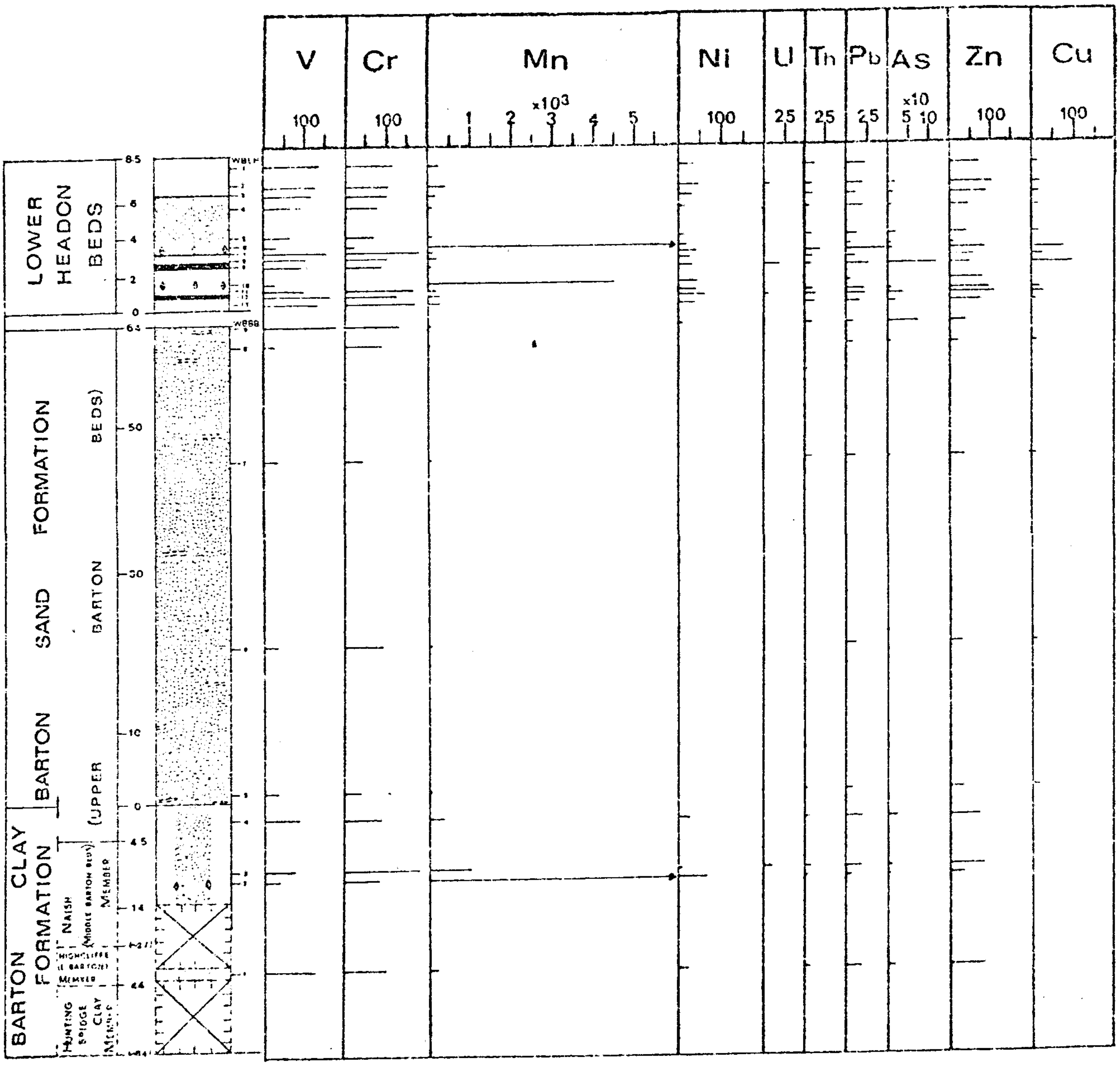
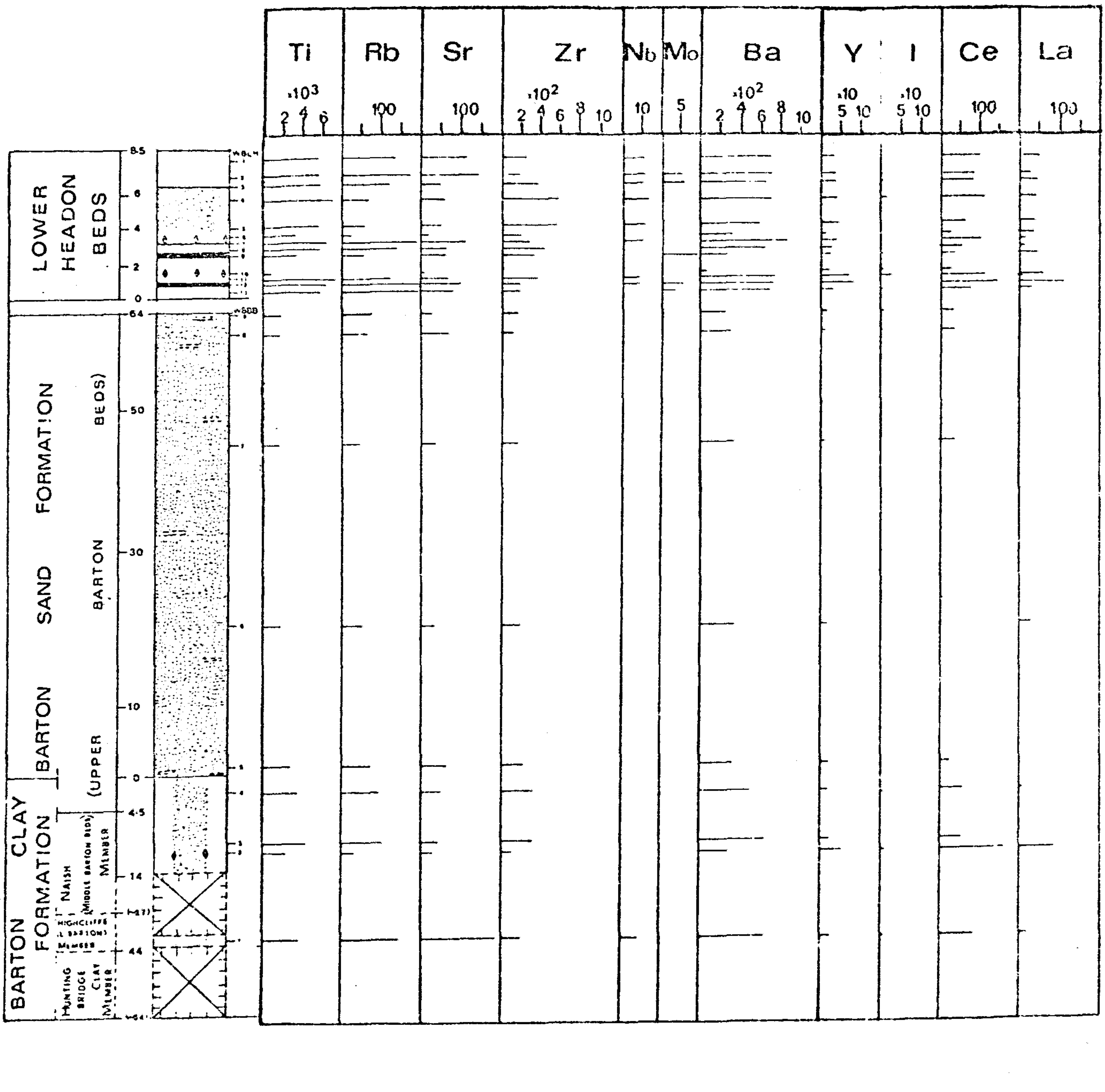


Fig.44c :Stratigraphical Variation of the Trace Element Composition; Whitecliff Bay,Isle of Wight (2).



In the Upper Eocene succession under study, vanadium occurs in concentrations varying from trace to about 300 ppm. The element correlates with clay minerals, pyrite and organic-C ($r \gtrsim 0{\cdot}6$); these would be the phases in which V occurs and/or is associated with. Concentrations in excess of 100 ppm mostly occur in the clayey sediments and the lignitic clays. It is only in the highly carbonaceous lignites, such as sample ABLH-11, that the highest vanadium concentrations (up to 309 ppm) were recorded. These provide indications of substantial contribution of V from organic (plant) matter.

The vanadium concentration in the sands and carbonate sediments is often $<$ 50 ppm. There is, however, a significantly high concentration of V (180-200 ppm) in the goethitic soil horizons ABBB-20 and WBBB-9 at the top of the Barton Sand at Alum Bay and Whitecliff Bay on the Isle of Wight. These high concentrations may signify the important role played by vegetal organic matter in the development of the palaeosols and their high goethite concentrations.

15.1.2 Chromium, Cr

Reported Abundances

Shales (Rösler & Range, 1972)	100 ppm
Sandstones (" ")	25 ppm
Carbonate Rocks (" ")	11 ppm
Calcareous Concretions (Gad et al., 1969)	19 ppm
Sideritic Concretions (" ")	45 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	75 - 162	106
" " Barton Clay Fm	76 - 432	122
Lignitic & Carbonaceous Clays	80 - 267	135
Sands, 'Lower Headon Beds'	30 - 128	61
" Barton Sand Fm	6 - 126	45
Red-Yellow Podzol Palaeosols	36 - 85	61
Freshwater Limestones	8 - 105	43
Calcareous Concretions	29 - 56	44
Sideritic Ironstones	trace - 86	76

Chromium possesses similar resistive and hydrolysing properties as Fe^{2+} and Al^{3+} because of their similar ionic sizes and charges. Generally, chromium is transported into depositional basins combined structurally in the lattices of degraded clay minerals (Hirst, 1962). In the various lithological units of the Upper Eocene succession under study, chromium correlates more strongly with kaolinite, anatase and, less significantly, with illite, mixed-layered clays, goethite and organic-C. It would have been derived with the clay minerals in addition to those associated with the organic materials and goethite. This would explain the abundance of Cr in the succession. The element occurs in insignificant ($<$ 10 ppm) quantities in the Barton Sand at Alum Bay; but occurs in higher amounts of up to 85 ppm in the more clayey and often ferruginous sands, particularly at Whitecliff Bay where the ferruginous loam sand, WBBB-9, contains 126 ppm Cr. The limited amounts of incorporated clastic (clays) materials in the carbonate sediments would account for the low (averaging ~ 40 ppm) chromium contents of the carbonates.

15.1.3 Manganese, Mn

Reported Abundances

Shales (Wedepohl, 1969)	850 ppm
Carboniferous Shales (Nicholls & Loring, 1962)	238 ppm
" " (Spear, 1964)	1,316 ppm
Sandstones, Russian Platform (Vinogradov & Ronov, 1964)	500 ppm
Sandstones (Clarke, 1924)	200 ppm
Carbonates (Rankama & Sahama, 1950)	2,600 ppm
Calcareous Concretions (Gad *et al.*, 1969)	594 ppm
Sideritic Ironstones (" ")	2,204 ppm
" " (Pearson *et al.*, 1975)	7,500 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	49 - 363	158
" " Barton Clay Fm.	61 - 978	201
Lignitic & Carbonaceous Clays	26 - 586	143
Sands, 'Lower Headon Beds'	14 - 88	40
" Barton Sand Fm.	5 - 49	27
Red-Yellow Podzol Palaeosols	21 - 89	42
Freshwater Limestones	270 -2853	967
Calcareous Concretions	1569 -3766	2665
Sideritic Ironstones	707 -9774	3882

Depending on the Eh and pH conditions, Mn often occurs as physico- and/or bio-chemically concentrated carbonates and/or oxides. Manganese as Mn^{2+} possesses chemical properties similar to Fe^{2+}, Ca^{2+} and Mg^{2+}; hence it does substitute for those cations, especially in their carbonate phases. Mn may also be transported as colloidal hydroxides in association with (or adsorbed on) iron-oxides, titania and other resistates or hydrolysates (Vinogradov, 1959, Katchenkov, 1967).

In the Upper Eocene succession, Mn correlates strongly with calcite, siderite and, to a lesser extent, aragonite. These, in the absence of manganese minerals, show that Mn occurs as a substituting cation in the diagenetic calcites, siderites and biogenous $CaCO_3$ forms. In fact, it only occurs in significant amounts of more than 100 ppm in the fossiliferous clastic sediments,and in substantially high amounts of 200-9774 ppm in the carbonate horizons. Mn concentrations of 200-500 ppm characterise the fossiliferous sediments such as those of the Naish Member of the Barton Clay at Barton and Alum Bay and, as well, some of the green and carbonaceous clays in the 'Lower Headon Beds'. The high, 978 ppm Mn recorded for the sandy-clay WBBB-3 at Whitecliff Bay is difficult to explain; although carbonaceous, the sediment lacks fossil shells, diagenetic carbonate minerals, nor does it contain detectable free iron-oxides which might have adsorbed it.

Mn occurs in very variable amounts in the limestones. The creamy 'Lymnae Limestone' on Hordle Cliff contains 2853 ppm Mn. This compares higher than the more variable 270 to 1151 ppm Mn concentrations in the How Ledge Limestone and other limestone horizons in the'Lower Headon Beds' at Heatherwood Point. In fact, low Mn concentrations actually characterise the lime-mud matrix and the fossil shell contents of the limestones. The lime-mud calcites are low magnesian, low ferroan and, in addition, only contain 0·1 mol% MnCO (Table 20, Fig. 36); whilst the Galba longiscata, the dominant shells in the limestone, are still wholly aragonitic and only contain about 160 ppm Mn.

The concentrations of Mn in the calcareous concretions are less variable, averaging 2665 ppm. The concretions at Barton possess the higher (2155-3766 ppm) Mn when compared with those at Alum Bay (with 1569-2493 ppm Mn). This reflects differential pore fluid compositions; those at Barton being relatively more enriched in manganese. The manganese contents of the calcareous concretions are mostly with the calcites. The analysis of the calcites of sample BBB-36 showed that only about 1 mol% $MnCO_3$ is in the low magnesian but ferroan microcrystalline calcite matrix; and about 0·5 mol% $MnCO_3$ is in the similarly low ferroan and low magnesian septarian calcites. There has been an apparent depletion of Mn in the pore fluids for the septarian calcite precipitation in the late growth phase of the concretions.

Mn occurs in very high concentrations of 707 to 9774 ppm in the sideritic ironstones. In general, the Mn concentrations are higher in the ironstones within the non-marine 'Lower Headon Beds'. But in order to determine what relationship exists between the Mn concentrations, ferrous iron contents and the extent of Mn substitution for the sideritic phases, the plots of Mn (ppm) vs % FeO (Fig. 45) and Mn (ppm vs mol% $MnCO_3$ (Fig. 46) were made. There are two trends of variation of Mn to ferrous iron. Firstly (Slope A, Fig. 45) the Mn increases with iron from the ironstones at Barton into those on the Isle of Wight. The second (Slope B, Fig. 45) concerns ironstones with high iron and Mn contents. In these, the Mn decreases from $>$ 8000 ppm in WBBB-2 and WBLH-6 with lesser iron contents ($\sim$ 25% FeO) to between 3000 and 6000 ppm in the more highly sideritic ($>$ 40% FeO) ironstones at Alum Bay and Whitecliff Bay. Figure 46 shows that, apart from WBBB-2 and WBLH-6 with high Mn concentrations and correspondingly high ($\sim$ 4 mol% $MnCO_3$) manganese substitutions, the mol% $MnCO_3$ of the siderite phases increases only very slightly with substantial increases (1000 → 7000) in the Mn contents of the bulk ironstone samples. The plot of Mn ppm vs mol% $MnCO_3$ (Fig. 46) further shows that the Mn contents of the ironstones and siderite phases are relatively higher in the non-marine 'Lower Headon Beds'. These ironstones, as discussed in Chapter 14, would have formed at very shallow burial depths, or even possibly in near-surface conditions within sediments accumulated in brackish and freshwater bodies. The manganese might have been derived with iron from non-marine depositional waters incorporated as pore fluids.

Finally, mention should be made of the 183 ppm and 89 ppm Mn respectively recorded in the goethite indurated horizons (vesons) of the red-yellow podzol palaeosol at Alum Bay. These are minor enrichments when compared to the average 33 ppm Mn contents of sandy sediments. In the absence of manganese minerals, the manganese would possibly be

Fig.45: Plot of Mn(ppm) vs. %FeO For Sideritic Ironstones.

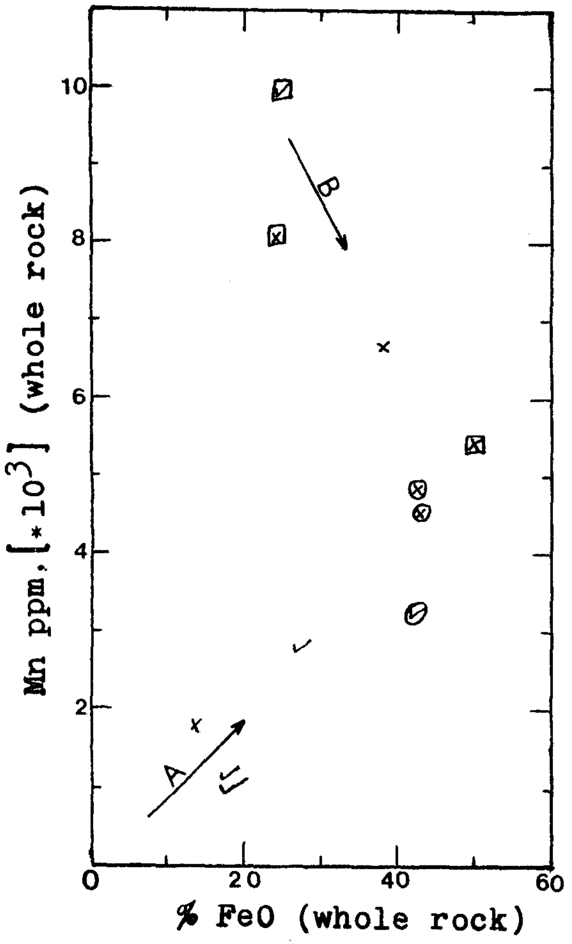
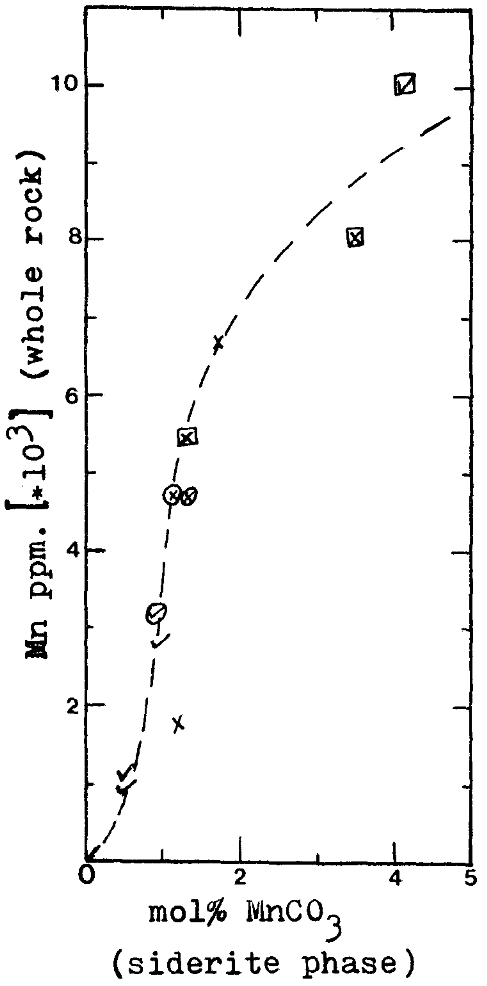
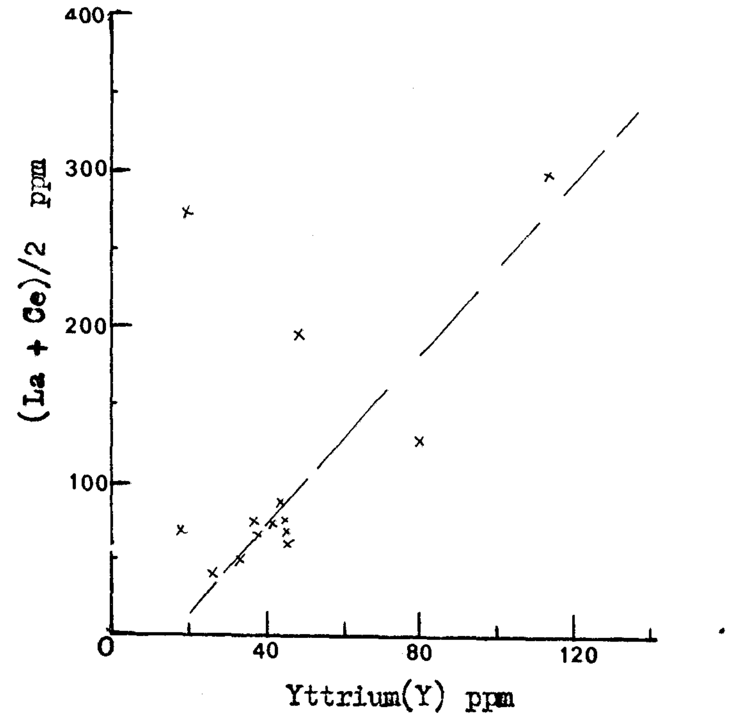


Fig.46: Plot of Mn(ppm) vs. mol% MnCO3 For Sideritic Ironstones



(see Fig.37. for key to symbols)

Fig.47: Plot of (La+Ce)/2 vs. Y Contents of Lignitic Clays



substituting for iron in the goethites that occur in high concentrations (10-44%) in the soils. Those amounts of Mn are, however, of little significance and the development of the soils did not involve high manganese mobilisation and accumulation.

15.1.4 Nickel, Ni

Reported Abundances

Shales (Wedepohl, 1969)	68 ppm
Nearshore Clays (Young, 1954)	47 ppm
Sandstone (Kranskpoff, 1958)	2-10 ppm
Carbonates (" ")	3-10 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	30 - 125	46
" " Barton Clay Fm.	11 - 125	40
Lignitic & Carbonaceous Clays	25 - 216	62
Sands, 'Lower Headon Beds'	trace - 19	7
" Barton Sand Fm.	trace - 11	3
Red-Yellow Podzol Palaeosols	trace - 29	16
Freshwater Limestones	trace - 31	12
Calcareous Concretions	5 - 61	28
Sideritic Ironstones	18 - 68	44

Nickel, during weathering, could be taken into solution and transported as bicarbonate or as a stable hydrolysate (Manskaya & Drozdova, 1968). During deposition, it can be adsorbed onto clay minerals, organic matter and/or incorporated into Fe^{2+} and sulphide phases (Keith & Degens, 1959, Luther _et al._,1980). It can also substitute for Mg^{2+} and Fe^{2+} in clays (Hirst, 1962).

In the succession under study, nickel occurs in small concentrations of trace to 30 ppm in the sands, limestones, calcareous concretions and podzols. It occurs, however, in higher amounts of 40-70 ppm in the clayey sediments. Substantially higher amounts of up to 216 ppm even occur in some very lignitic ($>$ 10% organic-C) clays. This distribution of Ni accounts for its strong correlation with, and suggests its occurrence in association with, the clay minerals, pyrite and organic-C.

15.1.5 Uranium, U

Abundance

Shales (Wedepohl, 1969)	3·7 ppm
" (Adams & Weaver, 1958)	3·2 ppm

Carboniferous Shales (Spears, 1964)	9·6 ppm
Sandstones (Rösler & Lange, 1972)	0·5 ppm
Carbonate Rocks (" " ")	2·2 ppm

Lignitic Clays	Upper Eocene Hampshire Basin	trace - 51 (av. = ~ 5)
Sands, Clays, Carbonates		trace - 12 (av. = ~ 2)

The uranium contents of sediments are usually very small and often $<$ 10 ppm. Uranium largely behaves as a resistate because it is often released, during weathering, in its sparingly-soluble hydrated U^{+4} oxide. Some uranium may also be taken into solution as basic salts of U^{+3} and U^{+6}, and which may be adsorbed onto Al, Fe and Mn hydrolysates (Rankama & Sahama, 1950), or onto organic matter (Manskaya & Drozdova, 1968). It is also possible that, during the reduction of U^{+6} to U^{+4}, within sediments, U may be precipitated from entrapped sea-water as carbonate, arsenate and phosphate (Vinogradov, 1959). Numerous uranium occurrences have also been related to its biogeochemical concentrations in plants and sulphides (i.e. Bloxam & Thomas, 1969).

In the Upper Eocene sediments, uranium was detected only in a few horizons. The horizons include parts of the Barton Sand at Barton (i.e. 'Beds I & K'), and also the lignitic and carbonaceous clays. The element occurs in amounts generally $<$ 25 ppm; the highest, 51 ppm U, being in the lignitic ABLH-11 at Heatherwood Point.

The element correlated weakly with quartz and organic-C. It has probably been concentrated with resistive coarse-grained materials in the sands, whilst its abundance in the lignitic sediments would certainly be due to its association with organic (plant) materials and sulphide (pyrite) phases.

15.1.6 Thorium, Th

Abundances

Shales (Wedepohl, 1969)	12 ppm
" (Adams & Weaver, 1958)	13 ppm
Sandstones (Rösler & Lange, 1972)	2 ppm
Carbonates (" " ")	2 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments	trace - 47	12
Lignitic & Carbonaceous Clays	7 - 31	16
Sands & Podzol Palaeosols	trace - 27	6
Freshwater Limestones	trace	-
Calcareous Concretions	trace - 5	3
Sideritic Ironstones	trace - 10	4

Thorium in sediments is mostly contained in monazite and other Th-bearing minerals which generally occur as heavy, coarse-grained, hydrodynamic mineral equivalents of resistates such as quartz and the feldspars. Thorium may also occur as a hydrolysate adsorbed onto clays and anatase. The ions of Th possess ionic radii close to those of Ca^{2+}, Ba^{2+}, Sr^{2+} and K^{+}; and they may substitute for those ions in their compounds such as the feldspars and clay minerals. Thorium is also an important growth stimulant in plants (Rankama & Sahama, 1950), and would be released and concentrated in soils and sediments upon the death and decay of plant materials.

The association of Th with clays and organic (plant) material would account for the occurrence of thorium in the sediments under study. The element occurs mainly in the clayey and lignitic sediments in amounts varying from trace to 47 ppm, and averaging <20 ppm. It is most abundant in the non-marine sections at Barton and Long Mead End, where carbonised plant materials and rootlets are common.

15.1.7 Lead, Pb

Abundances

Shales (Wedepohl, 1956)	20 ppm
Carboniferous Shales (Nicholls & Loring, 1962)	6 ppm
Limestones (Wedepohl, 1956)	9 ppm
Sandstones (Rösler & Lange, 1972)	7 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	7 - 36	23
" " Barton Clay Fm.	14 - 49	24
Lignites & Carbonaceous Clay	22 - 92	37

Sands, 'Lower Headon Beds'	trace - 21	13
" Barton Sand Fm.	5 - 15	25
Red-Yellow Podzol Palaeosols	trace - 28	14
Freshwater Limestones	trace - 28	8
Calcareous Concretions	trace - 12	8
Sideritic Ironstones	5 - 16	10

The mobilisation of Pb during weathering is limited because of the low solubility of its hydroxide and oxy-salts. It does, however, get taken into solution and transported as bicarbonate, while the similarity of Pb^{2+} to K^{+} in ionic sizes facilitates its occurrence in clay mineral lattices (Wedepohl, 1956; Gad et al., 1969).

In the Upper Eocene succession of the Hampshire Basin, Pb only occurs in substantial amounts of up to 90 ppm in the clayey and lignitic sediments, and only correlates significantly with the kaolinite and illitic phases (r = 0·7). The abundance of Pb in sands and carbonate sediments with low clay contents is generally low, averaging $<$ 10 ppm.

15.1.8 Arsenic, As

Abundances

Shales (Onishi, 1967)	13 ppm
Sandstones (Rösler & Lange, 1972)	trace
Carbonates (" " ")	trace

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	trace - 54	11
" " Barton Clay	9 - 46	17
Lignites & Carbonaceous Clays	trace - 154	52
Sands, 'Lower Headon Beds'	trace - 25	5
" Barton Sand Fm.	trace - 78	6
Freshwater Limestones	trace - 28	15
Calcareous Concretions	trace - 8	trace
Sideritic Ironstones	trace - 20	6
Red-Yellow Podzol Palaeosols	trace - 92	15

Arsenic is one of the rare constituents of the earth's crust. Arsenic released during weathering often precipitates and migrates with the hydrolysates and oxidates such as anatase and ferric iron hydroxides

(Rankama & Sahama, 1950). Arsenic may also be adsorbed on clay minerals or occur in them as lattice substitute for Al^{3+}, Si^{4+}, Fe^{3+} and Mg^{2+} (Escon et al., 1955; Onishi & Sandell, 1955). Under reducing conditions, As from decomposed organic (plant) matter could also become concentrated in sulphide phases.

In the succession studied, arsenic was undetected in most of the sand and carbonate sediments; but where detected, it is in concentrations of $<$ 20 ppm. In the clayey sediments, As occurs more consistently, but also often in amounts of $<$ 20 ppm. The element is particularly common in the glauconitic sandy clays, and is most abundant in the lignitic and carbonaceous clays, such as BLH-28, ABLH-11 and 13 and WBLH-9, with 100-154 ppm As concentrations. High arsenic concentrations (up to 89 ppm) also occur in the goethitic palaeosols at Alum Bay, and the ferruginous loamy top of the Barton Sand at Whitecliff Bay.

The above enumerated abundances of arsenic suggest that the element occurs in association with clay minerals, organic matter and free iron oxide (goethite) phases.

15.1.9 Zinc, Zn

Abundances

Shales (Wedepohl, 1969)	95 ppm
Sandstones (Rösler & Lange, 1972)	16 ppm
Limestones (" " ")	20 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	47 - 157	80
" " Barton Clay Fm.	38 - 130	70
Lignites & Carbonaceous Clays	17 - 197	80
Sands, 'Lower Headon Beds'	7 - 124	36
" Barton Sand Fm.	15 - 40	25
Red-Yellow Podzol Palaeosols	11 - 89	31
Freshwater Limestones	19 - 119	50
Calcareous Concretions	6 - 72	32
Sideritic Ironstones	5 - 86	32

The behaviour and migration of zinc is very similar to that of Ni^{2+}. Zn^{2+} could be adsorbed onto detrital clay minerals and/or substitute for Fe^{2+} and, to a lesser extent, Mg^{2+} in smectites and chlorites (White, 1957). Zinc is also an important physiological component of tissues of living animals. Upon the death and decomposition of organisms, Zn^{2+} could become concentrated as Zn-organic acid complexes and be incorporated into sulphide phases (Manskaya & Drozdova, 1969).

Zn, in the Upper Eocene succession, occurs in amounts varying from trace to about 200 ppm. It occurs in depleted amounts of < 30 ppm in the sands and carbonates; whereas its concentrations in the clayey sediments are much higher, averaging about 80 ppm. The element would, largely, be associated with the clay mineral phases. Zinc is significantly most abundant (> 100 ppm) in the lignitic and limestone horizons in the 'Lymnae Limestone Bed' on Hordle Cliff at Long Mead End. In these, the element could have concentrated with organic remains, and is possibly incorporated into the lime-mud calcites.

15.1.10 Copper, Cu

Abundances

Shales (Wedepohl, 1969)	45 ppm
" (Nicholls & Loring, 1962)	33 ppm
Sandstones (Rösler & Lange, 1972)	10 - 40 ppm
Carbonates (" " ")	4 ppm
Calcareous Concretions (Gad *et al.*, 1969)	3 ppm
Sideritic Ironstones (" " ")	11 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	5 - 43	24
" " Barton Clay Fm.	trace - 22	8
Lignitic and Carbonaceous Clays	12 - 320	63
Sands, 'Lower Headon Beds'	10 - 130	22
" Barton Sand Fm.	trace - 17	10
Podzol Palaeosol	11 - 36	12
Freshwater Limestones	trace - 22	7
Calcareous Concretions	trace - 9	2
Sideritic Ironstones	trace - 10	3

Cu is a very mobile element and could be migrated in solution as cupric sulphate (Rankama & Sahama, 1950; Strakov, 1967; Perel'man, 1967).

The element is also a common physiological component of organisms and plants; and its distribution and amounts in soils and sediments are often influenced by organic matter and associated sulphide phases (Arrhenius, 1959).

Cu occurs in very small amounts (< 10 ppm) in the carbonate sediments and < 40 ppm in most of the clastic sediments. In the very lignitic clays BBB-1, ABLH-11 and WBLH-9, Cu occurs in high amounts of up to 312 ppm. These contain high (> 10%) organic-C and pyritous materials into which the element would most likely be associated.

15.1.11 Titanium, Ti

Titanium has been discussed as titania in Chapter 12. The element is more abundant in the clayey sediments, where it averages over 5000 ppm compared to the average 2770 ppm Ti in the sands. It is mostly associated with the clay phases, possibly as finely disseminated or adsorbed material. Anatase was detected by XRD in many clayey sediments, while rutile grains were also commonly observed in the grain mounts of the sand sediments. Titanium abundance is very variable in the carbonate sediments, generally in sympathy with the amounts of clastic materials incorporated.

15.1.12 Rubidium, Rb

Abundances:

Shales	(Turekian & Wedepohl, 1961)	140 ppm
"	(Nicholls & Loring, 1962)	143 ppm
"	(Heir & Billings, 1970)	164 ppm
Carbonates	(Turekian & Wedepohl, 1961)	10 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	32 - 222	131
" " Barton Clay Fm.	61 - 201	140
Lignitic & Carbonaceous Clays	55 - 217	132
Sands, 'Lower Headon Beds'	8 - 126	47
" Barton Sand Fm.	trace - 79	40
Red-Yellow Podzol Palaeosols	trace - 111	39
Freshwater Limestones	trace - 28	8
Calcareous Concretions	24 - 71	44
Sideritic Ironstones	trace - 128	41

Rb, a very mobile element, is often adsorbed on clays and/or, because of the closeness of Rb^+ ionic radium to that of K^+, substitutes for potassium in illitic clay phases, micas and feldspars. These modes of occurrence of Rb are found in the succession under study. The greater concentrations ($>$ 100 ppm) of Rb occur in the clayey sediments. It is particularly high in abundance in the glauconitic sediments of the Barton Clay at Barton and some carbonaceous horizons in the 'Lower Headon Beds'. The Rb abundance is low ($<$ 40 ppm) in the carbonate sediments and most of the sands at Barton and Alum Bay. A relatively substantial amount of 40 - 76 ppm Rb in the sands at Whitecliff Bay would be due to their relatively higher feldspars and clay contents.

15.1.13 Strontium, Sr

Abundances

Shales (Wedepohl, 1969)	300 ppm
Carboniferous Shales (Nicholls & Loring, 1962)	74 ppm
" " (Curtis, 1969)	123 ppm
Limestones (Turekian & Kulp, 1956)	610 ppm
Calcareous Concretions (Gad *et al.*, 1969)	500 ppm
Sideritic Ironstones (" ")	250 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	54 - 167	87
" " Barton Clay Fm.	31 - 193	90
Lignitic & Carbonaceous Clays	32 - 247	99
Sands, 'Lower Headon Beds'	16 - 93	36
" Barton Sand Fm.	trace - 64	30
Red-Yellow Podzol Palaeosols	trace - 47	21
Freshwater Limestones	314 - 511	414
Calcareous Concretions	65 - 108	84
Sideritic Ironstones	8 - 127	49

In sediments, Sr could occur as adsorbed cations on clay minerals and as a lattice substitute for K^+ in illites, micas and feldspars (Perel'man, 1967). The element could also be biochemically partitioned into $CaCO_3$ (aragonitic) skeletons or physico-chemically precipitated with carbonates (Kinsman, 1969).

The abundance of Sr in the Upper Eocene succession is most significant in the fossiliferous clastic sediments with > 100 ppm Sr, and the freshwater limestones which contain 300-500 ppm Sr. In these sediments, the biogenous aragonite would account for most of the Sr contents; whilst some Sr may be associated with clay phases especially the illite and glauconitic-mica. The clay minerals and feldspars would most likely be the main phases containing the < 50 ppm Sr in the non-fossiliferous sediments in the succession.

The Sr contents of the fossil shells from the succession at Barton and Heatherwood Point are given in Table 14 and discussed in Chapter 11. Conforming with the established differential partitioning of Sr into $CaCO_3$ polymorphs (Kinsman & Holland, 1969), the obtained Sr concentrations were higher for the aragonitic shells. The Sr abundance, however, varies widely from ~ 2500 ppm in shells from the Naish Member of the Barton Clay ('Middle Barton') to ≲ 1000 ppm in shells from lower and upper parts of the Barton Sand and the 'Lower Headon Beds'. A significantly very low (500 ppm) Sr concentration was obtained for the Galba longiscata shells that predominate in the freshwater How Ledge Limestone at Heatherwood Point. The variations probably reflect increasing shallowness and equilibration to warm atmospheric temperatures of depositional water bodies up the Upper Eocene succession. It is also probable that animals possessing the lower Sr contents were physiologically more advanced. It has been realised that with increased physiological advancement, invertebrates generally become more efficient in excluding extraneous materials from their skeleton (i.e. Lippman, 1973). Deduction of a warmer late Upper Eocene would also agree with the palaeoclimatic inferences made by Hubbard & Boulter (1983) from palynological studies.

15.1.14 Zirconium, Zr

Abundances

Shales (Wedepohl, 1969)	160 ppm
" (Rankama & Sahama, 1950)	140 ppm
Limestone (Turekian & Wedepohl, 1961)	19 ppm
Calcareous Concretions (Gad et al., 1969)	30 ppm
Sideritic Concretions (" " ")	< 3

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	188 - 512	329
" " Barton Clay Fm.	186 -1042	450

Lignitic & Carbonaceous Clays	183 - 515	292
Sands, 'Lower Headon Beds'	39 - 927	441
" Barton Sand Fm.	11 - 339	140
Pebble Bed, Highcliffe	2110	
Red-Yellow Podzol Palaeosols	trace - 193	83
Freshwater Limestones	trace - 75	21
Calcareous Concretions	54 - 185	124
Sideritic Ironstones	trace - 304	113

The compounds of zirconium are mostly insoluble with the most common form being zircon, $ZrSiO_4$. Zircon often occurs as silt to sand-sized, resistate heavy mineral grains. It is the dominant phase in which Zr occurs in the Upper Eocene sediments under study; it was commonly observed present in the heavy mineral assemblages studied by Walder (1964) and Blondeau & Pomerol (1968). It is prominently seen in the grain mounts of the sand sediments (Plates 26, 27).

Enrichment of Zr in beach and related transgressive phase sandy sediments is indicated by the 2110 ppm Zr recorded by the sand matrix of the pebble bed at Highcliffe, and about 1000 ppm Zr in the immediately underlying Boscombe Sand and overlying glauconitic sandy clay - Huntingbridge Clay (BHB-2). The Zr content of the pebble bed at Alum Bay is very low (about 43 ppm), significantly indicating probable leaching of Zr during the contemporaneous development of the horizon as an acidic red-yellow podzol. The near-shore, sandy nature of the early Barton Sea sediments is still indicated by the high ~ 950 ppm Zr in the sand clays deposited over the pebble bed podzol.

The abundance of Zr in the sand sediments is of bimodal distribution. Enriched, ~ 800 ppm Zr concentrations occur in most of the sands within the 'Lower Headon Beds' at all the studied localities. These sands would be river-channel deposits probably re-worked from nearby zircon-rich sediments. Exceptions to the above are the 'seat-earth' sands with low (~ 100ppm) Zr contents. It is probable that these on deposition contain substantially higher Zr contents, but much of this became leached by acidic ground-waters during the development of their lignite covers as swamp soils. Similarly low Zr concentrations characterise the Barton Sand at Barton and Whitcliff Bay. These 'Barton Sands' are relatively less well sorted, and less intensive sorting conditions during their deposition might not have facilitated high zircon concentrations. The low Zr contents obtained for the white sand 'Barton Bed I' at Barton agree with the observation of zircon depletion made by Blondeau & Pomerol (1968) in the heavy mineral content of that deposit. A much lower <30 ppm Zr abundance in the Barton Sand at Alum Bay would, as stated earlier for the pebble bed at the same locality, be due to acidic leachings attending the contemporaneous development of podzol palaeosols on the sands and in nearby land areas.

The zircon contents of the clayey sediments generally vary narrowly between 200 and 500 ppm; it could be reflecting the siltiness and sandiness of the clay deposited compared to average shales. In fact, the very sandy horizons of the Barton Clay (i.e. ABBB-9 & 12) can be clearly differentiated by their high ($\sim$400 to $\sim$1000 ppm) Zr contents. These very sandy horizons can be regarded as deposits representing periods of eustatic drop of the Barton Sea levels attended by high current energies and greater concentrations of coarse-grained detritus.

Zr was largely undetected in the limestones in the 'Lower Headon Beds' at Heatherwood Point. These contain very small clay-dominated clastic materials. The 'Lymnae Limestone' at Long Mead End contain 75 ppm Zr and this is due to its much more substantial ($\sim$20%) clastic contents. The differential abundance of Zr in the limestones thus supports the earlier suggested (Chapter 13) differential conditions of accumulation of the limestones. Those at Heatherwood Point, especially the How Ledge Limestone, had accumulated in quieter water bodies receiving only very little muddy detritus. In contrast, the Lymnae Limestone at Long Mead End was accumulated closer to detritus-discharging streams.

Differences in the lithological nature of the matrix constituents of the calcareous concretions and the sideritic ironstones would account for their very variable contents of trace to 304 ppm Zr. The Zr contents of the ironstones were seen to increase from <30 ppm, where the matrix is very clayey (i.e. ABLH-8 and ABBB-13) to between 100 and 200 ppm in those with sand-clay and sand matrices. Zircon was undetected in the ironstone nodule WBLH-10, which is almost wholly composed of almost pure siderites; the ironstone would have developed in very low energy setting, or very close to the surface with incorporation of very little clastic materials.

15.1.15 Niobium, Nb

Abundance

Shales (Wedepohl, 1969) 18 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments & Lignites	trace - 29	11
Sands	trace - 19	4
Freshwater Limestones	trace - 7	trace
Calcareous Concretions & Sideritic Ironstones	trace - 18	4

During weathering, Nb could be taken into solution as soluble alkali niobates or as adsorbed hydrolysed Nb^{5+} salts on clay minerals. Nb^{5+} also has an ionic radius similar to that of Zr^{2+} and Ti^{4+}, and could occur with them as resistates and hydrolysates (Goldschmidt, 1954; Gordon & Murata, 1952).

In the Upper Eocene sediments under study Nb occurs in concentrations of $<$20 ppm and is more common in the clayey sediments. A geographical distribution difference is exhibited by Nb. It occurs more frequently at the type sections on mainland Hampshire, whilst it was largely undetected in most of the sediments in the succession on the Isle of Wight. It has particularly been depleted in the sands and the carbonate sediments.

The relative abundance of Nb and Zr (Nb/Zr ratios) has been employed as palaeo-climatic indicators. Parchadzhanov (1963) employed Nb/Zr ratios of 0·08 and 0·06 as limiting indicator values, for arid and humid climates, respectively. The Upper Eocene sediments under study are characterised by Nb/Zr ratio values of 0·2 to 0·7. This may be taken as equivalent to a very variable but essentially humid palaeo-climatic condition in the Upper Eocene Hampshire Basin. Such a deduction agrees greatly with similar inferences already made in the present study and, in addition, with those of earlier workers on floral contents of the sediments (i.e. Chandler, 1960, 1961; Fowler *et al.*, 1973).

15.1.16 Molybdenum, Mo

Abundances

Calcareous & Sideritic Concretions (Gad *et al.*, 1969)	$<$ 10 ppm
Upper Eocene sediments, Hampshire Basin	trace - 15 ppm (average $<$ 4 ppm)

In weathering zones, Mo can easily be taken into solution and migrated as hydrated oxide and/or colloidal complexes. In Ca-rich environments, Mo can be induced to precipitate as calcium salts of molybdic acid (Rankama & Sahama, 1950). Mo is also physiologically important in living tissues; and upon death and decay of organisms, the organically concentrated Mo can become adsorbed on clays (Manskaya & Drozdova, 1969).

In the Upper Eocene sediments, Mo was detected only in a very few lignitic and fossiliferous sediments; and even then, it is often in amounts of 4-15 ppm. The element would be associated with the various organic materials in the concerned horizons.

15.1.17 Barium, Ba

Abundances

Shales (Goldschmidt, 1954)	436 ppm
" (Curtis, 1969)	794 ppm
Sandstones (Engelhardt, 1936)	170 ppm
Limestones (" ")	120 ppm
Calcareous Concretions (Gad *et al.*, 1969)	90 ppm
Sideritic Ironstones (" ")	198 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, 'Lower Headon Beds'	304 - 879	712
" " Barton Clay Fm.	231 - 840	567
Lignitic & Carbonaceous Clays	254 -1086	659
Sands, 'Lower Headon Beds'	123 - 751	470
" Barton Sand Fm.	73 - 412	253
Red-Yellow Podzol Palaeosols	69 - 239	139
Freshwater Limestones	22 - 183	67
Calcareous Concretions	53 - 228	142
Sideritic Ironstones	84 - 480	290

During weathering, Ba behaves similarly to Sr and can easily be taken into solution to migrate as bicarbonates (Rankama & Sahama, 1950). As a hydrolysed ion, Ba^{2+} may adsorb on clay minerals, whilst by their similar ionic radii, Ba^{2+} can substitute for K^{+} in clay minerals and feldspars. Ba can also occur as carbonate and sulphates in marine and saline-water deposits.

In the present study, Ba is found to be most abundant in the clayey sediments, varying from about 300 ppm to over 800 ppm. In the sands, abundances of about 200-300 ppm Ba are more common. In these clastic sediments, correlation between the constituents indicates that Ba occurs in association with the illitic and feldspar phases. This mode of occurrence would account for the low ($<$ 50 ppm) in the Barton Sand at Alum Bay, which is depleted in feldspars and 2:1 clay minerals.

Sometimes, variations in Ba abundances in sedimentary sequence has been related to salinity differences (Kukal, 1971). This is not apparent in the Upper Eocene succession under study; most of the clayey sediments in the marine and non-marine parts of the succession are similarly characterised by $\gtrsim$400 ppm Ba.

Ba, however, occurs in low ($<$ 50 ppm) in the How Ledge Limestone and the ironstone nodule WBLH-10. These incorporated very little detritus. The higher clastic material contents of the other carbonate horizons would account for their high, 200-350 ppm, Ba contents.

15.1.18 Iodine, I

Abundances

Sedimentary Rocks (Rösler & Lange, 1972)	$<$ 2 ppm
Limestones (Vinogradov , 1956)	up to 430 ppm

Upper Eocene, Hampshire Basin

	Range (ppm)	Mean
Clayey Sediments, Lignites, Sands & Palaeosols	trace - 27	$\leq$ 4
Freshwater Limestones	73 - 181	113
Calcareous Concretions	8 - 55	22
Sideritic Ironstones	trace - 9	trace

Iodine is the only halogen determined in the present study. The element is a major physiological constituent of organisms, and is particularly much concentrated in seaweeds and marine organisms, notably the planktons (Day, 1963). It can occur as insoluble phenolic acids and metal-iodide (e.g. CuI) often concentrated in water, peats and humified soils (Vinogradov, 1956). It is most common in water bodies in the form of iodates and iodides, and generally increase in concentration with increases in salinity, and also changes towards more open marine waters (Day, 1963).

The importance of the biochemical concentrations of iodine is reflected in its abundance and distribution in the succession under study. Iodine occurs in amounts averaging $<$ 10 ppm in the ironstones and clastic sediments; but it is very substantial in the calcareous sediments. Exceptionally high amounts of 74 to 181 ppm I are contained in the limestones, while lower amounts of 10-55 ppm I are in the calcareous concretions. This iodine distribution would suggest either concentration of iodine from decayed organism tissues and/or fixation of iodine with calcium ions as a separate phase or very possibly in association with the $CaCO_3$ forms. Association with the remains of organisms may also account for the limited 4-30 ppm amounts of iodine in the marine sediments and some of the lignitic clays.

15.1.19 Rare-Earths: Yttrium, Y; Cerium, Ce; and Lanthanum, La.

Abundances	Y (ppm)	Ce (ppm)	La(ppm)
Shales (Minami, 1935)	28	46	18
" (Herrmann, 1970)	38	91	45
" (Ronov *et al*., 1967)	30	67	34
Sandstones (Rosler & Lange, 1972)	40	92	30
Carbonates (" " ")	30	12	$<$10

Upper Eocene, Hampshire Basin	Range(ppm)	Range(ppm)	Range(ppm)
Clayey Sediments, 'Lower Headon Beds'	24-70;$\bar{x}$=39	53-132; $\bar{x}$=84	trace-77; $\bar{x}$=40
" " Barton Clay Fm.	17-50;$\bar{x}$=31	53-149; $\bar{x}$=87	trace-70; $\bar{x}$=56
Lignitic & Carbonaceous Clays	17-123; $\bar{x}$=45	34-320; $\bar{x}$=120	11-244; $\bar{x}$=79
Sands, 'Lower Headon Beds'	5-56;$\bar{x}$=26	7-85; $\bar{x}$=55	trace-45; $\bar{x}$=23
" Barton Sand Fm.	trace-20; $\bar{x}$=8	4-64; $\bar{x}$=10	trace-49; $\bar{x}$=10
Red-Yellow Podzol Palaeosols	trace-19; $\bar{x}$=10	5-82; $\bar{x}$=34	trace-160; $\bar{x}$=31
Freshwater Limestones	4-49;$\bar{x}$=18	trace-44; $\bar{x}$=7	trace-57; $\bar{x}$=10
Calcareous Concretions	10-37;$\bar{x}$=20	trace-34; $\bar{x}$=6	trace-47; $\bar{x}$=14
Sideritic Ironstones	19-58;$\bar{x}$=35	35-159; $\bar{x}$=72	5-90; $\bar{x}$=45

Y, Ce and La are rare-earths; the La and Y being heavy (Yttrium-earth) and the Ce, a light (Cerium-earth) earth (Haskin et al., 1966; Rankama & Sahama, 1950). The elements have similar electronic configurations and hence similar chemical properties. They are strongly lithophile and often occur together in nature, usually by replacing one another in compounds or other minerals in which they occur. As trivalent ions, the elements in a weathering zone behave as hydrolysates, forming stable sparingly-soluble but mobile hydroxides. Y and Ce could form soluble bicarbonate complexes and be mobilised in association with phosphates and organic compounds. Y is the most mobile and is reported (Ronov et al., 1967) to increase in abundance seawardly, possibly as colloids and following Fe_2O_3 and P. There is a diadochial relationship between Ca and Y and, in addition but to a lesser extent, Ce. By this, Y tends to proxy for Ca in apatites, carbonate sediments and some marine calcareous shells (Day, 1963). Although the ionic sizes of the rare-earths (3+) are large (average 0·96Å) for them to conveniently replace Al^{3+}, Mg^{2+} or Fe^{2+} in clay minerals, the Ce-earth ions are relatively closer in size and could substitute, in substantial amounts, for K^+ in minerals such as the potash feldspars.

In the Upper Eocene succession under study Ce occurs in greater abundance, on average, than either Y or La. The three elements occur in greater concentrations in the clayey sediments and are particularly enriched in some highly ligniferous horizons. In the clayey sediments, there are no significant variations in the element concentrations in the marine and non-marine divisions. On average, the clayey sediments contain 35 ppm Y, 50 ppm La and 86 ppm Ce. The recorded higher average amounts of La and Ce in the lignitic clays are due to their exceptionally high concentrations in lignitic samples BLH-29, BBB-1, ABLH-11 and ABLH 13, and WBLH-12. These samples contain 90-302 ppm Ce and 100-244 ppm La. A plot of % Organic-C vs $[(La + Ce)/2]/Y$ ratio values has been made (Fig. 47) for the lignitic clays in the succession. The plot shows that in lignites with > 10% organic-C contents there are substantial enrichments of the rare-earths, especially the La and Ce. The plot further helps in differentiating the lignitic sediments as to their possible derivation from different plant materials and/or subjection to differential post-depositional diagenetic or alteration conditions. Perhaps the elements were primarily concentrated in high amounts with the plant materials of the lignites. However, many of these suffered penecontemporaneous leaching and oxidation. Substantial amounts of the elements remain retained only in the less leached lignites.

In the sand sediments, the concentrations of Y, La and Ce are much lower than in the clayey sediments, showing a systematic variation. At Barton the sand matrix of the pebble bed is the only material with high concentrations of La (76 ppm) and Ce (98 ppm). Sands in the Barton Sand Formation are characterised by $<$ 10 ppm Y, $<$ 20 ppm La and about 30 ppm Ce. Higher concentrations (10 to 50 ppm) of the elements are, however, contained in the sands of the 'Lower Headon Beds'. Contributions from organic matter are indicated by the higher amounts (up to 85 ppm) of Ce in horizons with plant rootlets and/or fossil shells (i.e. BLH-16 and 35). At Alum Bay, Y and La occur in depleted ($<$ 10 ppm) amounts, but the Ce concentrations and variations are similar to those at Barton. The clayey base of the Barton Sand at Alum Bay, however, has higher rare-earth concentrations similar to those of the underlying Barton Clay. At Whitecliff Bay, the sands are completely depleted of La, while Y and Ce are always present in small amounts as in the sands at Barton.

Correlation within the clastic sediments suggests that the rare-earths occur in association with organic-C, kaolinite, the illitic phases and, to a lesser extent, the feldspars. In addition, Y and La show a weak positive correlation with anatase and smectites respectively; whilst Ce, in the sands, also weakly correlates with calcite.

In the limestones, the rare-earths are largely undetected. It was only in the 'Lymnae Limestone' that concentrations of about 50 ppm were recorded. This distribution underlines the association of the rare-earths with the clastic materials which only occur in substantial amounts ($\sim$ 20%) in the 'Lymnae Limestones'. The concentrations of the elements in the calcareous concretions are very variable. With the exception of samples ABLH-4 and 5, with 15 and 34 ppm Ce contents respectively, cerium is largely undetected in the concretions. Y occurs in amounts of about 15 ppm; the smaller nodules ABBB-4 and BBB-42 containing higher, $\sim$ 35 ppm Y. La occurs in trace to 47 ppm. In general, the persistent occurrence of Y, albeit in small ($<$ 20 ppm) amounts, and the depletion of Ce, and to a lesser extent La in comparison with the host clastic sediments, would be due to the dilution effect of the diagenetic calcite constituents.

The pore fluids for the calcareous concretions were apparently not enriched in the rare-earths.

In the case of the ironstones, those in the Barton Clay contain higher (20 - 80 ppm) of each of the rare-earths compared to ironstones in the 'Lower Headon Beds'. The element concentrations are particularly substantial (58-159ppm) in the ironstone WPB-2 at Whitecliff Bay. There is, however, a general decrease of the elements abundance in ironstones within the 'Lower Headon Beds' from the mainland sections to the Isle of Wight; with Y and Ce being between 12 and 50 ppm, and the La largely undetected on the Isle of Wight.

15.2 Modes of Occurrence

From their distributions and correlations with other mineral and chemical constituents, the determined trace elements contents of the Upper Eocene sediments may be grouped into the following occurrence phases:

15.2.1 Resistates

Amongst the elements determined, only Zr has a distribution that typifies resistate phases (i.e. Rosler & Lange, 1971). The element is most abundant in the basal, transgressive pebble bed at Highcliffe, and also occurs in substantial concentrations in some very sandy horizons in the clayey sediments of the Barton Clay. It also occurs in very high amounts in most of the sands in the 'Lower Headon Beds'. These sediments could be considered as deposits of high energy and shallow-water bodies, the pebble bed being typical of beach deposit, and the sands being channel and/or fan-like.

Resistate elements of lesser significance are U and Th; their correlations to quartz were weak, but significantly positive. U occurs in parts of the Barton Sand at Barton (i.e. 'Beds I & K'), whilst Th occurs in many of the sand horizons except the white sands of 'Bed I' at Barton, and the Barton Sand Formation at Alum Bay and Whitecliff Bay.

15.2.2 Hydrolysates

Most of the determined elements behave as hydrolysates; they are V, Cr, Ni, Rb, Sr, Nb, Ba, Y, Ce, La, Pb, and probably, in addition, As, Cu, Th and Zn. They dominantly occur in high concentrations in the clayey sediments, but are relatively impoverished in the sands and carbonate sediments. The elements mostly correlate with the kaolinite and/or illitic clay phases. They also often correlate with the anatase, smectite and feldspars. Their occurrences would be as adsorbed hydrated ions on clays and anatase; and as cations substituting for structural and/or interlayer Mg^{2+}, K^{+}, Al^{3+}, Si^{4+}, Fe^{2+} and Fe^{3+} in clay minerals. Some, such as Rb, Sr and Ce may be substituting for K in potash feldspars.

Apart from the lithological differences in abundance, as mentioned above, the elements do not show any significant systematic variations between the marine and freshwater clayey sediments vertically or laterally. Major differences only significantly concerned variable enrichments of elements such as V, Cr, As, Zn and Sr in sympathy with the occurrence and abundance of fossil shells and/or carbonaceous materials. The elements concerned are considered further below. The general similarity of abundance of the hydrolysates in the clayey sediments suggests similar probable source(s) of their detritus, and no significant variations of the detritus compositions with change of depositional environments from marine to freshwater.

15.2.3 Sulphide/Organic Matter

The elements associated with organic matter and/or sulphide phases are As, Nb, Mo, Pb, Ce, Cu, I and, in addition, V, Cr, Mn, Ni, La, U, Th and Zn. Many of these elements (such as Mo, I and Cu) are physiologically important in living tissues, and could become concentrated in sediments upon the death and decay of organisms and plants. The elements would mainly concentrate and occur as metal-organic complexes. However, in reducing environments of poorly aerated or drained water bodies and/or skeletal enclosures, the trace elements may become concentrated, with reduced iron, into metal sulphides, notably pyrite. In the event of the sediment becoming better aerated, the elements may become associated with exogenously-produced iron-oxides, jarosite and, possibly, gypsum.

The trace elements, listed above, occur mostly in the clayey sediments and some are particularly enriched in the lignitic and fossiliferous beds. Enrichment was particularly high for Pb, Cu, I, Mo, U, Cr, Ce, La and As in very lignitic horizons, i.e. lignitic clays with >10% organic-C contents. These lignitic clays probably accumulated, and remained in relatively less aerated and drained conditions in comparison with the other lignitic clays with lower organic-C contents ($< 3\%$) and trace element concentrations. However, all the lignitic clays possess low, $<$ 20 ppm, Mo contents and similarly low, 0·47 to 1·42 V/Cr ratios and 1·5 to 4·8 V/Ni ratios. These are attributes close to those of 'gyttja organic substances' (Kukal, 1971), which could have accumulated with little air access within or close to oligotrophic or slightly eutrophic non-saline lakes and bays. Plant organic matter may be the original source of the As, Zn, V, Mo, Cr and, probably, Mn, enriched with goethite in the indurated pebble bed and Barton Sand podzol palaeosols at Alum Bay. Similar derivation may also account for these elements in the goethitic, loamy top of the Barton Sand at Whitecliff Bay.

15.2.4 Carbonates

The trace elements associating with the carbonate phases and sediments are Mn, Y, Ce, Sr, Mo, I and, in addition, U, Pb and Zn. In fossil shells, Sr and Mn can be biochemically partitioned into calcite and/or aragonite phases; hence substantial amounts of these elements occur in many fossiliferous clastic sediments. Also Mg, Ca, Mn, Fe can, in solid solutions, replace each other in physico-chemically and/or biologically induced precipitated calcites and siderites. There is also a diadochial relationship between Y, Ce and Ca ions; while it is probable that some of the elements were derived as soluble bicarbonates, but which became precipitated as disseminated insoluble carbonates with the $CaCO_3$ and $FeCO_3$ phases. Some elements, such as iodine, could actually have been concentrated from decayed tissues of fossil animals, and possibly the charaphyte algae in parts of the 'Lower Headon Beds'.

The dominant trace element, occurring in amounts of up to 9774 ppm, is Mn. Its higher concentration occurrences are in the sideritic ironstones where it is mainly substituting for Fe^{2+} in the siderite phases. Each of the other elements associated with the carbonates mostly occurs in amounts of $<$ 100 ppm. They are mostly hydrolysates and, as enumerated earlier, their abundances are dependent on the amount of clastic materials incorporated into the carbonate sediments. The incorporations were least for the How Ledge Limestone, and the sideritic ironstones in the 'Lower Headon Beds' at Alum Bay and Whitecliff Bay. That limestone would have accumulated in quiet water bodies with little detrital input, while the ironstones would have developed close to the sediment-water interface and would have incorporated very little clastic matrix materials.

15.3 Summary

Twenty-one trace elements have been determined in the sediments of the Upper Eocene Hampshire Basin. The elements showed characteristic variations with the sediment lithology. In the clayey sediments, the hydrolysates predominate, with no significant systematic variations from marine to non-marine clayey sediments. The observed abundance variations concerned (i) Ni, Cu, Pb and Zr, which were higher in the Lower Headon clayey sediments than those of the Barton Clay; (ii) Sr that was lower in the Lower Headon clays; (iii) La, Ce, Y, Zn, Pb, Cu and Ni that were variably enriched in the lignitic clays, particularly those highly carbonaceous with > 10% organic-C contents; (iv) low Ni, Cu and Sr, but substantially higher Zr contents in the Huntingbridge Clay compared to the rest of the Barton Clay Formation.

Most of the elements present in the sands are also hydrolysates. But they largely occur in impoverished abundances, probably in sympathy with their lower clay mineral contents, in comparison with the clayey sediments. Probably leaching at detrital sources and/or upon deposition may also have contributed to the elements' low concentrations in the sands. The depletion of the elements was severe at Alum Bay where acid soil formations occurred; and in the 'seat-earth' sands underlying the lignitic clays. The only important resistate element, Zr, occurs in very high concentrations in the transgressive pebble bed at Highcliffe, very sandy clays in the Barton Clay, and in most of the sands in the 'Lower Headon Beds'. These sediments would be high energy deposits.

The clayey base of the Barton Sand at Alum Bay contains trace elements in greater concentrations than the impoverished whiter sand above it. Its trace element contents are similar to those of the underlying Barton Clay. This illustrates the gradual change to sand deposition as the Barton Sea started shoaling.

In the red-yellow palaeosols at Alum Bay and Whitecliff Bay, V, Cr, Mn, Zn, As, Ce and La were concentrated along with goethite, probably having been derived from plant remains.

The carbonate sediments also contain variable amounts, but mostly in depleted quantities, of the hydrolysate elements. The elements would be mostly associated with the incorporated clastic matrix materials. Mn is the dominant trace element in the carbonate sediments; it is enriched to several tens of times the amounts in the host clastic sediments. The Mn concentrations are highest in the sideritic ironstones, particularly those at Alum Bay and Whitecliff Bay. The element is mainly structurally contained in the siderite and, to a lesser degree, in calcites and aragonites. Sr was also enriched in the limestones. However, the low 300-500 ppm Sr contents of the limestones is difficult to explain. Perhaps the Sr was mainly in the fossil shells; and the shells, which are wholly aragonitic, make up less than one-fifth of the limestones and, in fact, contain low ($\sim$ 500 ppm) Sr. The low Sr of the shells may be due to their being physiologically advanced, and inhabiting land and shallow warm waters within which the limestone accumulated.

CHAPTER 16

PALAEOSOLS

16.1 Introduction

Palaeosols are 'fossil' soils that are of pre-Holocene (> 10,000 years) age (Mackenhausen, 1973). They may be considered as materials that have been subjected to surface and/or sub-surface weathering and the pedogenic actions of climate and vegetation during periods of geological stasis with no noticeable sedimentation or erosion. Palaeosols are thus widely recognised as sensitive indicators of palaeo-climate, and hence are of great importance in palaeo-environmental interpretations.

Palaeopedology, the recognition, designation and study of palaeosols, has only been established in recent years (Pettijohn, 1975; Terrugi & Andresis, 1971; Yaalon, 1971; Mackenhausen, 1973; Buurman, 1975). Buurman (1975b), in his presentation of a case for the recognition and establishment of palaeopedology, gave some important characterising features of palaeosols, such as the presence of: i) rootlets; ii) distinct horizons of abundance and accumulation of vegetational organic matter; iii) strong coloration; iv) clay skins; v) accumulation of iron, silica and alumina; and vi) mottles.

Field recognition of palaeosols is often not easy because many soils are not well developed. Many of their pedogenic features could also have been destroyed or substantially altered either by erosion and multiple weathering immediately following formation or by diagenesis following burial. Palaeosols of Devonian to Lower Carboniferous ages (400 - 300Ma) described by Wright (1980) from Wales, and Riding & Wright (1981) from the English Midlands, are probably the oldest soils so far recognised. These comprise calcretes, calcareous soils and rootlet-bearing pyritous gleysol complexes. Rootlet-bearing soils have also been reported in the Upper Carboniferous of Germany (Roeschmann, 1962 - reference in Mackenhausen, 1973). A very few soils have been recognised in the Permian, Jurassic and Lower Cretaceous Systems. Most of the well-established palaeosols are Tertiary to Pleistocene in age. They are mostly latosols and podzols, and include: i) silcretes in the Netherlands (Van den Broek & Van der Waals, 1967) and Britain (Isaac, 1983b); ii) ferruginous and kaolinitic soils (latosols or ferralitic or siderolitiques), red-yellow podzols and red-earths (Terra rossa or Mediterranean Red Soils) in Central and Western

Europe (Millot, 1970; Pomerol, 1973; Mackenhausen, 1973); and iii) podzols, hydromorphic soils and gleysols in Britain (Buurman, 1981; France (Freytet, 1971, 1973), and the Netherlands (Vink & Sevink, 1971).

In the Upper Eocene succession of the Hampshire Basin, southern England, pedogenic features occur at some horizons. These include the following:

I) Humified, ferruginised and sometimes pyritised rootlets in growth-position occurring in

a) the mottled clay and ferruginous sands in the upper 2m of 'Bed K' of the Barton Sand on Beacon Cliff at Becton Bunny (Fig. 48).

b) the brown ferruginous sand and clayey silt of the Leaf Bed on Beacon Cliff at Long Mead End;

c) the purplish-brown, ferruginous sand occurring some 4m above the 'Lymnae Limestone Bed' on Hordle Cliff, Long Mead End;

d) the ferruginous, loose and cemented sands at the top of the 'Lymnae Limestone Bed' and its lateral equivalent, the mottled clay around Hordle House;

e) the ferruginous sand at the base of the Chara Bed around Hordle House.

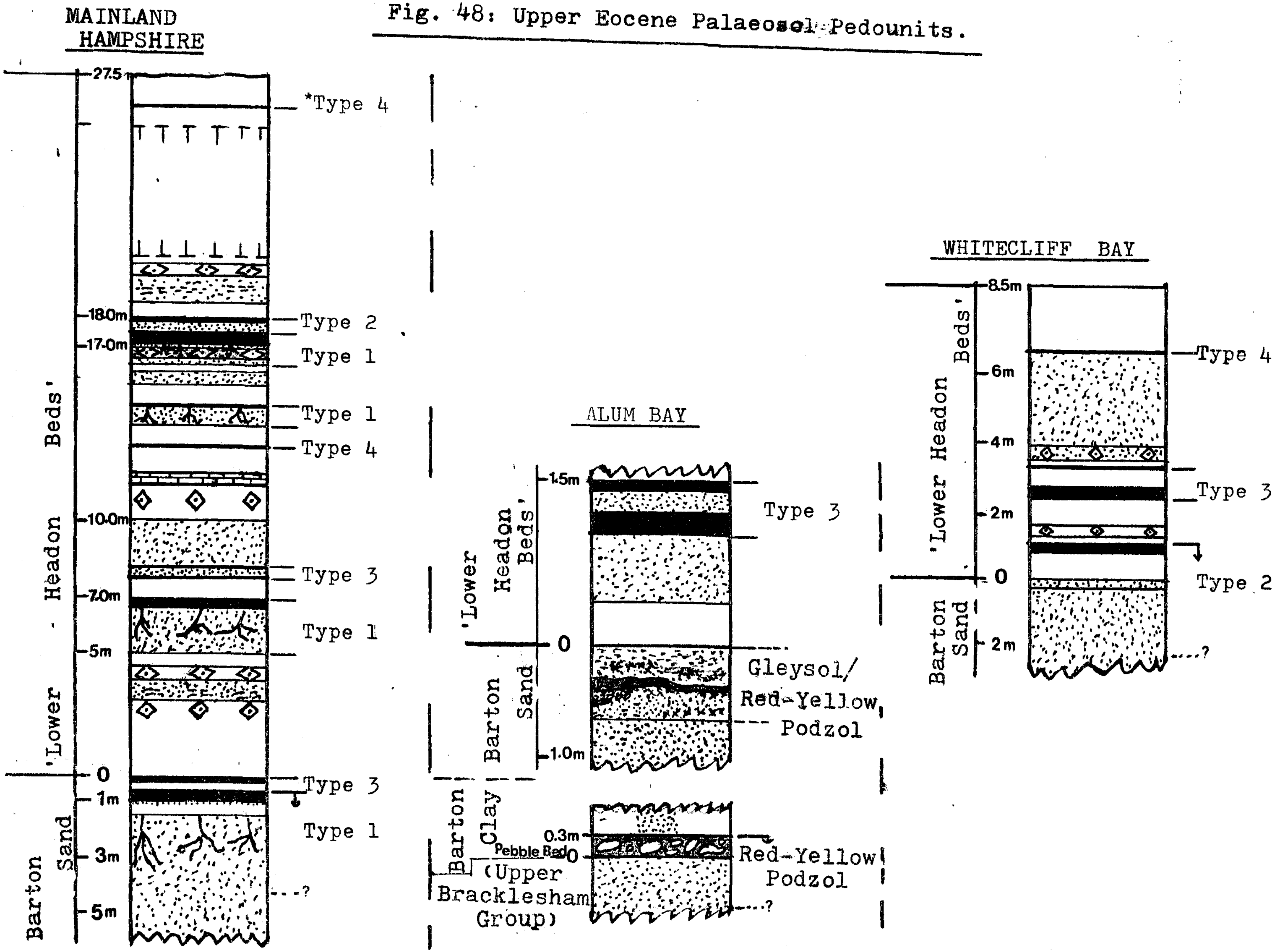
II) Plant-debris accumulations in substantial amounts, typified by lignitic clays and muds, most of which occur in association with rootlet-bearing horizons or sandwiched between mottled green clays (Fig .48;cf.Figs.5-7). This category excludes dispersed plant debris such as drift-wood and infall litter.

III) Strong coloration and iron-oxide concentrations such as those characterising:

a) the yellow, reddish-brown and purplish horizons marking the top of the Barton Sand in Alum Bay (Fig. 48), where they are associated with rootlets, reddish iron mottles, goethite-cemented bands, pallid patches and lenses of kaolinite;

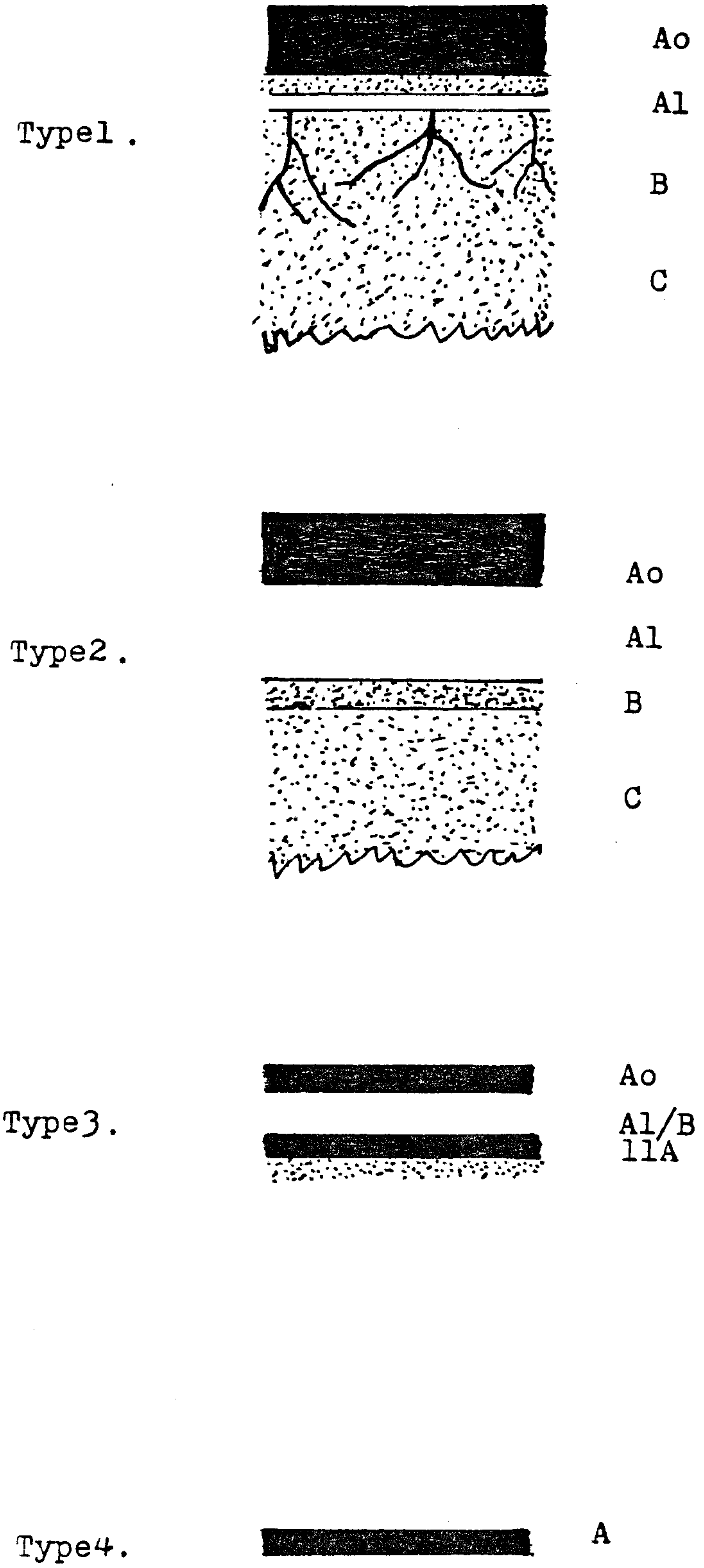
b) the dark-red, goethite-cemented pebble bed at the base of the Upper Eocene succession in Alum Bay;

Fig. 48: Upper Eocene Palaeosol Pedounits.



*Hydromorphic Swamp pedounits (see Fig.49 for profile types)

Fig. 49: Profile Types of Hydromorphic Swamp Palaeosol



c) the thin brownish-yellow ferruginous, loamy clayey-sand at the top of the Barton Sand in Whitecliff Bay. This is sandwiched between the ferruginous yellow sand in the upper part of the Barton Sand and the lignitic and carbonaceous clay at the base of the 'Lower Headon Beds' (Fig. 48 ; Plate 24).

The pedo-characteristics listed above have been assigned to three of the major types in the soil classification of U.S.D.A (1967) and Fitzpatrick (1971). They are:

i) the Red-Yellow Podzols, at the top of Barton Sand and the pebble bed at Alum Bay;

ii) the Gleysols, above the Barton Sand red-yellow podzol at Alum Bay; and

iii) the Hydromorphic Soils of marshes, swamps and tidal flats. These comprise the lignitic horizons and associated rootlet-bearing ferruginous sands and mottled clays.

In view of their palaeo-environmental significance, those horizons have been studied in some detail. Their morphology and compositions are described and discussed below. Detailed definitions of pedological terms used are contained in Brewer (1964).

16.2 The Red-Yellow Podzols and Gleysols

16.2.1 Morphology

The general description of the pebble bed and the palaeosol top of the Barton Sand at Alum Bay has been given in Chapter 2. Two similar soils, Profile A at Heatherwood Point (Plates 18a, b) and Profile B (Plates 19a,b) some 50m further south were recognised at the top of the Barton Sand. These soil profiles consist of two incomplete pedounits that, earlier in Chapter 2, have tenuously been classed as Rossosol grading into Arenosol (both equivalent to Red-yellow podzols), and Gleysols (Fig. 6b). The soils consist of loose, yellowish sandy arenons (C, IIB3 and IIC); brownish to yellowish sandy rossons (IIB22 and C); the vesons, made up of an upper part of hard, dark red goethite-concentrated bands ($IIB21_{ir}$), and a lower part of red mottle-containing, friable or yellowish-red goethite-cemented sands ($IIB22_{ir}$); the mottled purple, clayey-sand argillon ($B2_t$); and the gleysons with patches, lenses and bands of greyish-white pallid sands and red-goethitic mottles ($B2_g$ and

IIC_g). Fine laminations, inherited from the parent sand body, are still preserved in the arenons and rossons. The laminations, however, became less pronounced with an increase in the iron-oxide accumulation and induration in the veson. The argillon is a mass of apedal clayey-sand with no sedimentary structure preserved. The veson of Profile A contains void-filling specks and small ($\lessdot$ 1 cm) lenses of 'flint-clay' kaolinite (Plates 18c, d).

Plant remains are common, especially as pedotubules. These are most abundant in the veson of Profile B, and generally occur as tubular, hollowed and knobbed roots and rootlets (Plate 20) The pedotubules measure 2-5 cm in length, 0·2-0·6 cm in diameter, and possess thin (0·5 mm thick) walls. The walls are dark-coloured (humified or carbonised?) and rimmed externally by thin layers of red mottles. Their hollows are empty or filled with loosely agglutinated sand-sized grains and red goethite mottles.

Also common in the vesons, rossons and argillons are aeration channels, thin (1-3 mm) but variably long (< 5 mm to 2 cm), and with dark red goethite linings or fillings.

The pebble bed is a composed of 30 cm thick sand-supported flint pebbles, cemented by goethite. It probably developed pedogenically along with the immediately underlying goethitic, yellow sand equivalent to the Boscombe Sand at Highcliffe (Gardner, 1879). The pebble bed may be regarded as the indurated (veson) horizon to the underlying sand (arenon). The basal part of the Huntingbridge Clay that immediately succeeds the pebble bed is a very sandy clay which, although carbonaceous, does not possess typifying pedogenic features.

16.2.2 Micromorphology

Optically, the soil horizons were seen to be largely characterised by granular fabric (texture) with sand-sized skeletal materials (and pebbles in the pebble bed) and undulic plasma (matrix) composed of voidan-goethite and clay argillons (Plates 40, 41, 45-50). The plasma of the argillons is, however, much more argillosepic, vosepic and skelsepic (cf. Brewer, 1964).

The skeletal grains consist mostly of sand-sized (200-500 μm), spherical sub-rounded and sub-angular quartz grains (Plates 40, 47, 49). A few coarser ($\gtrsim$ 600 μm) and finer (< 150 μm) grains are also present, especially in the vesons and argillons. Coarse sand-sized flints also occur in the vesons, particularly making up to about 10% of the pebble bed (i.e. Plates 40, 41). Many of the skeletal grains are pitted (i.e. Plates 54a, b) and, in addition, possess goethite-filled surface cracks which would suggest their subjection to leaching processes. Surface cracks on the pebbles are often very extensive (see Plate 41); their development having probably been enhanced by displacive growth of goethite. Such cracks and displacive growths are common in caliche soils (cf. Watts, 1978). The goethite-filled voids are large, well-connected and often continuous as bands in the pebble beds where the skeletal grains are more sparse and often clustered.

There are also a few skeletal grains of fine to coarse silt-sized, sub-rounded to sub-spherical feldspars. These are often deeply etched or corroded. Some are so intensely corroded that they have broken, along their cleavage planes, into pieces of 0.5 - 3 μm thick and 10-30 μm long blocks or plates (Plates 54c - e). These are features of incongruous dissolution in soil environments (Wilson, 1975).

16.2.3 Voids

Voids are only discernible in the Barton Sand palaeosols. They comprise simply packing voids and aeration channels. They are generally vesicular or channelled, and have assumed numerous attitudes, which include the mammillated, inter-connected, circular, arched and planar forms.

The packing of the skeletal grains was very high in the arenon and rossons, hence most of the packing voids in these are small, 5-30 μm in size, and mostly discrete. In the vesons, where there are fewer but much coarser grains, the voids are larger, 50 to > 200 μm, and interconnected, as to occasionally form continuous > 2000 μm - wide bands. In the argillon, the grains are fewer and more dispersed, with the resulting large spacing between the grains becoming a matrix. This matrix is composed of clay (clay argillons) and with fine-sand to silt-sized quartz grains.

The aeration channels were better observed in the argillon. They are elongated, > 2000 μm to < 100 μm, and circular, 0·2 to 0·5 μm in diameter. There were also a few bigger channels or planar voids. They would all have been root channels.

16.2.4 Voidal and Non-Skeletal Material

In thin section, the voids were observed to be predominantly filled with goethite. Only in the argillon are there domains of weakly birefringent clay argillons, but inter-mixed with quartz grains; and both predominate over the goethite (Plate 46). Under the SEM, the voidal materials occur as irregularly oriented, intimately-mixed, discreet and/or clusters of goethite crystals and floccules of clays (Plates 51 - 53). In addition, fine silt-sized quartz grains and feldspars were also occasionally observed.

The goethite occurs in various forms detailed in Chapter 9. The forms include lath or acicules, interwoven laths and glaebules (Plates 51e-j;52d-h; 53a-h). The goethite laths, in stacks or discreet, occur in all the soil horizons, whereas the intricately-interwoven forms mainly occur in the rossons and vesons. These are the horizons of high iron-accumulation (illuviation) and induration.

Clays also occur in the voids, either as discreet floccules of 2-5 µm sizes, or aggregated floccules of 5-30 µm sizes (i.e. Plates 51d, 52c). Kaolinite specks and lenses, in the veson of Profile A, consist of 0·3 to 0·5 µm platy crystals and vermicules of 2-10 µm-sized platy crystals (Plate 56). The platy morphology and open-texture of the kaolinite are, as previously described in Chapter 7, characteristic of weathering profiles in humid, warm climatic regions (cf. Keller, 1982, 1983). In the pebble bed, loosely-stacked, 3-5 µm sized kaolinite plates (Plate 51d) occur with filamentous clays thought to be illite.

Vegetal remains are most common in the veson of Profile B. Under the SEM, they are seen as 3 µm thick by 5-20 µm long pieces of rootlets (or rhizomes) with smaller-sized anastomising offshoots (Plates 52g,h The rootlets are often coated by glaebular goethites and/or clay floccules.

16.2.5 Mineralogy

Kaolinite is very abundant in the clays of the red-yellow podzols and gleysols (Tables 7e,f). This phase dominantly comprise the clay mineralogy of the lower pedounit of Profile A in the Barton Sand palaeosols; whereas in all the other associated units, the clay mineralogy is composed of a relatively constant mixture of about 35% kaolinite, 56% illite and 8% illite-smectite. However, in the veson of Profile B, there is enrichment of illite at the expense of the interstratified illite-smectite. The clay contents of the pebble bed and underlying sands are composed of equal amounts of kaolinite and illite.

The bulk mineralogy (Tables 8e,f) is composed of quartz, clays, goethite and infrequent small amounts of feldspars. Excluding the vesons, which are very goethitic, the mineralogy is dominated by quartz, averaging 80 ± 8%. Next abundant are the clays, averaging 6%, but varying widely from trace amounts in the lower pedounit of Profile B, through 6% in the arenons and rossons, to between 10% and 25% in the argillons and the pebble bed. K-feldspar is the dominant feldspar, averaging about 3%; amounts that compare higher than the 0·8% average sodic feldspar content. The feldspars are significantly absent in the vesons, possibly because they have suffered alteration and dissolution during the formation of the authigenic kaolinite. Goethite occurs in amounts of 3·5 to 11·5% in most horizons, but it constitutes 21% of the pebble bed 29% and 44% of the vesons of Profiles B and A respectively

The mineralogical data suggests that the soils developed from quartz-rich sand deposits by goethite and kaoline enrichments, and loss of some feldspars and 2:1 layered clay phases.

16.2.6 Chemical Composition

The chemical composition of the palaeosols (Table 15e,f) is dominated by silica, alumina and ferric iron-oxide. The goethitic vesons are the least siliceous with about 50-70% SiO_2, but most ferruginous with about 20-35% Fe_2O_3. The other horizons possess an average of 82% SiO_2 and 5% Al_2O_3. Greater amounts of alumina (8-11%) occur in the more clayey argillons. Ferric iron in these horizons varies widely from about 10% in the arenons and rossons to $\leq$ 7% in the argillons, and $<$ 1% in the pallid gleysons. Other elemental oxides occur in small amounts, none $>$ 0·3%. These are probably contained in, or adsorbed on, clays, goethite and feldspars. CO_2, determined for some of the samples, is mainly $<$ 2% and indicates the presence of very small amounts of carbonised organised matter in the soils. Thus, the loss on ignition (L.O.I) values recorded would be the structural water contents from the clays and goethite. The higher L.O.I. values are in the vesons and rossons; this is a consequence of their higher goethite contents.

Of all the trace elements determined, only Ti, Zr, V, Cr and Mn in the Barton Sand palaeosols, and As, Zn and Mn in the pebble bed occur in significant amounts. Ti concentrations of over 1000 ppm typify the gleysons and argillons. The other elements occur in varying amounts, up to 200 ppm. Many of these elements are also possibly associated with the clays or have concentrated with goethite during soil development. The low abundance of Mn indicates that the soils developed in acidic conditions with no significant manganese accompanying the iron-oxide accumulation.

16.3 Hydromorphic (Swamp/Marsh) Soils

16.3.1 Morphology

The stratigraphical position of the observed lignitic and rootlet-bearing horizons and their profile types are shown in Figures 5,6a,7,48 Although the depth to which the rootlets penetrate is observable, it was rather difficult to determine the lower limits of the units. This is because most of the horizons are thin and often grade rapidly into other sediments. The units have, however, been sub-divided as follows:

A_0 - the lignitic sediment.

A_1 - the immediate seat-earth sands and/or clay; variable in thickness but usually very thin ($<$ 2 cm), or absent.

B - extending from the base of A_0 or A_1 to the lowest limit of the rootlets or to the top of the next, lithologically-different, underlying sediment.

C - where the B horizon is thick ($>$ 50 cm), the C-horizon may be that below the rootlet limit; especially when ferruginous brown or yellow.

The sequence in which these horizons occur, in the studied sections, is diverse but may be differentiated into four profile types (Fig 49). These are:

Type 1 - Profiles with A_0, A_1, B and C horizons

Type 2 - Profiles with A_0, A_1, B_2, B_3 and C horizons.

Type 3 - Incomplete profiles of Type 1 or Type 2. They are often superimposed on another complete or similarly incomplete profile.

Type 4 - Lignitic horizon underlain by sediments not possessing or exhibiting any pedogenic features.

The lignites are dark-coloured but may be lustrous grey when dry. Some with high clay contents are less dark but much more greyish-brown. The lignitic clays contain humified, carbonised and/or pyritised plant matter, which includes wood, leaves and seeds. The floral content has been studied by many authors, including Chandler (1961), Edwards (1967) and Fowler et al. (1973). It consists of warm temperate - tropical plants, many of them aquatic or water-loving species.

The seat-earth sands underlying the lignites are loose brownish or ferruginous-yellow and of variable thickness. Very thin (1-2 cm thick) ones may constitute only the A_1 horizons; whereas those about 50 cm or more may include the B- horizons. An example of the former is the base of 'Bed L' and of the latter is the sandy basal part of the Leaf Bed in the mainland type-section (Figs. 5, 48).

Other sandy horizons included with the hydromorphic soils are 1) the loamy brownish-yellow sand top of the Barton Sand at Whitecliff Bay and ii) the dark-brown iron-oxide cemented sand underlying the Chara Bed on Hordle Cliff (Plates 11, 12). Rimming this indurated sand are a few layers of thin, hardened, dark-brown scales of iron-oxide (goethite and lepidocrocite). The scales and some other features and components of the hydromorphic soils under consideration are arguably penecontemporaneous with the Upper Eocene sedimentation, or post-Miocene uplift in age (see Chapters 9 and 10).

Mottled clays associated with the lignitic horizons display variable green, yellow or brown colorations. They are often fossiliferous, with a fauna of brackish/freshwater gastropods and pelecypods. Although they may be regarded as gleyey (cf. Fitzpatrick, 1971; Buurman, 1980a), their mottling would be due to burrowing and feeding activities of organisms rather than to iron mobilisation and accumulation which appear to be poor and patchy.

Rootlets in A_1 and/or B horizons are mostly tubular, hollowed and often ramifying with long lateral extensions. Many occur as poorly preserved humified or pyritised material. Goethite and gypsum have replaced pyrite in some, the time of the alteration being difficult to ascertain. Aeration channels,possibly left by decayed rootlets, are often observed. They are filled with sand and rimmed with reddish or yellow iron oxides (i.e. Plate 12). Small sized ($\lessdot$ 5 cm) concretionary bodies occur in the basal sand of the Chara Bed on Hordle Cliff. The bodies are associated with rootlets and shells. They are yellowish-green with jarosite and bands and rosettes of gypsum crystals.

16.3.2 Micromorphology

The lignitic clays are composed of fine sand and silt-sized quartz grains within a matrix (undulic plasma of Brewer, 1964)of admixed organic matter, clays and, in places, iron oxides. Gypsum rosettes (Plates 34-36) are also common. The quartz grains are often clustered into lenses, although substantial amounts are also dispersed within the plasma. The gypsum rosettes comprise $< 30\ \mu m - \sim 250\ \mu m$ sized prismatic crystals. Rosettes in soils are believed (Brewer, 1964) to be solution features and would have precipitated within confined enclosures. The enclosures, in the presently studied materials, are defined by organic materials, particularly hollowed centres of rootlets.

The mottled clays exhibit variable micromorphology. Their fabrics are much more argillasepic (Brewer, 1964), although in places they could be vosepic and skelsepic. Those on the Beacon Cliff sections are apedal, but that of sample WBLH-13 at Whitecliff Bay possesses micropeds (Plate 33). The micropeds are separated by cutans of diffused, dark to brownish organic matter. In all, skeletal grains are mainly fine-sand to silt-sized quartz. These are sometimes coated with organic matter and/or iron-oxides. Occasionally gypsum rosettes and swirl tectures (Plates 32, 34) are observed in the matrix. Also, fossil shells (Plate 32) are seen; they are evidence for initial sedimentation in aquatic environments.

16.3.3 Composition

The clay mineralogy is essentially illite-smectite-kaolinite-illite/smectite mixed layers and, in places, traces of chlorite. This assemblage applies to the greater part of the Upper Eocene succession of the Hampshire Basin (Tables 7a,b,d,g) previously described in Chapter 5. It has been argued that the clay assemblages were derived mainly from less-intensely weathered illite and/or smectite-rich sources under humid and warm climatic conditions.

Illite is the predominant clay phase in the soil profiles, occurring in variable amounts of between 27% and 80%. Only a few horizons, however, contain $>$60% and these are mainly on the Isle of Wight. Smectite constitutes 20-57% of the clays, although it is significantly absent in the profiles at Alum Bay. Kaolinite generally occurs in amounts of $\leq$ 15%, but is enriched, up to 36%, in some lignitic horizons, possibly as a result of in situ penecontemporaneous leaching and alteration of silicates. In fact, leaching may account for the very poor crystallinities of the clay minerals in many of the soil profiles (see Chapter 5). Kaolinite is absent in the ferruginous loamy top of the Barton Sand at Whitecliff Bay; this is a reflection of the generally low amounts of the phase in the Upper Eocene succession at that locality. The illite-smectite mixed layers constitute between 10% and 15% of the clays. Another mixed phase recorded is the 'chlorite-like' smectite. This occurs only in three of the lignitic horizons (BBB-1, BLH-28 and WBLH-9). The phase could have been formed as an alteration product of other clay phases, probably under reducing conditions and catalytic influence of organic matter (Rich, 1968).

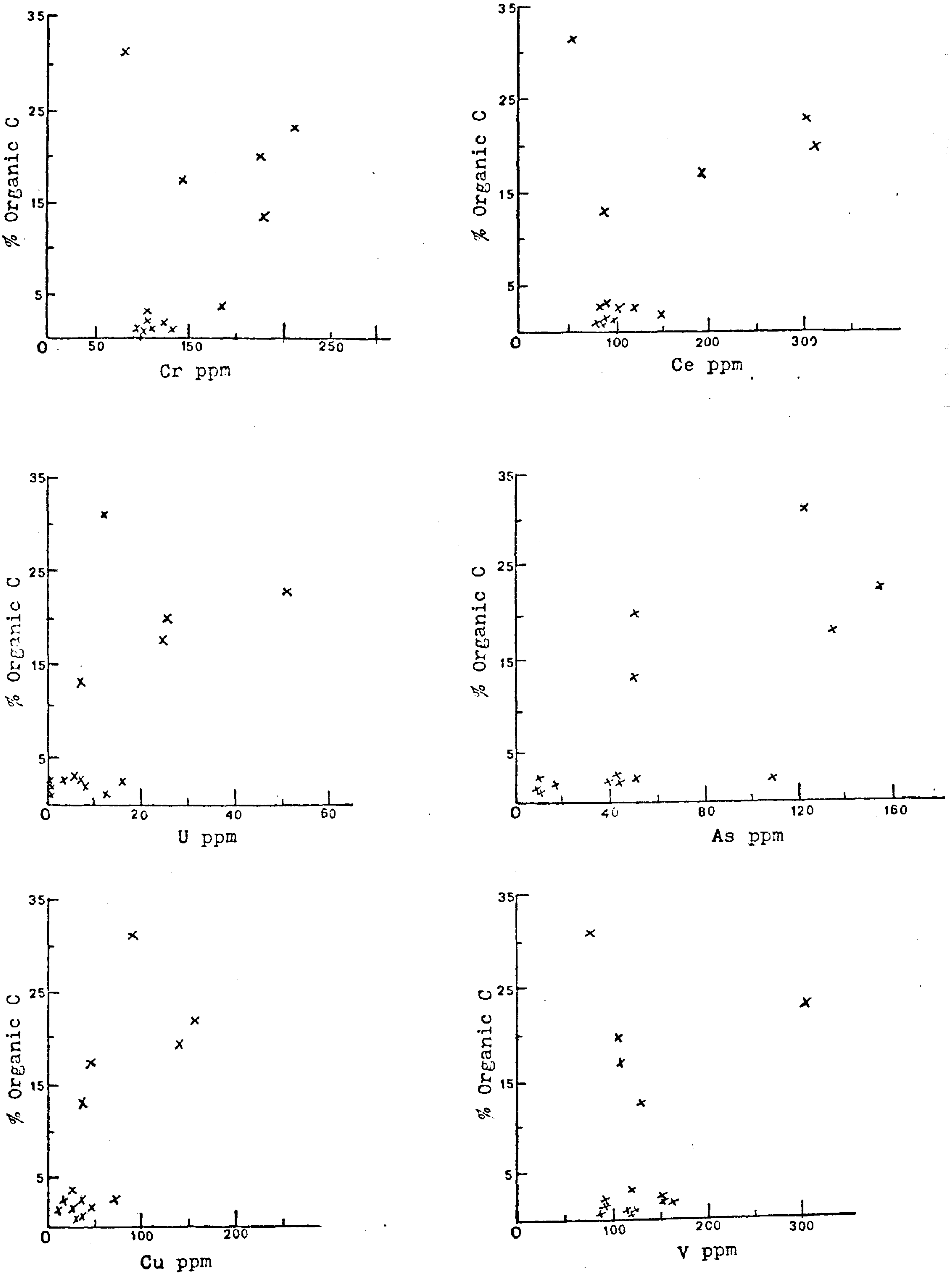
The bulk mineralogy (contained in Tables 8a,b,d,g) is dominated by quartz, clays and organic-C, with feldspars, calcite and pyrite being present in minor amounts. The organic-C content is very variable. The mottled clays and sands contain from $<$ 1% to 5% organic-C. Similarly low amounts of organic-C occur in the lignitic clays on Beacon and Hordle Cliffs. Substantially higher (13-31%) amounts of organic-C, however, occur in the other lignitic horizons, especially on the Isle of Wight. Quartz amounts vary from 25% in the highly carbonaceous horizons (i.e. WBLH-9) to 40-56% in the mottled clay and 78-88% in the sands. The clay contents vary inversely with quartz, being $<$ 6% in the sands but 30-60% in the clays and lignites. The feldspars are mostly of the potassic variety and achieve 2-5% in most horizons, although 8-11% feldspars occur in some of the sands. Calcite from fossil shells occurs in a few horizons, including the carbonaceous clays BLH-25 and 27 on Hordle Cliff. Pyrite is also less common, occurring mainly in the lignites and in amounts of $<$ 5%.

The quartz, clays and feldspar contents of the soil profiles are primarily deposited clastics, whilst the organic-C is essentially carbonised plant materials. The pyrite has formed in reducing conditions within which accumulated organic materials were bacterially being decomposed. Poor water-drainage or waterlogged conditions and poor aeration during lignite accumulation could also have facilitated the reducing conditions for pyrite formation.

In addition to the above minerals, there are exogenous phases comprising goethite, gypsum and jarosite in the soil profiles. Goethite, the main free iron-oxide detected, occurs in amounts of 4-14% in the profiles on the Isle of Wight. The indurated sand, BLH-12, on Hordle Cliff (Plate 11), however, contains 10% goethite and 7% lepidocrocite. This sand also possesses a dark brown scaly covering. The scales comprise a mixture of goethite and lepidocrocite (Plates 89, 90). Detectable free iron-oxides are, however, significantly absent in most of the brownish to yellowish sands which, in the field, were thought to be ferruginous. Gypsum and jarosite occur mainly in the lignitic horizons; the former in amounts of $<$ 5%, whilst the latter is mostly in trace amounts. The exogenous phases, especially the gypsum and jarosite, are often in association with weathered pyrites. The pyrite weathering and time of formation of the exogenous phases have been discussed in Chapter 10; much of these might be Recent. Very small amounts ($\sim$ 3%) of siderite also occurs in the sand BLH-12. This could be a relict of a low-scale siderite (or fermentation zone) diagenesis in that horizon.

The chemical composition of the hydromorphic profile is dominated by silica, alumina and ferric iron (see Tables 8a,b,d,g). SiO_2 and Al_2O_3 average 54% and 14% respectively in the lignites and mottled clays. In the sands, silica and alumina generally contribute $>$80% and $<$ 5% of the composition respectively. They are quartz sands, and hence are similar to other sand deposits in the succession (cf. Chapters 4 & 12). The potash contents are $<$ 3%, mostly contained in the illitic phases. The ferric iron varies from 1% to 6%, and generally accounts for 80-98% of the total iron content. Relatively higher proportions of ferrous iron occur in some lignites, particularly those still containing pyrite. In the goethitic horizons, Fe_2O_3 occurs in considerable amounts of 9-16%. The non-ferruginous nature of the variously-coloured sands is further stressed by their low ($\lesssim$ 1%) Fe_2O_3 contents. MgO, CaO and Na_2O generally occur in low concentrations ($<$ 1%). The fossiliferous and/or gypsiferous horizons, however, display higher (2-6%) lime contents. Sulphur varies between 0·6 and 3·8%, generally in sympathy with the abundance of pyrite and its alteration products. As highlighted during the consideration of clastic sediment geochemistry (Chapter 12), the plot of organic-C vs sulphur (Fig. 32) shows that much of the sulphur, particularly in the lignites, has been denatured.

Fig.50: Plots of Organic C versus Cr, Ce, U, As, Cu and V Contents of Lignitic Clays.



The trace elements generally occur in concentrations of $<$ 1000 ppm, although substantially higher concentrations of As, Ce, Cr, Cu, La and Mn occur in some of the lignitic clays and the indurated sand BLH-12 (see Tables 25a,b,d,g). The lignites also contain uranium in amounts of up to 50 ppm. Elements such as Ce, Gr, Cu, La and As are hydrolysates and would mainly occur in association with the clay phases. Those elements are, however, physiologically important in living tissue; they could become concentrated upon death and decay of organisms and plant materials. They may, thus, also be occurring as organo-metal complexes and/or in pyrite (the only sulphide phase in the soils) and its exogenous alteration products, especially goethite. The significant association of Cu, V, Cr, Ce, U and As with organic matter is clearly indicated in the plot of the concentration of each of those elements against the organic-C content of the lignitic clays (Fig. 50). It is seen that one or more of those elements are enriched where organic accumulation is high, i.e. $>$ 10% organic-C.

Mn is mainly associated with the carbonate phase - the fossil shells - and, in BLH-12, siderite. The high, 1161 ppm Mn in BLH-12 is essentially due to Mn^{2+} substituting for Fe^{2+} in the siderite structure. There is no Mn-enrichment in any of the other horizons. This significantly shows that, as in the podzols, the soil developments did not involve manganese concentrations.

16.4 Discussion

16.4.1 Comparison with Established Soil Types

The pebble bed and the lower pedounits of the palaeosol top of the Barton Sand at Alum Bay (Fig. 48) are thought to be red-yellow podzols. These are acid soils (Hunt, 1972) believed to have formed by the process of alluviation, homogenisation, iron-liberation and fluctuating ground-water movements (Buurman, 1980b). They could form in warm climatic areas with abundant ($>$ 600 mm) rainfall, forest cover and/or largely deciduous vegetation (Hunt, 1972). In these soils, leaching could be intensive but the breakdown of silicates may be minimal and loss of liberated iron from the soil may be checked by rapid oxidation and precipitation of hydrated oxides (Hunt, 1972). Red-yellow soils are also thought to be transitional to laterites (Grim, 1968), which are common in present-day tropical climatic regions (Fitzpatrick, 1971).

Typical examples of red-yellow podzols are the sandy soils occurring over shallow water-tables in the humid, warm temperature and tropical regions of south-east U.S.A. (Hunt, 1972; Joffee, 1949). These possess thin, dark, greyish-yellow or brown A_1 and A_2; dark coloured B-horizons with organic matter and iron accumulations close to the fluctuating ground-water table; pale coloured C-horizons with variously coloured mottles. The soils underlie both forest and grassland.

Other red-yellow soils include those developed on acid meta-sediments in south-east Sulawesi, Indonesia (Dai et al., 1980). This region has pronounced relief, good drainage, 4-6 month dry periods (with 60-100 mm precipitations) but abundant annual precipitation of 1050-1600 mm, and high average temperatures of 24·6 - 26·7°C. The soils on the plains are more hydromorphic; whereas in the better drained elevated areas, the profiles are deeper and often include clay alluviation. The organic content of the soils is very low, and their B-horizons vary from poorly developed to well-developed, with high iron accumulations.

The gleysols above the podzols on the Barton Sand (Fig. may be related to the red earths or soils that are commonly called Terra Rossa or Mediterranean Red Soils (Fitzpatrick, 1971). These soils are very common as pre-Holocene palaeosols in central and western Europe (Mackenhausen, 1973). They are hydromorphic soils in which the ground-water table is close to the surface and the sub-soils could be water-saturated, sometimes permanently. The pH is drainage-dependent, acidic (pH 4·5 - 6) in better drained profiles, but neutral to alkaline (pH 6·5 - 8) in poorly drained settings.

The lignites and associated horizons (Fig. 48), also regarded as hydromorphic soils, would be swamp or marsh soils (USDA, 1967). Indeed, the consideration of lignitic sediments as kinds of soils is debatable. Sedimentalogically, lignites and carbonaceous clays could be regarded as stratified accumulations of vegetal, carbonaceous materials in swampy or marshy environments (Greensmith, 1971; Pettijohn, 1975). But, according to Joffee (1949), swamp sediments become soils as soon as they are elevated above the lowest tide level and vegetated upon. The vegetation could vary from grasses to woods; most would, however, be water-loving or aquatic species. The presence of in situ plant rootlets in the profiles under study thus satisfies the vegetational criteria. Swamp soils belong to a miscellaneous group of intrazonal soils whose pedological characterisations are poorly defined (USDA, 1967). Closely related, or synonymous, soils include Histosols, Groundwater podzols, Peat or Bog soils (USDA, 1967; Carroll, 1970; Fitzpatrick, 1971). These often have high water tables and are poorly drained. They commonly occur in low-lying coastal or flood plains, including the coastal marshlands and seaward portions of the Coastal Plain from Virginia to Texas in south-east U.S.A., and parts of tropical Indonesia and Borneo (Carroll, 1970; Fitzpatrick, 1971).

16.4.2 Development of the Soils

16.4.2A Environmental Settings

The development of palaeosols in the Upper Eocene succession of the Hampshire Basin required that the sediment horizons concerned lay in terrestrial environments which supported abundant vegetation. The general palaeo-environments of the depositional areas of the Upper Eocene Hampshire Basin have previously been described in Chapters 1 and 2. The environment in the late Middle Eocene times is believed (Curry, 1965; Murray & Wright, 1974) to be mainly that of an accreting, shallowing embayment, with clear water bodies and sand depositions in areas westward of Alum Bay. Non-marine conditions in places are manifested as rootlet-bearing lignitic horizons. The onset of the Barton Sea transgression in early Upper Eocene times was marked by a sandy-pebble beach deposition at Alum Bay and Highcliffe. Fisher (1862) suggested that the deposit recorded a long interval of marine conditions during which very little clastic sedimentation took place. It is the view of the present author that the pebble bed was most probably deposited by a short-lived marine incursion, prior to the main Barton Sea transgression. When the sea withdrew, the pebble bed at Alum Bay, with part of the underlying sand and any sediment cover (which, possibly, were thin and sandy) would have become exposed. Colonization by plants could have ensued with accompanying soil formation. Thus the pebble bed could have constituted part of a viable pedological unit.

The Barton Sea later became effectively established, with an initial shelf sedimentation of the Barton Clay, followed later by the deposition of the Barton Sand. Curry (1965) and Murray & Wright (1974) believe that the Barton Sand is a shoal bar or barrier sand deposit in a silting-up embayment. Crustacean burrows indicate deposition of the Barton Sand in littoral marine conditions (Daley & Edwards, 1973), but the sea bottom could have been close to the mean sea-level (Edwards, 1967). Indeed, the layers of carbonised plant matter associated with pipe clays in the sands would suggest very shallow water bodies, which allowed aquatic (?) vegetation to develop and accumulate. Nearness to vegetated land areas is also indicated by the abundance of disseminated plant matter throughout the sand. The silting-up of the Barton Sea could thus lead eventually to the creation of flood-plain environments. Floral studies (Chandler, 1961; Edwards, 1967; Fowler _et al_., 1973) have indeed indicated the probable existence of flood-plains during the deposition of the uppermost Barton Sand sediments and much of the 'Lower Headon Beds'. These authors believe that the environments were not dissimilar to present-day coastal plains of south-east Asia and south-east U.S.A., especially the Florida Coastal Plains, where diverse surface processes are operating (Wanless, 1976a,b). They include differential sediment stripping, shifting and accumulation. In places, newly laid sediments are brought into ground-water zones, colonized by plants and subjected to variable surface and sub-surface drainage. There are also swamps, marshes, podzols and other related hydromorphic soils (Carroll, 1970; Hunt, 1972; Fitzpatrick, 1971). Similar situations possibly existed upon the silting-up of the Barton Sea in the Upper Eocene Hampshire Basin, thereby making the palaeosols' development possible.

16.4.2B Soil Processes

Information on soil processes in the Upper Eocene Hampshire Basin is mainly provided by the red-yellow podzols and gleysols at the top of the Barton Sand, Alum Bay; they are the most evolved and well-differentiated palaeosols under study. Each of the soil types is, however, considered below.

a) Red-yellow Podzols: These constitute the lower pedounits of the Barton Sand palaeosols (Fig. 6b). In the soil profiles, there is a pallid and mottled gleyson at the base; it is better developed in Profile B and represents the lowest ground-water table. The horizon would have been continuously wet, resulting in substantial reduction and mobilization of iron. Thickness of the gleyson has been taken as an indicator of the extent of fluctuations of ground-water tables (Mohr & van der Baren, 1954). The Barton Sand gleysons are very thin, indicating that water-table fluctuation was minimal, and possibly reflecting the prevalence of tectonic quietness in the Hampshire Basin during the development of the soils. Very possibly there was also a seasonal variation of temperature and precipitation because of the existence of an upper water table now represented by the vesons. During a drier season, the ground-water table would possibly be lowered, but the very porous nature of the sand deposit could, however, have ensured retainment of high capillary fringe. But the greatest iron accumulation generally occurs at the upper water table (Gidigasu, 1976); hence the vesons with the highest goethite contents would represent upper water levels. Fluctuation of the water table would also have enhanced precipitation of iron in the intervening horizons (the arenon and rosson); hence their intense coloration.

Iron in the podzol accumulated only as goethite $[\alpha FeOOH]$, a form of hydrated iron-oxide which is abundantly formed in present-day weathering profiles of humid and warm climatic regions (Mohr & van der Baren, 1954; Eswaran & Deconnick, 1971). The initial iron-oxides could have been the amorphous iron-oxides (i.e. $Fe(OH)_3$ and $Fe_3(OH)_8$) which are unstable but would, with time and maturity, dehydrate to goethite (Slayer & Schuylenborgh, 1970).

The existence of strong oxidising conditions in the soil would have induced the high goethite precipitation. Other conditions believed (Gidigasu,1976) to be capable of promoting iron precipitation include good aeration, relatively rapid loss of percolating waters, minimal biological activity and low concentrations of organic matter. In the podzols of the Barton Sand, sub-aerial aeration would have been effected through packing voids of skeletal quartz grains, channels and root-walls. Possibly, vegetation cover was very dense and the A-horizons (not preserved) were very thin. Oxidation of organic accumulates was rapid, as reflected in the low ($\leq$ 0·5%) organic-C contents of the soils. This sort of strong oxidative condition is common in the acid sandy soils of south-east U.S.A. (USDA, 1967; Hunt, 1972).

Local topographic factors, in addition to aeration, could have been responsible for the higher goethite contents and deeper coloration of podzols of Profile A compared to Profile B. Aeration and immobilisation of iron could, respectively, have been more intense and faster in Profile A. This profile may also have occurred at a lower elevation relative to Profile B. This could have induced gradient flow of ion-charged ground-water towards Profile A. Such topo-induced features have been described by Hardon (1938; quoted in Joffee 1949, p.415) from a low-lying plain in south-east Borneo. It involved substantial accumulation of iron and aluminium, with the formation of hard pan, in hydromorphic soils developed on a very sandy parent sediment with very little clay or iron-bearing mineral content. Similar lateral migration is typical of some African tropical lateritic soils studied by D'Hoore (1954) and Maignien (1966).

The crystal forms in which the goethite occurs in the podzols would have depended on the level of iron-concentration in the horizons. With an increase in available iron, the form could have changed from discreet thin laths to stacks of laths and interwoven laths and plates, and possibly glaebules as well. The interlocked goethite crystals would be mainly responsible for the induration of the vesons. Such crystals have been shown by Alexander & Cady (1962) to constitute the bulk of the hardened crusts of laterites. The mottles, being $<$ 3mm-sized masses of diffused or thick goethite accumulates, could represent locally migrated and accumulated iron.

Hydrolysis and alteration of silicate phases, particularly feldspars, mixed-layered phase and, to some extent, illite, would have led to the enrichment of kaolinite in the soils. Incongruously dissolved (etched and broken up) feldspars are present in the vesons of Profile B. Such dissolution features are common in soils; an example is that described by Wilson (1975) from Scotland. The dissolution processes would have been more intense in Profile A, where the kaolinite masses have formed. Conditions for kaolinite enrichment include acidic pH (4 to 5·5), good drainage, rapid loss of released bases (K^+, Na^+, Mg^{2+}, etc.) and the presence of alumina and silica in 1:2 proportion (Millot, 1970; Lukashev, 1972). Topo-induced ground-water recharge in Profile A may also have influenced greater kaolinite precipitation there than in Profile B.

The climatic regime deduced from the podzol compositions and morphology was seasonal, warm and humid. It is difficult, however, to ascertain whether it is tropical or sub-tropical. Vermiform kaolinite is most common in the weathering zones of present-day tropics (Fitzpatrick, 1971). But vermiforms also feature in the warm sub-tropics (Chukrov et al., 1972) and have, indeed, been observed in in situ soils from acidic rocks in Europe (Keller, 1983). Kaolinite enrichment in palaeosols has most often been attributed to tropical conditions. Such is the case for the

Tertiary palaeosols in Devon (Isaac, 1983) and vermiform kaolinites in residually-weathered pebbles, of Tertiary age, in Scotland (Koppi & Fitzpatrick, 1980). Goethite is less restricted to a particular climatic region, as long as it is warm and humid. It is, however, less favoured compared with haematite in hotter and drier conditions (Chukrov et al., 1973).

b) Gleysols: After evolving with their indurated vesons, the Barton Sand podzols could have been flooded and/or swept by tidal waters. The result was not only the loss of any probable topmost units (organic-rich A horizon) of the podzols, but also the deposition of new materials from which the upper pedounits (Profiles A and B) could have developed. It is even probable that the new materials were derived from, or translocated from, nearby areas undergoing similar pedogenesis to the earlier podzol of Profile B.

The presence of greyish, pallid patches and lenses in the arenons, rosson and gleyson, along with red mottles within the purplish argillon, are characteristic of hydromorphic gley soils (Buurman, 1980). They suggest intermittent water saturation of the soils, with the ground-water tables fluctuating very frequently and over variable depths. The aeration would have been 'amphibious' (see Mohr & van der Baren, 1954, p.294) but still accompanied by localised mobilization of iron and goethite precipitation.

The similarity of the compositions of the gleysol units to those of the arenon and gleyson of Profile B podzol indicates that their pedogenic factors were similar. Leaching and silicate alteration was moderate, and perhaps the pH was less acidic (i.e. ~ pH 5·5).

The gleysols, having evolved, could have been flooded by water-bodies within which their organic-rich top units were lost. The flooding further led to the deposition of the overlying green-clay base of the 'Lower Headon Beds', at Alum Bay/Heatherwood Point.

c) The pebble bed podzol: As stated earlier, the pebble bed at Alum Bay (Fig. 48) would not, on its own, have constituted a viable soil unit. Its development as a soil would have involved part of the immediately underlying sand deposit and, very possibly, a sediment cover. Within the soil, acid leaching would have caused alteration of the silicates, resulting in complete loss of the feldspars, and enrichment of kaolinite. The pH was probably ~ 5. Iron accumulation was very substantial, so aeration would have been very good, a direct consequence of the large packing voids between the pebbles and the coarse sand grains. The highest ground-water table would have coincided with the pebble bed, hence the high iron concentration and induration of the horizon.

After the soil had evolved, it must have been flooded by the transgressing sea. Erosion during transgression caused the loss of the non-indurated horizon above the pebble bed. The Barton Sea was swiftly established, initially with deposition of the carbonaceous sandy-clay, and subsequently of glauconitic sandy clays that comprise the lower part of the Barton Clay at Alum Bay. Carbonaceous matter in the earlier deposit is mostly plant deposit, which could easily have been derived from the A_0 horizon of the podzol.

d) Swamp soils: The swamp soil profiles (Fig. 48) are dominated by lignites which would have primarily accumulated as peats admixed with detritals. In places, the clastics have been current-concentrated into lenses or laminae of sands and clays. Differences in types of vegetation and/or sub-surface aeration would probably account for the variations in the organic-C contents and enriched trace-elements (Cu, V, Cr, U and As) in the lignitic horizons. The highly carbonaceous horizons (with > 13% organic-C) could have accumulated from similar, more abundant vegetation and in less leached conditions. Vegetation in the less organic-rich horizons could have been scanty, or, if substantial initially, much of the primary accumulates had been oxidised.

Poor drainage and water-logged conditions prevailed, and the established reducing conditions facilitated pyrite formation. But the occurrences of exogenous minerals (goethite, gypsum and jarosite) are indications that more oxic and better drained conditions prevailed on occasions. These sorts of drainage and aeration changes are typical of present-day acid sulphate soils, otherwise called cat-clays or Thiosols (Moorman, 1962; Fitzpatrick, 1971; Dones & Lynn, 1977). In cat-clays, pyrites formed during the early stage reducing conditions could become oxidised and hydrolysed in the latter stage oxic conditions. This often leads to the production of ferric sulphate, sulphuric acid, and the formation of exogenous minerals. Gypsum and jarosite are also common in many other present-day hydromorphic and saline soil types (Fitzpatrick, 1971).

Buurman (1980) has described jarosite pseudomorphs on pyrite from pseudogleys palaeosol in the Reading Formation at Alum Bay. Gypsum has also been observed pseudomorphed by calcite in hydromorphic palaeosol in Languedoc, France (Freytet, 1971, 1973).

In as much as the above would suggest a penecontemporaneous (Upper Eocene) age of the exogenous minerals, there are, however, strong arguments for a Recent age. Gypsum, in particular, would not be expected to be stable in under-saturated (with respect to sulphate phases) ground-waters. There is also no evidence of the existence of hypersaline water bodies, nor conducive arid conditions, during Upper Eocene times in the Hampshire Basin, although these prevailed in the Paris Basin in France (Pomerol, 1967). The Palaeogene sediments in Hampshire were uplifted in the Miocene culmination of the Alpine orogeny (White, 1921; Jones, 1981). So surficial weathering of pyrites to form the exogenous minerals would have followed, on exposed sediment sections.

In general, the swamp soils are poorly developed. Leaching has been insignificant, and iron mobilization and accumulation were very limited in scale and extent.

16.5 <u>Summary</u>

In the depositional areas of the Upper Eocene Hampshire Basin, newly laid sediments were penecontemporaneously exposed to terrestrial conditions, colonized by plants and acted upon by pedogenic processes. These are preserved as palaeosols. The horizons concerned in the Upper Eocene succession are the pebble bed and the top of the Barton Sand at Alum Bay that developed into red-yellow podzols and gleysols. Others are the lignites and associated rootlet-bearing mottled clays and sands that constituted hydromorphic, swamp soils. Surface and sub-surface drainages have been variable, being better for the podzols and poor for the hydromorphic profiles. Aeration and iron (goethite) accumulation have also been substantially higher in the podzols, along with acidic leaching and alteration of silicates. These conditions have also favoured the enrichment of authigenic kaolinite in the podzols. Leaching and iron-mobilization have been very limited in the hydromorphic profiles; these can be regarded as immature soils. The palaeosols are palaeo-environmentally significant. They indicate that the non-marine environments in the Upper Eocene Hampshire Basin were essentially vegetated, low-lying coastal plains.

The existence of warm, humid tropical - sub-tropical climatic conditions is also indicated, especially by the podzols with their high authigenic goethite and kaolinite contents. These deductions agree with those of earlier workers (i.e. Chandler, 1961; Edwards, 1967; Fowler et al.,1973; Keen, 1977; Hubbard & Boulter, 1983) from palaeontological studies.

CHAPTER 17

DISCUSSION

The present mineralogical and geochemical investigation of Upper Eocene sediments from the Hampshire Basin has provided information on the prevailing palaeoclimatic conditions, nature of the sediments' derivation and deposition. In addition, new data on mineral authigenesis in surficial and shallow-burial conditions has been obtained. These are discussed below.

17.1 Palaeoclimatic Conditions

The present work is the first to examine in detail the relationship between the mineralogy and geochemistry of the Upper Eocene sediments with inferred palaeoclimatic conditions. The mineralogical and geochemical data are consistent with a warm, humid sub-tropical climate. There are also indications that the early depositional waters were cool, shelf seawaters. These silted up, subsequently changing to estuarine and freshwaters, which were in equilibrium with the warm sub-aerial conditions.

17.1.1 Regional Palaeoclimate

A) Previous Floral-based Reconstructions

Previous palaeoclimatic reconstructions of the Eocene of southern England, which lay in the mid-latitudes, at ~ 40°N (Smith et al, 1981), during Eocene times have mainly been based on floral assemblages. The floral assemblage of Lower Eocene times in the region is characterised by mangrove taxa related to modern Nipa, the Rhizophoraceae, and reed swamp elements such as Scirpus and other Cyperaceae (Reid & Chandler, 1926; Collinson et al., 1981). This vegetation closely resembles those of present-day tropical south-east Asia. The vegetation later changed into a dominantly deciduous fern-conifer assemblage in Middle and Upper Eocene times. The mangrove taxa was initially interpreted (i.e. Reid & Chandler, op.cit.) as indicative of a prevailing rainy tropical palaeoclimate (cf. Fitzpatrick, 1971, Table 1). Daley (1972) reviewed the floral data and argued that the presence of temperate species (or 'extra-tropical'), such as Cantitila, Cupressinites, Araucarites and Sambucas in considerable ($\geqslant$ 11%) quantities is probably due to a seasonal variation in a prevailing 'tropical-like' climatic condition in which the temperature was most likely slightly lower than the ~24-27°C of present-day tropical regions. The fern-conifer assemblage, including Pinus, Sequoia, Gyptostroxylon species were interpreted (i.e. Edwards, 1967; Fowler et al., 1973) as an indication of a prevailing humid sub-tropical climate such as that characterising the coastal region of south-eastern U.S.A. Collinson et al. (1981) regarded the vegetational changes as manifestations of the gradual deterioration of the Lower Eocene climate. This view was shared by Hubbard & Boulter (1983), who, from sporomorph evidence, identified 'warm episodes' within the deteriorating climate, which was sub-divided into palynological climate zones. The early Upper Eocene coincided with the top of 'cooling zone d', which commenced in Middle Eocene times during the deposition of much of the Bracklesham Group. The late Upper Eocene was a 'warm sub-stage - Zone e', with temperatures of $\sim 15^{\circ}-20^{\circ}$C. In general, the Eocene climate was, according to Hubbard & Boulter (op.cit.), characterised by mild equable winters but very variable summers with mean annual temperatures of $\sim 10^{\circ}-20^{\circ}$C. The floral data is, however, inadequate for a definitive interpretation that the Eocene palaeoclimate was tropical or humid sub-tropical. In contrast, the floral assemblage of the succeeding Oligocene times is definitely non-tropical (i.e. Pallot, 1961). Daley (1972) and other authors hold a consensus view that the Oligocene flora indicate the establishment of a markedly cooler climate than that of the Eocene; and this was typically humid sub-tropical or 'Eastern Margin Warm Temperate'.

B) Previous Mineralogical-based Reconstructions

Previous mineralogical evidence for warm but variable sub-aerial conditions in the Tertiary period have mostly been obtained from studies of sediments and palaeosols in Cornwall and Devon, south-western England. Isaac (1981, 1983) identified advanced, lateritic-weathering of Cretaceous sedimentary rocks in east Devon. Such deep weathering requires either high year-round humidity or alternating very wet and dry conditions. The weathering was dated as being of latest Cretaceous - early Tertiary age (i.e. Palaeocene), and produced goethitic and kaolinite-rich residual soils which were believed to have been eroded in Middle and Upper Eocene times to form nearby gravel deposits (i.e. the Tower Wood Gravels). There is no evidence, however, that this lateritic weathering occurred all over southern England; although Isaac (1983) correlated it with similar weathering in Antrim, Northern Ireland (cf. Wright, 1924; Montford, 1970). The occurrence of laterite in Ireland and the Faroes (i.e. Nielsen & Kerr, 1978) at high, $\sim 45^{\circ}$N, latitudes supports the floral data in indicating the prevalence of almost global warm, humid conditions during early

Tertiary times; occurrences of dry, hot conditions and evaporite accumulations being very limited (see Frakes, 1979).

Isaac (1983) and Freshney et al. (1982) also found less advanced weathering profiles developed over Upper Palaeozoic metasediments in east Devon and Cornwall. The profiles comprise 'young or immature' soils, which the authors interpreted as typical of sub-tropical weathering profiles. They were believed to have developed in the Eocene-Oligocene times and were penecontemporaneously eroded to form the late Eocene-Oligocene fluvio-lacustrine sedimentary deposits in the Dulston, Petrockstow and Bovey Basins of south-western England. Similarly weathered Palaeozoic rocks in Wales most probably contributed to Tertiary sediments in the Cardigan Bay Basin (Mochras Farm) (Woodland, 1971).

A study of palaeosols in the Reading Formation of the Hampshire Basin at Alum Bay on the Isle of Wight was made by Buurman (1980a). The author identified hydromorphic gleysols and pelosols, but whilst highlighting their palaeogeographic and stratigraphic importance, he did not make any palaeoclimatic interpretations. This may be due to the azonal nature of such soils (cf. Carroll, 1970; Fitzpatrick, 1971). However, the palaeosols contain horizons with enriched kaolinite contents. This would suggest the prevalence of warm humid sub-aerial conditions conducive to kaolinite formation from the leaching of pre-existing silicate minerals.

Another probable indicator of the palaeoclimate are the 'sarsens' that commonly occur over the Devon Plateau and Chalk Downs of southern England (i.e. Clarke et al., 1967; Isaac, 1979, 1983b; Summerfield & Gouldie, 1981). The 'sarsens' (or silcretes) are relic silica - and/or iron oxide - cemented blocks of sandstones often consisting of Chalk-derived materials including pebbles (i.e. Jones, 1980, p.26). However, unlike silcretes, which commonly constitute soil profiles in present-day hot, dry, semi-arid areas of Namibia, South Africa and Australia, the 'sarsens' mostly occur as strewn boulders and rarely in place. The sarsens are also characterised by textural features mostly typifying non-weathering (or diagenetically formed) silcrete profiles (i.e. Summerfield & Gouldie, 1981). These silcrete types are, however, near-surface phenomenon requiring hot and humid sub-aerial conditions for effective mobilisation and accumulation of silica and/or iron oxides. Isaac (1983b) has, in fact, found that the silcretes from Devon possess features typifying both weathering and non-weathering profiles. The author thus suggested that the silcretes have probably had complex evolutionary history involving several sub-aerial weathering and sub-surface diagenetic stages.

C) Reconstruction from Present Study

In the Upper Eocene succession under study, the nature of the clay assemblage and the occurrence of palaeosols and associated pedogenic kaolinite and goethite provide mineralogical evidence for the prevailing palaeoclimatic conditions. Further evidence is also provided by the presence of micritic-mud calcite, glaucony and early diagenetic siderite and ferroan calcite.

i) Clay assemblage

Clay assemblages in sediments result from many, often inter-related, factors which include climate, source rock composition, depositional conditions and alteration after deposition and burial. In the case of the Upper Eocene succession under study, the sediments have only been shallowly buried (i.e. to $\sim$150-200m, see Table 1), and therefore not subjected to elevated temperatures and pressures. In addition, no evidence has been found for diagenetic alteration of the clastic mineral constituents. The predominating clastic sediments in the succession are also characterised by closely similar bulk compositions and relatively constant clay mineralogy, which would suggest little changes in the sediments' provenance (see Section 17.3). As such, the clay mineralogy is useful for palaeoclimatic interpretations (cf. Singer, 1980).

Clay products of weathering vary with climatic zones. In humid climates, chemical weathering predominates (Ollier, 1969) with intense weathering and mature soils containing substantial amounts of iron-oxide, kaolinite and/or gibbsite, typifying tropical regions; whilst poor to moderate weathering with soils rich in silicate phases, particularly feldspars, illite and smectite, characteritse the sub-tropical and warm temperate regions (see Dixon & Weed, 1977).

The clay assemblage of the Upper Eocene succession consists of degraded or poorly crystalline illite $\geqslant$ smectite $>$ kaolinite $\simeq$ illite-smectite (Tables 8a-h). This is considered to be a result of relatively moderate weathering of illitic and smectitic rocks. Such an assemblage would be typical of humid, warm sub-tropical and temperate climates. Alternatively, it might also be the product of immature soils of a tropical climate because, in present day tropical regions, lower parts of deep weathering are often characterised by low kaolinite abundance and little alteration of primary silicates and 2:1 clay phases (i.e. Kronberg <u>et al.</u>, 1979; Calvert <u>et al.</u>, 1980; Eswaran & Bin (1980). Such characteristics were also observed by Isaac (1983) in the lower parts of the lateritic Palaeosols from east Devon.

The latter suggestion would imply that the Hampshire Basin and adjoining areas had been subjected to intense tropical weathering, but that erosion had been very active, removing the soils before they could evolve to maturity, and that the resulting clay assemblage was as now observed. Such interpretation would be grossly inconsistent with the floral data enumerated earlier. It is also unlikely that erosion would not have equilibrated with weathering on the one hand and sedimentation on the other. There are no indications that sedimentation involved high rates of clastic supply, as would be expected for a rapidly eroding hinterland. The rate of erosion must have been moderate and in-phase with sedimentation. Therefore the relatively uniform clay assemblage of the Upper Eocene sediments, which accumulated over ~ 5 m.yrs (i.e. 40→ ~ 35 Ma, see Table 1), is probably an 'equilibrated assemblage' resulting from the prevailing sub-aerial conditions. Hence the lack of extensive kaolinite and/or gibbsite makes it seem likely that the climate was not tropical.

ii) Palaeosols

More definitive evidence for the prevailing conditions is provided by the residual palaeosols observed in the succession. Three different types present were identified as red-yellow podzols, gleysols and hydromorphic swamp soils (Figs.6b,48). The podzols and gleysols are zonal soils (i.e. Plates 18,19; cf. Fitzpatrick, 1971), and hence more useful for palaeoclimatic interpretation. These are $\lesssim$ 1m-thick and are characterised by a high abundance of authigenic kaolinite and goethite (Tables 7e, 8e). Most certainly, they correspond to the kaolinite-goethite facies weathering of Chesworth (1975). These palaeosols are equivalent to present day Red Earths or Terra Rossa, which predominantly formed from moderately intense weathering in humid sub-tropical climates (cf. Fitzpatrick, 1971; Hunt, 1972). Although a few have been reported from the tropics in south-east Asia (i.e. Soepraptohardjo & Ismangum, 1980), these soils are not characteristics of the tropics.

The penecontemporaneous development of the palaeosols, considered in detail in Section 17.2.2D, was consequent as a result of eustatic falls of the sea level attended by localised emergence of freshly laid sediments. The red-yellow podzols and gleysols are characterised by clay contents with more kaolinite ($\sim$ 35-100%) than the rest of the succession ($\leq$ 15% kaolinite). The localised occurrence of these soils, at Alum Bay, raises the question as to whether they were typical of the land areas bordering the Hampshire Basin. The relatively intense weathering producing the palaeosols was certainly facilitated by the porous nature of the sandy parent sediments. This allowed good drainage and aeration, with considerable fluctuations of the ground-water table, and hence extensive leaching of the pre-existing silicates. In contrast, the hinterland would mainly comprise extensive exposure of low-lying to moderate-relief calcareous rocks, particularly the Chalk. These could have had high water-tables and ground-waters rich in liberated Ca^{2+} ions. These would not be expected to allow extensive acidic leaching. The result would be little evolved soils, possibly hydromorphic types, with little or no kaolinite formation. The lack of high kaolinite does not imply that warm, humid sub-tropical conditions did not prevail in the basin and surrounding areas. The development of the red-yellow soils is, in fact, a pointer to sub-tropical conditions. Similar red-yellow soils are widely developed on sandy parent materials along the south-eastern coastline of the U.S.A. (i.e. Hunt, 1972). This is supported by the similarity between the vegetation of the Upper Eocene Hampshire Basin and that of the sub-tropical south-eastern U.S.A. (i.e. Fowler et al., 1973). It seems that the in situ palaeosols observed might not have been widely developed, since high kaolinite concentrations are only observed locally.

Another important aspect of the palaeoclimate is its probable seasonal variation that the horizons comprising the red-yellow podzols palaeosol would suggest. Although incompletely preserved, the profiles (Fig.6b) is characterised by a lower gleyson/arenon (11Cg) and an upper veson (IIB 21ir) horizon. The former constitutes the horizon of the lowest ground-water table (cf. Buurman, 1980a). Being continuously water-logged the horizon is much leached, and contains pallid patches, but low accumulation of iron oxide and lesser authigenesis of kaolinite. The veson constitutes the highest ground-water table, and is characterised by a high accumulation of iron oxides and kaolinite authigenesis (cf. Gidigasu, 1976). The fluctuation of the water table within the profile is thus reflected in an increase in iron-oxides, and hence intensity of coloration, from the gleyson to veson (cf. Plates 18 and 19). Slager & Schuylenborgh (1970) and Mohr & van Baren (1954) have described similar water-table fluctuations and coloration variation from coastal plain soils respectively from Surinam and tropical south-east Asia.

Ground-water tables are, amongst several factors, influenced by climatic conditions, with changes in the water tables being more pronounced in regions with markedly dry-wet seasons. Often, ground-water tables are at their lowest levels during dry (and hot) seasons, although water may still rise to the soil surface by the capillary-rise effects of evaporation. Whilst non-observation of cryogenic features precludes frosty conditions, the palaeosols are, however, inadequate to indicate whether the seasonal variations of the Eocene palaeoclimate were of equably 'cool winter' and a 'more variable warm summer', as suggested by Hubbard & Boulter (1983).

iii) Freshwater biomicritic limestones

The microfloral-induced precipitations of micritic calcite and the accumulation of limestones in ponded hard waters of the late Upper Eocene non-marine environments may be considered as indicators of 'seasonal variations' that affected the atmosphere and, in addition, the depositional water bodies. Probable variations in the palaeo-temperature of the Upper Eocene depositional waters is considered later. It should be stated, however, that the freshwater biomicrite limestones in the 'Lower Headon Beds' are marl-lake type micritic-mud accumulations (i.e. Murphy & Wilkinson, 1980, see Section 1.7.5.2). They are similar to the Holocene calcareous tufa described from the area of Southampton (i.e. Hudson & West, 1972). Marl lakes are commonly found in warm sub-tropical and temperate regions of the U.S.A. (i.e. Feth, 1964). Terlecky (1974) has found, in Littleville Lake in New York State of the U.S.A., that micritic calcite precipitation ensuing from the lowering pCO_2 effect of photosynthesis activities of aquatic green algae (i.e. Charaphytes) is greatest during the warm 'summer' seasons. It is during the summer that the algae bloom; whilst the warming up of the water body further causes losses of CO_2 to the atmosphere, thus contributing to the lowering of pCO_2.

iv) Fe-rich authigenic phases

The presence of a prevailing warm, humid palaeoclimate in the

Upper Eocene Hampshire Basin is manifested in the occurrence of iron-bearing mineral phases comprising detrital goethite, high Fe-containing glauconitic mica, and diagenetic siderites and ferroan calcites. The formation of iron-rich glaucony and siderite particularly has been correlated with the prevalence of intense advanced weathering and the presence of high iron influx in the Cretaceous-Tertiary rock of the USSR (Shutov et al., 1970b); the Holocene Black Sea (Hsu & Kelts, 1982); the Japanese Palaeogene (Matsumoto & Iijima, 1981); and the Carboniferous of England (Pearson, 1979). The significance and confirmation of such inferences for the Hampshire Basin would, however, require further investigation of similar iron-rich mineral phases occurring in other parts of the Palaeogene succession.

v) Comparison with the Paris Basin

The inferred warm, humid palaeoclimate of the Hampshire Basin is different from that of the Paris Basin of France where pronounced alternating warm-wet and hot-dry climatic conditions have been established as prevailing during the Palaeogene (i.e. Chatteauneuff, 1980). The dry conditions are attended by the existence of saline water bodies within which chemical sedimentation and authigenesis of gypsum and fibrous magnesian clays occur.(Fontes & Lucas, 1968; Millot, 1970; Pomerol, 1973). Widespread lateritisation and abundance of rainy-tropical floral species have also been shown to occur during the wet climatic period (i.e. Chatteauneuff, op.cit.). Daley (1972) considered the problems arising from the different contemporaneous climates in the Palaeogene Hampshire Basin and Paris Basin. These problems are not resolved but may be due to relative movements of the ocean currents and the trade winds, as a result of latitudinal shifts in the Eocene climatic belts. Further studies are called for.

17.1.2 Depositional Waters Palaeo-Temperatures

A) Previous Deductions

The palaeotemperature of the depositional waters is also important in palaeoclimatic reconstruction. Water temperatures, particularly of the seas, depend on several factors that include depths, current patterns and sub-aerial temperatures. In the Eocene of southern England the nature of the depositional waters has previously been assessed from fossil assemblages. Curry (1965), from molluscan assemblage, and Murray & Wright (1974), from foraminiferal assemblages, found the Palaeogene seas to vary.

These include a 100-350m deep, cool ($\sim$ 16-18°C) London Clay Sea in the Lower Eocene times; a variably deep (up to 250m), but warm ($\gtrsim$ 18°C) Middle Eocene Bracklesham Sea; and a shallow ($\sim$ 50m) cool ($\sim$ 16-18°C) Barton Sea of the early Upper Eocene times. These variations were supported by Burchardt (1978) from studies of oxygen isotope composition of molluscan shells from the area of north-western Europe. The temperature of the seas did not, therefore, necessarily reflect the prevailing sub-aerial conditions, although the subsequent cool ($<$ 10°C) Oligocene waters coincided with a global climatic change (i.e. Burchardt, op.cit.).

The variation in the Palaeogene waters was essentially brought about by the interplay of water circulation between cool northern seas and warm southern seas. Whilst the opening of the North Atlantic Ocean and the Norwegian-Greenlandic Sea facilitated circulation of cold polar waters to the low latitudes(i.e. Cita, 1971), the Tethyean Sea was dwindling and closed to through-going warm equatorial circulation (Kennett et al., 1975; Van Andel et al., 1975).

B) Deductions from Present Study

i) Sr contents of aragonitic fossil shells

Some indications of the water palaeotemperature in the present study is provided by the Sr content of aragonitic fossil gastropod and pelecypod shells, and the occurrence of authigenic glaucony. Sr incorporation in invertebrate skeletons is biochemically controlled. The biochemical processes concerned are not well understood (i.e. Lippman, 1973). Nevertheless the amount of Sr incorporated has been found to be influenced by the phylogenetic level, the temperature of the water habitat and, perhaps, the water salinity (i.e. Lowenstram, 1954; Dodd, 1967). Molluscs are highly evolved and their shells are characterised by $\leq$ 2500 ppm Sr incorporation (i.e. Kinsman, 1969). Decrease in the incorporated Sr contents, with increasing temperature, has been established for Mytilus (Dodd, 1965) and Cardium edule (Hallam & Price, 1968). Utilisation of the Sr contents of shells for palaeotemperature deduction is, however, restricted because fossil shells are often subject to diagenetic dissolution and alteration on burial. Only in very few instances, as in the present study, where no alteration of the shells is observed, can palaeoclimatic utilisation be feasible. Although the ideal situation in which the shells concerned are of the same species is not met in the presently studied succession, a significant systematic decrease was nevertheless found in the Sr contents of the various shells up the succession (see Table 14). The highest Sr concentrations, 2450 → 2000 ppm occur in shells (i.e. Clavilithes, Crassatelites and Corbula) from the Barton Clay. Shells from the Barton Sand formation, and the brackish Mammal Bed at the base of the 'Lower Headon Beds' are characterised by 2000 → ~1300 ppm Sr. The shells, which include Cardita, Chama, Battilaria, Cyrena and Viviparus, are essentially estuarine to tidal flat species. Occurring higher up in the freshwater clays and limestones of the 'Lower Headon Beds' are shells including Viviparus and Galba, possessing 750 → 550 ppm Sr concentrations. These Sr variations are tentatively regarded as an indication of a relative increase in the temperature of the depositional water up the succession. Thus the high values can be equated to the cool waters of the early Barton Sea. This warmed up as it shallowed - or silted up (see Curry, 1965), and is reflected in moderate Sr values. The subsequently established non-marine conditions in which the waters equilibrated with the prevailing warm sub-aerial conditions show the low Sr values.

It should, however, be noted that changes in Sr contents might be related to changes in salinity, although a convincing relationship between the two parameters has never been demonstrated (see Hallam & Price, 1968; cf. Dodd, 1965 & 1967). Support for the deductions is given by the correlation with respect to the molluscan and foraminiferal assemblages which also indicate a cool early Barton Sea. The later warm, shallow waters are also supported by the warm episode 'Zone e' of Hubbard & Boulter (1983) and, in addition, by the precipitation of micritic calcite for the freshwater limestones. Further investigation of other Palaeogene fossil shells, also believed to be preserved unaltered, should be undertaken in order to obtain more information.

ii) Occurrence of authigenic glaucony

The widespread formation of glaucony in the early Barton Sea provides further support for the presence of cool, non-tropical shallow waters. Recent glaucony occurs in passive shelf and continental slope environments between latitude 50°S and 60°N. Their formation is, however, optimum in water columns with 15-20°C temperature, ~ 30-500m depths and essentially receiving little clastic supplies or distant from drainage outlets (Odin & Matter, 1981). The shallowest water depths considered (i.e. Cloud, 1955; Fairbridge, 1967) conducive to the formation of glaucony are between 30 and 50m in cool seas, but at much deeper (~ 250m) depths in warm tropical seas.

In the case of the early Barton Sea, the foraminiferal assemblage has indicated (Murray & Wright, 1974) the water depth to be shallow, often ~ 50m and most probably < 100m. In addition, the nearness of a drainage outlet is indicated by the occurrence of abundant disseminated drifted plant materials and stray estuarine shells (Chandler, 1960; Curry, 1965). These hydrological conditions would not normally be expected to have favoured extensive glauconitisation observed in the Barton Clay. The fact that glaucony was formed at these depths suggests that the Barton Sea must have been cool. In addition, there must have been a high abundance of detrital iron-oxides and low supply, and hence slow sedimentation rate, of clastic detritus. If the water had been warm, and the detritus supply high, berthierine, a 7Å layered-silicate previously called chamosite (Brindley <u>et al.</u>, 1968) would have been expected. Berthierine, unlike glauconies, is predominantly limited to shallow (off river mouths and deltas), warm (> 20°C) tropical waters along the West African and north-eastern South American coastlines (Porrenga, 1967; Odin <u>et al.</u>, 1981). Berthierine was not detected in the Upper Eocene sediments studied, and has never been reported from the Palaeogene sediments of southern England. Perhaps further detailed search may reveal it. The absence of berthierine is unlikely to be due to a diagenetic transformation to 14Å chlorite (Velde, 1977) because chlorite is only found in trace amounts in the sediments. Because of its low abundance, it is difficult to ascertain whether the chlorite is detritally derived or diagenetically formed, as suggested by Gilkes (1966).

17.1.3 Summary

In summary, the study showed that the prevailing palaeoclimate of the Upper Eocene Hampshire Basin and adjoining areas was warm, humid and probably sub-tropical. In addition, the depositional waters were initially those of a cool sea, but later changed into warm estuarine and freshwaters. Further studies of the Palaeogene succession in the basin from mineralogical and geochemical point of view should provide some information on the prevailing palaeoclimate. Attention might particularly be paid to the ferruginous and kaolinite-rich Lower Eocene 'Bagshot Beds' and parts of the Middle Eocene Bracklesham Group. They will probably contain 'zonal' palaeosols useful for palaeoclimatic interpretations.

17.2 Palaeogeography and Sedimentological Conditions

17.2.1 Previous Palaeogeographic Reconstructions

A) Regional Palaeogeography

Palaeogeographic reconstruction of Tertiary southern England has been predominantly based on litho- and bio-stratigraphic studies. Recently, further significant contributions have come from geomorphological (i.e. Jones, 1981) and regional tectonic (i.e. Ziegler, 1962) studies. Jones (1981) showed that three main environments existed in the region during Tertiary times. These comprised uplands of moderate relief (~ 400-700m), lowlands and coastal plains, bordering depositional (basinal) areas of the London and Hampshire Basins (see Fig.25). The basins were subjected to interplay of marine incursion and regression and cyclical deposition of marine, brackish and freshwater facies (Stamp, 1921). Drainage was essentially eastwards and was dominated by the 'Proto-Thames' to the London Basin and the 'Solent River' to the Hampshire Basin (Fox 1862; West, 1980; Jones, 1981). Plint (1983) has further suggested the existence, at least in Middle Eocene times, of a limited number of small tributaries to the 'Solent River' draining areas of the present day English Channel to the south.

The Hampshire Basin, which is the north-western part of the Hampshire-Dieppe Basin, is a large flat-floored NW-SE trending synclinal structure (Groupe Norois, 1972). This is bounded by the Portsdown anticline and the Weald-Artois anticline to the north and north-east, and the Purbeck-Isle of Wight-Bembridge-St.Valery monoclinal flexures to the south and south-west (Smith & Curry, 1975; Stoneley, 1982; Plint, 1983). Further away, the Cornubian Massif occurs in south-western England and the Amorican Massif in northern France and Brittany, whilst the 'North Sea' occurred to the east. This was connected to the cold Greenlandic-Norwegian Sea to the north, the dwindling warm Tethys Sea and the opening Arctic North Atlantic Ocean (Ziegler, op.cit.) to the south and south-west.

B) The Upper Eocene Depositional Environments

Detailed palaeogeographic conditions of the Hampshire Basin and the Upper Eocene depositional settings have been deduced on the basis of several palaeontological studies. These include the floral assemblage (Chandler, 1926-1964; Fowler et al., 1973), the molluscan fauna (i.e. reviewed by Curry, 1965); foraminiferal assemblage (i.e. Murray & Wright, 1974); ostracods (Keen, 1977, 1978) and mammalian remains (i.e. Cray, 1973; Hooker et al., 1980). Some information has also come from both clay assemblage studies (Gilkes, 1966) and heavy mineral assemblage studies (Blondeau & Pomerol, 1968). Murray and Wright (1974) and Plint (1983) showed that in the latest Middle Eocene times, a shallowing marine embayment probably existed in areas stretching from Dorset in the west of the basin to, and beyond, the Isle of Wight in the east. Floral assemblages (Chandler, 1960) suggests that the embayment was bordered by well vegetated coastal lowlands.

Curry (1965) and Murray & Wright (1974) further showed that the earliest Upper Eocene time was marked by the onset of the Barton Sea transgression onto the pre-existing embayment. A coastline was initially established in the west of the basin, running through Alum Bay, Highcliffe and Hengistbury Head. This was followed by the establishment of tidal marsh to shelf environments. Occurrences of abundant Rotaliina sp. (i.e. Cibicides pygmens) foraminifera and ostracods, including Cyamocytheridae ssp (Keen, 1978) indicate the depth of the established Barton Sea to be probably of the order of ~50m, and certainly less than 100m. The Barton Sea later started to silt up. Curry (op.cit.) and Murray & Wright (op.cit.) believed the silting-up to result from the build-up of shoal or barrier sands in areas located south-east of the Isle of Wight. Similar Middle Eocene silting was suggested by Plint (1981) as probably being due to the existence of a submarine tectonic or tectonically-controlled barrier south of the Isle of Wight. The silting changed the Barton Sea into a shallow, estuarine-lagoonal water with bodies characterised by Chama, Olivella branderi, Polymesoda (Cyrena), Battilaria and burrows of the crustacean Ophiomorpha (Burton, 1931; Daley & Edwards, 1973). Subsequently, coastal flood plain environments similar to the present day coastal plain of the present-day south-eastern U.S.A. were established. There is an abundant but diverse fossil content, which includes Charophytes (Feist-Castel, 1977); Viviparus, Unio, Galba and Planorbina ssp gastropods (i.e. Edwards, 1967); Candona, Cypridopsis, Moenocypris, Cytheromorpha and Neocyprides ostracods (Keen, 1977); rodents, crocodile, turtle and bird remains (see Hooker et al., 1980) and plant assemblages that Chandler (1961) grouped as 'gregarious genera and species'. These suggest environments consisting of sluggish streams, rivers, swamps and ponds (Edwards, 1967; Fowler et al., 1973; Cray, 1973; Keen, 1977). They also indicate the variability of the water bodies from fresh (oligo-haline) to brackish and estuarine (poly-haline) (Keen, 1977).

17.2.2 Deductions from the Present Study

Contributions from a mineralogical and geochemical basis in the present study are generally consistent with the previous reconstructions. The data, however, are of much less value for systematic palaeoenvironmental reconstruction than the palaeontological data. Facies changes are very weakly expressed, although the data has been sufficient to recognise sub-aerial and submarine conditions, and also to provide information on the relative hydrological conditions, i.e. water depths and prevailing current energy. Some appreciation of tectonic influence on the palaeogeography can also be made.

A) Facies Variation

Facies analysis is one major use to which sediment composition is often applied. This involves identifying and relating significant compositional variations within a suite or succession of sediments to differential prevailing conditions or environments within a sedimentary basin. There are, however, no well established compositional criteria; both mineralogical and geochemical criteria have been used. Those commonly employed include basinward increase in the abundances of clay minerals; Al_2O_3, K_2O, MgO as well as trace elements such as B, I, V, Cr, Ni, Ba and Ga (i.e. Hirst, 1962; Kukal, 1971). The concept involved is that greater deposition of finer grained detritus occurs in the lower energy regimes of drainages, and seawards from drainage outlets.

Also important is the shelfwards differential flocculation and settling first of kaolinite, and then illite and smectite (Porrenga, 1966; Krumm, 1969). Those basinward clay variations are also often geochemically mirrored by a number of elements. In particular, K and Mg not only normally occur more in the 2:1 layered clays (i.e. Weaver & Pollard, 1973); they could, in addition, be adsorbed from sea-water into the interlayer portions of degraded illite and smectite (i.e. Nicholls & Loring, 1960). Furthermore, 2:1 clay phases, which are generally characterised by higher contents of structurally-held trace elements (i.e. Hirst, 1962) may adsorb more of the dissolved trace elements in sea-water. These might be manifested as shelfward increase in the abundance of hydrolysate trace elements (cf. Hirst, 1962; Rosler & Lange, 1971; Wedepohl, 1971). However, the significant dependence of sediment composition on the nature of provenance, modes of derivation and deposition, and diagenetic history (i.e. Potter et al., 1980) has led to contentious considerations of the usefulness of trace elements for facies analysis (i.e. Walker, 1972; Potter et al., op.cit.).

The Upper Eocene succession is predominantly (~ 95-98%) composed of marine and non-marine clastic sediments, i.e. clays and sands. The other lithologies being freshwater limestones and diagenetic carbonate bodies. The probable mode of sediment derivation is considered later (Section 17.3). They are, however, found to be dominantly composed of quartz, with lesser clays and small amounts of potassic feldspars (Fig.20a-c). With respect to average sands and shales, the clastic sediments are more siliceous (sandy) but less abundant in alkali and alkaline earths. The clay sediments are characterised by (Quartz + Feldspar)/(Quartz + Feldspar + Total Clay) or (Q+F)/(Q+F+Cl) ratios of 0·4 to 0·6 (Figs.21a-c & 22), the quartz and feldspars being mainly of silt to medium sand-sized (< 600 µm) grains. Employing the (Q+F)/(Q+F+Cl) ratio values as a substitute (tenuous) index of particle size distributions, the Upper Eocene clay deposits would be regarded as sandy to very sandy clays (cf. Krumbein & Sloss, 1963 - Fig.5-7; Fuchtbauer, 1974 - Fig.21). The sand sediments are typified by (Q+F)/(Q+F+Cl) ratios of 0·75 to 0·98 (Fig.22a) and are dominantly composed of medium sand-sized quartz grains. These are quartz-sand type sediments.

In general, the bulk sediments mineralogy (Fig.20) shows no significant systematic differences to exist between the marine and non-marine clastic sediments. This is similarly reflected by the clay mineralogy. The clay assemblage generally consists of detrital illite $\gtrsim$ smectite $>$ kaolinite $\simeq$ illite smectite; deviations occur only where recognisable sub-aerial in situ leaching has enriched kaolinite (Figs.23a-c). Illite and smectite, together, constitute about 70-80% of the clays, the illite being slightly more abundant in the non-marine 'Lower Headon Beds'. In parts of the Barton Clay, the illite estimates include substantial amounts (unestimable) of structurally similar but authigenically formed glauconitic mica of clay-sized glauconies. Smectite occurs in relatively higher amounts in the succession at Whitecliff Bay, the lower parts of the Barton Sand on mainland Hampshire, and in a few horizons within the Barton Clay at Alum Bay. This distribution of smectite, along with the constancy of abundance of the kaolinite and mixed-layered illite-smectite phases throughout the succession, shows the absence of differential flocculation.

The relatively small changes in the clay mineralogy, along with the low abundance of sodic feldspars in the succession, is geochemically mirrored by small changes in the alkali and alkaline earth abundances. Mg/Al ratios of $\sim 0{\cdot}1$, and Na_2O/K_2O ratio values of $< 0{\cdot}1$ characterise the shelf Barton Clay sediments, compared with $< 0{\cdot}1$ Mg/Al ratios and $\sim 0{\cdot}1$ Na_2O/K_2O ratios for clayey sediments in the 'Lower Headon Beds' and the 'Barton Sands' (Figs. 21a-c). These differences, albeit very small, are significant in that they correlated with the differential crystallinities of the clay minerals in the succession (cf. Tables 8a-c). More degraded clay phases characterise the non-marine 'Lower Headon Beds'. Several works, including those of Nicholls & Loring (1960), and Altschuler et al. (1963), have shown that clay phases could be liable to degradational loss of potassium and magnesium in non-marine environments. In marine environments, however, clay minerals could remain stable as derived, or, in the case of 2:1 phases, undergo structural reconstitution (aggradation) by adsorbing Mg^{2+} and K^+ into their interlayer position (see Grim, 1968; Millot, 1970). The possibility of leaching in the Upper Eocene non-marine environments is indicated by the occurrence of several palaeosol units. These palaeosols contain substantial amounts of exogenously formed minerals; these are considered further in Section 17.2.2D). In the marine environments, however, better preservation of 2:1 clays rather than extensive Mg^{2+} adsorption would account for the relatively higher Mg/Al ratios of the Barton Clay sediments. The only significant clay reconstitution and/or neoformation concerns the authigenic glaucony, and would have involved the utilisation of substantial amounts of iron and potassium. The glauconitisation processes are considered in detail in Section 17.5.3.

In the case of the trace elements, the elements determined were found to be mostly hydrolysate. These occur in $\sim$ 50-500 ppm concentrations, and show strong correlation with the detrital clay minerals and feldspars. In addition, there is an association between plant materials and As, Ce, Cr, Cu, Zn, I and Pb in the lignitic horizons, and between biogenic (fossil shells) material and Sr, Mn, Ce, Pb, I and Zn in the fossiliferous horizons. However, neither the abundances of the hydrolysate elements, nor their relative ratios (i.e. Cr/Ni, Ba/Al) show significant systematic facies-related variation within the clayey sediments. Similar variations of the hydrolysates, but with lower absolute abundances, also exist in the sand sediments. These findings lend support to the contentious suggestions of inadequacy of trace elements for facies analysis (i.e. Walker, 1972). This deduction could not, however, be ascertained for boron (B), which has much wider application (i.e. Kukal, 1972), but not estimated in the present study.

In general, the compositional data obtained for the Upper Eocene clastic sediments is inadequate for facies analysis. The only probable indicator of salinity changes is the extent of Mg^{2+} substitution in the diagenetically formed siderites. Sideritic ironstones were developed in both the marine and non-marine sediments; their probable modes of formation are considered in detail in Section 17.5. The siderites, although dominantly Ca-substituted (see Figs. 19, 36) are characterised by variable amounts of Mg^{2+} substitution (cf. Figs. 36, 38b). Whilst the extent of Mg^{2+} substitution will depend on the abundance of Mg^{2+} relative to Fe^{2+} in the pore fluids at the time of precipitation, it appears that the Mg^{2+} is essentially dependent on the Mg-content of the original depositional waters. Normally, sea-water contains more ($\sim$ 1300 ppm) Mg^{2+} than fresh-waters ($\sim$ 11 ppm). Therefore the observed $\lessapprox$ 2 mol% $MgCO_3$ in the non-marine ironstones siderites compared with the 3-5 mol% in the marine ironstones is considered to be a facies variation manifestation. Weber & Williams (1965) also reported a similar variation in Mg from the bulk chemical composition of some Carboniferous sideritic nodules in the U.S.A.

The previously highlighted poor facies differentiation with respect to the bulk sediments composition will probably be due to two main factors. These are the constancy of the provenance and mode of sediment derivation, and the existence of closely similar hydrogeological conditions throughout the Upper Eocene times of the Hampshire Basin. The sediments were predominantly derived from very nearby land areas; details of these are given in Section 17.3. Aspects of the prevailing hydrogeologic conditions are considered below and in Section 17.4.

B) Water Depths and Current Conditions

Compositional parameters of significance to the inter-related water depths and current conditions include the relative abundances of the silicate phases and quartz (see Figs.21a-c) and the occurrences of pebbles and high zirconium concentrations.

As previously stated, the clastic sediments are characterised by high quartz contents, small abundances of clay minerals, and little amounts of feldspars (Tables 7a-g, Figs.20a-c). With the (Q+F)/(Q+F+Cl) ratio values of 0·4 to 0·6 characterising the clayey sediments, and values of 0·75 to 0·98 typifying the sands, the Upper Eocene succession is essentially comprised by moderately well-sorted sandy-clays, and well-sorted quartz sands. These are characteristics of sedimentation ensuing from, or attending the prevalence of relatively strong to very strong current conditions (cf. Krumbein & Sloss, 1963; Folk, 1951).

Davis (1983 - Ch.2, 10 & 11) has highlighted the significant influences of tide- and wave-generated currents in coastal and shelf sedimentary processes. Current patterns are often variable and complex, and a region may be either tide-dominated, storm (wave)-dominated or influenced by a combination of both. Nio (1977) has inferred, from occurrences of large-scale sand cross-bedding, that the Tertiary basins of north-western Europe, including Southern England, were tide-dominated.

Tidal currents run perpendicular to coastlines, effecting considerable sediment transportation off- and on-shore over extensive period of time, and often in a regular cyclic fashion. This produces large scale sediment bodies, often aligned normally to coastlines and with bi-directional stratification. Davies (1964, 1980) and Cram (1979) have also found that the strength and influence of tidal currents vary sympathetically with tidal ranges (i.e. scale of water level fluctuations). Tidal ranges, however, also vary temporally and spatially from < 2m (microtidal) to 2-4m (mesotidal) and > 4m (macrotidal) with increasing width of shelves. The Hampshire Basin was broad and would most probably have had mesotidal and macrotidal ranges (cf. Nio, 1977). The North Sea is a typical modern-day example of such tidal ranges (see Kenyon & Stride, 1970). Tidal ranges would also be thought to be affected by eustatic fluctuations of the sea-level; the tide being more pronounced and extensive during periods of high sea-level rise (i.e. in the shelf Barton

Sea). Sea-level fluctuations have, in fact, had a profound control over sedimentation in the Hampshire Basin (i.e. Plint, 1983); these are considered in detail in Sections 17.3 and 17.4.

Wave-generated currents would also be expected to have operated, although temporally and to a lesser degree compared to tidal currents. Davis (1983) indicates longshore currents and ripple currents to be dominant along coasts and on shelves. Longshore currents run and transport materials parallel to coastlines. Their influence in the Hampshire Basin is widely recognised (i.e. Fisher, 1862; Plint, 1981) in the distribution of pebbles during initial phases of transgressions. Ripple currents make orbital motions, causing much sediment stirring-up and transporting materials shelfwards. In general, wave actions are limited to about 10m water depths (wave base) in normal shelf conditions. During storms, however, large waves may be generated to affect the whole shelf environment.

The extent to which both tidal and wave current processes occurred in the Upper Eocene Hampshire Basin cannot be ascertained from the present work, which is outside the scope of the more informative detailed studies of sedimentary structures. The commonly observed structures of significance are the burrows and mottlings produced from the bioturbational activities of benthic organisms. Mottling is most common in the Barton Clay and the 'Lower Headon Beds', whilst burrows and shell-borings are more obvious in the Barton Sand. Bioturbational features are amongst major characterising aspects of shallow shelf ($<$ 50m - i.e. Reineck & Singh, 1980) and coastal lowlands (i.e. Evans, 1965). Benthic organisms are significant for their unhomogenising sediments being deposited, for pelletising ingested fine-grained materials; and, by stirring up sediments, cause dispersal and suspension of materials which might then become liable to transportation by currents.

The foregoing is a generalised picture of the gross sandy nature of the Upper Eocene clastic sediments. It should be indicated that some horizons are characterised by lower, 0·25 to 0·4, (Q+F)/(Q+F+Cl) ratio values. The horizons include the greyish-brown clays close to the top of the Barton Clay at Barton-on-Sea and Alum Bay ($\equiv$ 'Beds E & F' of Burton, 1929 - see Fig.5); the pipe clays in the Barton Sand at Alum Bay; and some laminated and mottled green clays from the 'Lower Headon Beds' on Hordle

Cliff and Whitecliff Bay (cf. Figs. 5, 6a & 7). These horizons may be taken as an indication of deposition in relatively lower current energies and either deeper or protected water bodies.

Protected waters can be justified for the pipe clays and the 'Lower Headon' clays. The latter, in particular, often have in situ plant remains and, as well, land and aquatic mammalian remains (Edwards, 1967; Cray, 1973; Hooker et al., 1980), which are typical of tidal flat settings. In these, periods and places of low tides will be attended by higher depositions of finer grained materials, often mud.

The conditions for the marine grey-brown clays cannot, however, be ascertained to be deep or protected waters. The deposits contain several thin layers and pockets of shell drifts, particularly on mainland Hampshire. Shell drifts are storm phenomenon and are not restricted to any particular aquatic environment. In fact, there are several drift horizons in the deposits, which would mean a high frequency of storm occurrences. This is mostly expected in nearshore environments of open seas. A probable explanation of the relative higher clay deposition for 'Beds E & F' would be changes of physical processes within the source areas. Detailed consideration of the sediment derivation is discussed later.

There are also some compositional differences in the sand sediments. The sand-supported pebble beds, which Fisher (1862) established to be transgressive beach deposits, contain a high abundance of coarse quartz and flint grains and, in addition, at Highcliffe, a very high ~ 2100 ppm Zr concentration. Zirconium, as zircon, is a resistate often found occurring in greater abundances with strong currents, coarse-grained sediments (Deer et al., 1962). In fact, the transgressive aspect of Zr is further observed in the succeeding very sandy 'Huntingbridge Clay' sediments which possess ~ 700-1000 ppm Zr compared to the ~ 140-500 ppm Zr of the rest of the Barton Clay. The 'Barton Sands' are essentially bar sands (Gardner et al., 1888; Daley & Edwards, 1973). These will be expected to be uniform in character laterally. This is the case in respect of their very similar quartz-sand type composition and low, < 300 ppm, Zr contents. The deposit at Alum Bay, however, differs significantly from the other localities by containing a greater occurrence of pipe clays and small, well worn disseminated pebbles. There are also indications that it has been subjected to sub-aerial pedogenic processes. This is discussed later. The pipe clays indicate that the sands accumulated within very shallow water bodies, since such pipe clays would only have accumulated slowly within small hollows in the sand bodies. The disseminated small pebbles are probably localised in derivation, indicating a nearby drainage outlet and/or strong tidal drift to the locality.

The sand sediments in the 'Lower Headon Beds' comprise channel sands, although a few constitute 'sea-earth' beneath the lignites. The latter are affected by near-surface leaching and are discussed later. The channel sands are characterised by high ~ 800 ppm Zr and may reflect coarser-grained clastics than the Barton Sand. In places, the sands show lamination or shell drifts as an indication of localised storm conditions.

C) Submarine Conditions

The only mineralogical indicator of the existence of marine conditions in the Upper Eocene times is the occurrence of authigenic glaucony in parts of the Barton Clay. Glaucony is a layered-lattice silicate (clay) believed to form only within passive shelf conditions (i.e. Odin & Matter, 1981; Irwin & Hurst, 1982). The glaucony, which grades from thin films to clay- and sand-sized grains, possesses no iron-oxide coatings that would suggest derivation as re-worked material. A detailed consideration of the probable mode of formation of the glaucony is made in Section 17.3.3.

An important aspect of the glaucony is its irregular distribution, both vertically and laterally. Altogether, it occurs in about 20-30m of the Barton Clay Formation. The irregular distribution has consequences with regard to the hydrological conditions believed to prevail for Barton Clay deposition. In particular, the proposed prevalence of relatively strong current conditions would not be expected to facilitate the formation of glaucony. This is believed (Odin & Matter, op.cit.) to require, in addition to little clastic sedimentation, protracted periods of low current agitation. With the Barton Sea being a shallow shelf, minimal current agitation would only have been attained when the sea bottom lay below the wave base level. In normal shelf conditions, this occurs at about 10m water depth (Davis, 1983).

The implication is thus that the hydrogeologic conditions have probably varied considerably during sedimentation in the Barton Sea shelf environments. It would further suggest that there has been significant variation in the eustatic sea-level, basinal subsidence and rates of sediment derivation and accumulation. It is thus probable that there were periods when the sea was shallow and attended by high detritus supply and rapid sedimentation. In other alternating periods, there were deeper waters with little clastic supply and hence low sedimentation. These and other aspects of the basinal conditions are further considered in Sections 17.3 and 17.4.

D) Sub-aerial Conditions

Recognition of pedogenic features in the field and from laboratory investigations provides evidence for the existence of sub-aerial conditions in the very early, and much of the late Upper Eocene times.

Two notable features recognised in the field are:

i) *in situ* vegetation consisting of rootlets in the growth position and/or abundant accumulation of non-drift plant remains;

ii) high iron oxide (goethite) accumulation causing strong yellowish to brownish coloration and, in places, induration.

Such features are amongst those considered to be characteristic of palaeosols (i.e. Buurman, 1975). Other supporting features include the presence of kaolinite lenses in some of the indurated horizons; altered pyritised fossil shells and plant rootlets (i.e. pedotubules - see Brewer, 1964); and iron oxide scales and crusts on altered sideritic ironstones. These features were recognised at various horizons, including the basal pebble bed at Alum Bay; the top of the Barton Sand at all the localities studied; and many horizons within the 'Lower Headon Beds'. An attempt was made to characterise the palaeosols on the basis of modern soil classification schemes. They appear to closely resemble the acid red-yellow podzols (i.e. arenosol/rosossol - Fitzpatrick, 1971) and red-earths or terra-rosa (i.e. gleysol) and hydromorphic swamps (see Figs.6b, 17).

These palaeosols show petrographic and compositional features suggestive of leaching and alteration, which are typical of soils and/or sub-aerially exposed sediments. The red-yellow podzol and gleysol palaeosols contain etched and pitted skeletal (quartz, feldspars, zircon) grains (Plates 54a & b); congruously dissolved and broken-up feldspars (Plates 54c & d - cf. Wilson, 1975); kaolinite plate and vermiculitic book in open textural aggregations (Plate 56, cf. Keller, 1982); and goethite of glaebular, discrete and interwoven lath and platy forms (Plates 51, 62, 63; cf. Meyer, 1976; Schwertmann, 1977). In the hydromorphic palaeosols, patchy iron mobilisation and very little accumulation has occurred. Exogenous phases are, however, common. These include jarosite, gypsum, goethite and lepidocrocite formed from altered pyritised fossil shells and plant materials and, in places, sideritic ironstones. Although interpreted as penecontemporaneous, the exogenous minerals might as well have resulted from Recent surficial processes on the faces of sediment exposures studied (cf. Gallois & Horton, 1981; Taylor & Spears, 1981). Cored materials that might provide confirmatory information were not available for the present study. The minerals occur either disseminated, or intimately admixed with each other around the altered material and/or organic matter and clay minerals (i.e. Plates 34, 35). The jarosite is mainly of clay sizes and petrologically less distinctive from the admixed organic matter and clay minerals. The gypsum varies from micro- to ~2mm-sized discrete crystal and rosette aggregations of prismatic crystals, the rosette morphology being most typical of soils (i.e. Brewer, 1964). Goethite occurs mainly in dispersed masses, and occasionally in glaebular forms and pyrite pseudomorphs (i.e. Plates 34, 55c). The iron-oxides formed from an altered sideritic ironstone in the section at Whitecliff Bay (Plate 25) were, however, found to comprise steel-grey scales composed of thin platy geothite crystals pseudomorphed after the rhomb-form and spherulitic aggregations of the altered siderites (Plate 88). In addition, there are also orange-brown earthy encrustations on the goethitic scales. These consist of clods of clay-sized lepidocrocite crystals which, in places, appear to differentiate into boxwork of platy goethite (Plate 89). Another steely-scaled iron-oxide from the Hordle Cliff section comprises a flowery mass of interwoven, star-twinned lepidocrocite plates and laths, and euhedral prismatic crystals of goethite (Plate 90). These appear to have differentiated (or recrystallised?) from masses of cryptocrystalline iron-oxides (i.e. Plates 90c & 90h).

The effects of the surficial processes were more severe for the acid palaeosols, as shown by their enriched contents of authigenic kaolinite (35-100% of clay fraction) and goethite (up to 44%). The kaolinite enrichment has occurred at the expense of 2:1 clay minerals and feldspars. These soils must have had good drainage and aeration development conditions (cf. Mohr & von Baren, 1954). Similar kaolinite enrichment occurs in the sands immediately underlying those palaeosols at Alum Bay, most probably as a result of leaching by acid meteoric waters draining down from the soil horizons.

The hydromorphic palaeosols are poorly evolved and leaching is minimal. Nevertheless, the clay phases are more degraded than in the rest of the succession. Only in a few horizons is kaolinite enriched to between 20 and 35%. Small amounts of hydroxy-chlorite, and probably halloysite, occur in some of the lignitic horizons (i.e. Figs.10b & c). Rich (1968) has described such a clay phase from present-day water-logged (soils) conditions. The clay phases thus complement the previously mentioned exogenous phases as indicative of variable drainage and aeration conditions in the hydromorphic palaeosols. Such variability is typical of many present-day lowland soils, including marshes and cat-clays (cf. Fitzpatrick, 1971; Slager & Schuylenborgh, 1970; Dones & Lynn, 1977).

The above shows that significant and frequent penecontemporaneous emergence of freshly deposited sediments occurred during Upper Eocene times in the Hampshire Basin. This was attended by substantial sub-aerial alteration. Indications of similar emergence in other parts of the Palaeogene period within the basin are given by the frequent occurrences of rootlet-bearing horizons, particularly lignites. Closer examination of these and, in addition, the ferruginous sands in the Palaeogene succession (i.e. White, 1915; Edwards, 1967; Plint, 1983) would probably indicate other occasions of penecontemporaneous emergence. Unfortunately, the lack of such data prevents comparison with the Upper Eocene occurrence described in the present study.

Sediment emergence would mainly be expected within the shoreline complex and non-marine parts of a depositional basin. This could result from a number of factors, in particular eustatic sea-level fluctuations, tidal current variations or differential local responses to tectonic factors. Emergence is particularly feasible and more common where low-lying coastal plains border the sea. A typical present-day example is the coastal plain of south-eastern U.S.A. Here, diverse sedimentary processes, including differential sediment stripping, shifting and accumulation, occur (i.e. Wanless, 1976b). Swamps, ponds and sluggish streams occur on the landward side of the shoreline, whilst sand-bars/barriers occur shelfwards. In such settings, newly-laid sediments may emerge when the tide is low or sea-levels fall. Once brought into ground water zones, colonisation and surficial processes would take place, including the alteration and leaching of pre-existing and unstable mineral phases, with the consequent authigenic formation and accumulation of exogenous minerals (cf. Loughnan, 1969; Slager & Schuylenborgh, 1970). The types and extent of processes occurring will depend on a variety of factors, including variations in the local topography and drainage. The sediments' lithology will also be important.

In relatively well elevated and/or porous sediments, such as ridges of sand bars, there would be good aeration and drainage of the ground waters. Their levels (water table) would be low and fluctuate readily. Leaching by soil acids would hence be more effective, resulting in high iron accumulation and abundant kaolinite. The acid palaeosols described above are typical of such weathering phenomenon, which also occurs on sandy parent sediments along the coastal plain of south-eastern U.S.A. (cf. Hunt, 1972).

In depressed areas, the water table will be high, causing water-logged or hydromorphic conditions to prevail. Leaching and mineral alteration will be low, and the soil evolution poor. The drainage and aeration may, however, improve so as to allow oxidation and hydrolysis of unstable minerals, which will include sulphides formed during the earlier water-logged conditions. In the case of the Upper Eocene environments, there would also have been alteration of siderite, whose formation has been found (see Ch.14 and Section 17.5) to occur very close to the sediment surface.

The recognised penecontemporaneous emergence of the Upper Eocene sediments is indicative of eustatic sea-level tidal fluctuations and the existence of differential geomorphological sub-aerial conditions. It could thus be inferred that:
the initial transgressing Barton Sea was not only very shallow, but also ineffectively established or short-lived, particularly at Alum Bay.
The development of the pebble bed at Alum Bay, along with parts of the underlying sand sediments of the uppermost Bracklesham Group, into red-yellow podzol suggests the emergence and geostasis for about 10^4 years (cf. Kronberg et al., 1979). The soil development was terminated by a substantial eustatic rise from which the shelf Barton Sea environments

were effectively established in the area of the present study. At the end of the Barton Sea existence and cessation of the attending marine sedimentation, a substantial fall of the eustatic sea-level caused the emergence of the Barton Sand at all the localities studied. Topographical and drainage differences existed between the area of mainland Hampshire, which was low-lying and characterised by high water tables and flooding, and the areas of the Isle of Wight which were relatively more elevated and better drained, particularly at Alum Bay. The red-yellow podzols (Plates 18, 19) developed at Alum Bay suggest the emergence of $\sim 10^4$ years. The development of this soil was most probably terminated by a tidal surge, which, at Alum Bay, either deposited a $\sim$50 cm thick clayey sand or translocated an already evolving soil or weathering mantle from nearby areas. The translocated or deposited material then became emerged and developed into a gleysol (i.e. Plates 18, 19). Gleysols are related to red-yellow podzols (Fitzpatrick, 1971) and might also have taken up to 10^4 years to evolve. On mainland Hampshire, however, swamps and high plant accumulation occured with little active leaching. Actually, two lignitic horizons occur, separated by a mottled brown clay with small sand lenses ($\equiv$ 'Bed L' of Burton, 1929 - see Plate 7 and Fig.5). These lignitic horizons are time equivalents of the red-yellow podzols/gleysols at Alum Bay. The top of the Barton Sand at Whitecliff Bay is marked by a thin, $\sim$ 5 cm thick, yellowish-brown, loamy, goethitic clayey sand. This is a poorly evolved soil that suggests either only limited emergence or erosion at Whitecliff Bay. The horizon is, however, immediately succeeded by $\sim$ 2·5m lignitic and carbonaceous clays of the 'Lower Headon Beds' (see Plate 24, cf.Fig.7). It would thus appear that water-logged conditions prevailed for a considerable length of time at that locality.

The development of soils over the Barton Sand was terminated by an inundation from which the greenish-clay base to the 'Lower Headon Beds' was deposited. The inundation was most likely tidal and was most effective in the lower lying areas of mainland Hampshire. Variations in tidal/drainage conditions in the late Upper Eocene coastal plain environments led, in time and space, to several occasions of emergence of the sediments into swamps with high plant accumulation.

17.3 Sediment Derivation

17.3.1 Previous Deductions

Very few of the numerous works on the Palaeogene Hampshire Basin have considered the derivation of the sediments in detail. The exceptions are on the clay assemblages (Gilkes, 1966, 1978) and the heavy mineral assemblage (Walder, 1964; Blondeau & Pomerol, 1968). These authors suggest the presence of three main source areas, consisting of:

i) the Cornubian Massif to the south-west in Cornwall and Devon. This comprises low grade pre-Mesozoic metasediments and granites which are, in places, kaolinitised. They were thought to have supplied kaolinitic and illitic clays, as well as zircon, tourmaline and rutile.

ii) the Mesozoic sedimentary rocks in the area of the English Midlands, western England, and south-eastern England. These comprise illite-rich pre-Upper Cretaceous sandstones, clays, calcareous and glauconitic sediments; and Upper Cretaceous Chalk that predominantly consists of biogenic $CaCO_3$ with small amounts ($<$ 5%) of smectite-rich non-carbonate contents. These were believed to have supplied illite, smectite and heavy minerals dominated by granitic assemblages.

iii) the Amorican Massif, a metamorphic complex, occurring to the south in northern France and Brittany. Contributions from this are thought to be small, possibly including chlorite, garnet, andalusite, staurolite, sphene, brookite and epidote.

In addition, Blondeau and Pomerol (1968) suggested some derivation of certain heavy minerals, i.e. garnet, epidote and zoisite via the North Sea; whilst Gilkes (1968) suggested intrabasinal derivation of neoformed illites in the late Upper Eocene and during the Oligocene times. Other works of importance to the consideration of provenance include those of Curry (1964) and Plint (1982, 1983). Curry, from the foraminiferal content of a pebble in the late Middle Eocene Boscombe Sand, and Plint, from sedimentological studies of the Middle Eocene Bracklesham Group, inferred that some derivation of sediment occurred from the Upper Cretaceous Chalk in areas of the English Channel south of Dorset. The detritus includes flint pebbles and coarse-grained material.

The present work, from mineralogical and geochemical bases, suggests that some modifications can be made in respect of the previous works. It also highlights some aspects of the material supplied to the basin such as the influx of iron-oxides and dissolved $CaCO_3$, as well as the controlling influences of the palaeoclimatic, palaeomorphological and tectonic factors.

17.3.2 Deductions from the Present Study

As a result of the shallow burial history, relatively low scale diagenetic alteration has occurred. Hence the clastic constituents would be expected to be controlled by the nature of source rocks and modes of detritus supply. The clastic material dominantly comprises silt to medium sand-sized quartz and potassic (microcline) feldspar (i.e. Plates 26, 27) as well as a poorly crystalline (or degraded) clay mineral assemblage consisting of illite, smectite, kaolinite, illite-smectite and trace amounts of chlorite (Figs.23a-c). Other clastic materials occurring in minor amounts, and/or of limited distribution, are sodic (albite-oligoclase) feldspars, anatase and flint pebbles. The heavy minerals are silt to coarse sand-sized and commonly include zircon, tourmaline, garnet, staurolite and rutile (i.e. Plates 26-28, 30). The heavy minerals were not studied in detail. Information on sediment derivation is also provided by some of the authigenic phases, particularly goethites in the palaeosols, glauconies, Ca-siderites and ferroan-calcite.

17.3.2A Nature of the Source Rocks

The clay minerals, pebbles and goethite proved most useful in deducing the nature of the source rocks. However, the coarser clastic grains of dominantly silt to medium sand-sizes, being sub-spherical to rounded, indicate a water-transported derivation from older sedimentary rocks rather than direct derivation from crystalline source rocks (cf. Krumbein & Sloss, 1963). In addition, the low abundance of feldspars ($\lesssim$ 8% averages) which mainly comprise the potassic variety, with the virtual absence of calcic plagioclase, suggests either low feldspathic source rocks and/or that, in the prevailing warm-humid regional palaeoclimate, weathering was intense enough to differentially remove plagioclase and some of the more resistive alkali feldspar (cf. Goldrich, 1938). The clay assemblage, which is dominantly ($\sim$ 70%) illite $\geqslant$ smectite with small (8-15%) kaolinite $\simeq$ illite-smectite and traces of chlorite (Figs. 23a-c), however, suggests that the regional weathering was generally poor to moderate (see Section 17.1). Such a clay assemblage would mainly be derived from the smectite-rich Upper Cretaceous Chalk and the older, but more illitic Mesozoic rocks in the region bordering the Hampshire Basin.

Direct contribution from the Cornubian Massif, in particular the kaolinitised granites of Cornwall, is almost certainly less significant than previous believed. Gilkes (1966) considered such sources as providing the bulk of kaolinite to the Hampshire Basin. The present study suggests that the prevailing warm-humid sub-tropical climate would be sufficient to account for the bulk of the kaolinite present. High abundance of kaolinite has been found to occur only in the palaeosols, where in situ penecontemporaneous sub-aerial acidic leaching and pedogenic processes occurred. The increase in kaolinite is accompanied by depletion of feldspars, smectite, illite-smectite and, in places, illite (cf. Tables 7e & f; 8e & f). The kaolinite enrichment in the Barton Sand at Alum Bay has probably resulted from the leaching action of acidic meteoric waters percolating from the acid red-yellow podzols and gleysol palaeosols developed at the top of the sand. Alternatively, the kaolinite could be derived from areas undergoing similar pedogenesis. In fact, the similarity of the kaolinite $>\geqslant$ illite $>$ illite-smectite clay assemblage of the bulk of the Barton Sand, its pipe clays and the gleysol palaeosol at Alum Bay, may represent the 'equilibrium' clay contents of locally derived materials. Localised derivation to Alum Bay is also indicated by the occurrence of disseminated small flint pebbles and goethitic moulds of plant materials within the Barton Sand at Alum Bay. These materials, particularly the flint pebbles, do not occur in the deposit at the other localities studied. The probable sources, discussed later, are most probably intrabasinal and located nearby to the south of Alum Bay.

The importance of the pre-Upper Cretaceous rocks to the north and west of the basin with respect to sediment supply has been stressed by Gilkes (1966). Gilkes' (1978) suggestion that some illite was derived from re-worked or in situ neoformed illite is, however, improbable. Gilkes assumed that periods of hot, dry, sub-aerial conditions conducive to illite neoformation in ponded waters existed in the late Upper Eocene and Oligocene times. There is, however, no floral and sedimentological support for the existence of such conditions. The floral assemblage is predominantly of deciduous vegetation typical of warm-humid climates (i.e. Hubbard & Boulter, 1983), whilst the sedimentation was essentially of clastics with occasional lime-mud accumulations (cf. Edwards, 1967; Plint, 1983). A few gypsum occurrences (i.e. Daley, 1967, 1973; this study) are very localised, micro-scale phenomena probably formed from penecontemporaneous sub-aerial alteration of sulphide and carbonate material during brief emergence of the sediments (see Section 17.5.1). The Hampshire Basin palaeoenvironment differs significantly from the very extensive hypersaline water with chemical sedimentation of primary gypsum of the Palaeogene Paris Basin, whose palaeoclimate has, floristically, been shown (i.e. Chatteauneuff, 1980) to be an alternating warm-wet and hot-dry to semi-arid one.

An alternative explanation of the relatively higher abundance of illite in parts of the 'Lower Headon Beds' and the succeeding Oligocene sediments would be a possible change in the relative importance of the different source areas contributing to the Hampshire Basin. The change(s) apparently occurred after the last major marine Palaeogene sedimentation, in the basin, of the Barton Clay and Barton Sand Formations. It appears to involve decreased contribution from Chalk sources relative to the older sediments and probably intrabasinally-exposed earlier Eocene sediments.

Gilkes (1966) only envisaged smectite derivation from Chalk exposures located to the north of the basin. These cannot, however, account for the smectite abundances and distribution in the Palaeogene succession (see Table 10). The clay mineralogical data of Burnett & Fookes (1974) for the London Clay Formation and that of Gilkes (1966) for the Palaeogene succession show smectite to be the dominant clay phase in more than 300m of clayey marine sediments. Considering that the denudation rate of the early Tertiary southern England landscape was $\sim$15m/Myrs (i.e. Jones, 1981, Ch.4), it is unlikely that more than 600m Chalk could have been eroded. This would not be expected to produce, uniformly regionally, more than 30m of smectite-rich clay deposits, since the Chalk is predominantly composed of coccolith $CaCO_3$ and usually with $<$ 5% smectite (i.e. Hancock, 1975).

Since the smectite shows facies-dependent variation with higher abundances correlating with the transgressive marine facies, it is most likely that other sources, possibly Chalk rocks located to the south of the basin, and/or re-worked submarine smectite-rich sediments, made some contribution. Ziegler (1982) has shown that the latest Cretaceous tectonic 'inversion' of basinal Mesozoic sediments occurred in some areas of north-western Europe. One of such inversions occurred in the English Channel; this might have been uplifted and eroded. The possibility of such an emergence is indicated by the structural features of the English Channel (i.e. Curry & Smith, 1975; Stoneley, 1982). This shows that the Purbeck-Isle of Wight monoclinal Chalk fold forming the southern margin of the Hampshire Basin has a mirror image at about 60 km to the south in the English Channel. Melville & Freshney (1982) have suggested that regional

Tertiary tectonics probably raised the area between the two outward facing folds into a horst. Indeed, the area was most probably emergent in Tertiary times to supply flint pebbles and coarse-grained 'fan' deposits to parts of the Middle Eocene Hampshire Basin (Curry, 1964; Plint, 1983). An indication of the probable emergence of the horst structure in the Upper Eocene time is also provided by the occurrence of flint pebbles in the basal transgressive deposit, and also in the Barton Sand at Alum Bay. By their proximity, the Chalk exposures would have been subjected to similar palaeoclimatic and weathering conditions previously inferred (in Section 17.1). The weathering products would include dissolved $CaCO_3$, flint pebbles, smectite-rich clays and other clastic material.

Probable submarine derivation of smectite would most likely be from ash-bearing early Tertiary sediments in areas of the North Sea (i.e. Jacques & Thouvenin, 1975), and south-east England (i.e. Ellison, 1971). The submarine alteration of ash usually leads to the formation of zeolites and smectite (Stonecipher, 1978). Clinoptinolite zeolite occurs in the marine facies of the Bracklesham Group at Whitecliff Bay (Gilkes, 1966). This suggests the re-working and entrainment of altered ash materials in sea waters transgressing into the Hampshire Basin. It would thus appear that derivation via the North Sea is very probable, as first suggested by Blondeau & Pomerol (1968) from heavy mineral studies. Morton (1982) has made similar deductions for some heavy minerals from Late Palaeocene-Early Eocene sediments in the London Basin.

The importance of the Chalk as a source rock is further highlighted by occurrences of foraminifera that closely resemble Upper Cretaceous forms (Prof.D. Curry - pers.comm., 1982) in the flint pebbles of the Upper Eocene sediments. Plint (1981) believed similar flint pebbles in the Bracklesham Group to have been directly shed into the Hampshire Basin Palaeogene seas and distributed by longshore waves. This is probably the case, at least for the basal pebble bed at Alum Bay, where the pebbles show up to 30 cm long axis dimensions. These are larger than the $<$ 10 cm-sized pebbles in the equivalent horizon at Highcliffe. The supply of pebbles to Alum Bay would mostly have been provided by the Chalk exposure to the south of the Isle of Wight monocline. The larger pebbles would have remained in the vicinity of Alum Bay, whilst tidal currents would have transported smaller sized ones westward to Highcliffe and Hengistbury Head, and probably also eastward towards Whitecliff Bay. Although not observed during the present study, Keeping (1887) has also described occurrences of pebbles from the lower part of the Barton Clay at Whitecliff Bay.

In the case of the pebble bed base of the Upper Eocene succession at Hengistbury Head and Highcliffe, Hooker (1977) suggested the pebbles as probably being re-worked from intrabasinally exposed older pebble beds in the area of Dorset. Those older pebble beds often show a more exotic assemblage (Plint, 1982), suggesting derivation from a variety of source rocks, including the Jurassic Purbeck Limestones and the Cretaceous 'Greensand'. Hence a wide variety of lithologies might be expected if Hooker's theory is correct. Only the section at Highcliffe was presently studied, and only one small weathered chert pebble was found in the pebble bed, the rest being flints. Whilst not invalidating the probable exposure of older pebbly sediments in Dorset, the rarity of non-flint pebbles at Highcliffe would suggest insignificant contributions from such sources. Perhaps their exposure was limited and/or that the existing hydrologic condition was inadequate for effective or long-distance transportation. Re-working of earlier pebbly Eocene sediments located to the south in the English Channel would, however, account for the small ($<$ 2 cm-sized) disseminated smooth-worn flint pebbles limited to the Barton Sand at Alum Bay. The mode of derivation of this is considered later.

Disseminated iron-oxide is also an important material derived for the Upper Eocene Hampshire Basin. This remains preserved mainly as goethite in parts of the succession where oxidising conditions continued to prevail after deposition. This is particularly the case of the How Ledge Limestone and much of the Barton Sand, where, on the Isle of Wight, goethitic plant moulds also occur. Considerable quantities of iron-oxide deposited in other parts of the succession have been utilised for extensive authigenic formation of iron minerals. These include glaucony and, in places where Fe^{3+} is reduced to Fe^{2+}, pyrite, siderites and ferroan-calcite are found. If the scales of iron accumulation observed in the Upper Eocene palaeosols reflect the regional situation, it could be said that iron would mostly have been derived from the well-elevated, better-drained and/or porous source rocks. The most prolific source of iron would include the glauconitic Cretaceous 'Greensands' in the hinterland to the basin and any intrabasinal exposure of earlier Eocene ferruginous sand and glauconitic sediments (see Melville & Freshney, 1982). The low-lying coastal hinterland to the basin could have been very important as a source of iron, irrespective of the local lithology. As a result of tectonic changes and/or eustatic fluctuation, the land-drainage patterns were probably subjected to alternate conditions of water-logging and better drainage. Oxidation and hydrolysis of earlier formed reduced-iron phases (i.e. pyrite, siderite) would have occurred, providing detrital iron when eroded. This alternating drainage would account for the goethitic plant moulds in the Barton Sand on the Isle of Wight. The plant materials would have been shed into swamps in the nearby areas. There, the plant structure would be replaced by pyrite as the organic matter decayed. Fowler et al. (1973) have, in fact, recognised this process to account for the pyrite-preserved plant cells and structures from the top of the Barton Sand on mainland Hampshire. When the drainage improved, the pyrite would become rapidly oxidised to goethite, preserving the plant structure. The goethitic mould would then become durable for re-working, probably by storm or tidal currents.

17.3.2B Mode of Derivation

In addition to the type of source rocks, sediment derivation would also be influenced by several environmental factors, including the prevailing regional climate (humidity in particular), vegetation, geomorphology and drainage patterns (Holeman, 1968). The last two factors may also be influenced or controlled by the regional tectonic conditions.

a) Constancy of source

In the Upper Eocene Hampshire Basin, there were four main phases of mud or sand sedimentation. These successively comprise:

(i) sand and pebble for the basal sand-supported pebble bed;

(ii) grossly muddy detritus for the Barton Clay Formation. Although characterised by high clay contents (i.e. $Q/Cl < 2$), the SiO_2/Al_2O_3 ratios (Figs.21a-c) indicate this sedimentation phase as commencing at Alum Bay and Highcliffe with more siliceous (or sandier) materials. Similarly siliceous materials also later occurred occasionally at all the localities studied.

(iii) a predominantly sand derivation for the Barton Sand Formation. The initial stage of this phase was generally slightly muddy, but rapidly changed to well-sorted quartz-rich clastics. The deposits at Whitecliff Bay and mainland Hampshire are relatively rich in clay and feldspars compared to Alum Bay. This difference in the Alum Bay area is, however, not reflected by other compositional parameters such as Q/Ti and Zr/Ti (see Figs.21a-c); the difference is thus a localised phenomenon not related to the general regional sedimentation. On mainland Hampshire, a period of muddy sedimentation occurred about half way up the Barton Sand, whilst much smaller muds accumulated as pipe clays in shallow hollows within the sands on the Isle of Wight.

(iv) a variable muddy and sand accumulation for the Late Upper Eocene 'Lower Headon Beds'.

An important aspect of the deposits is their lack of significant compositional variation laterally from mainland Hampshire to the Isle of Wight. Sediment supply seems to have taken place from similar sources throughout the Upper Eocene times. This suggestion is strongly underlined by the constancy of the clay assemblage. With the exception of the localised loss of 2:1 clay phases as a result of in situ penecontemporaneous surficial process, the clay assemblage remains uniform as an illite-smectite-kaolinite-illite/smectite assemblage in the succession. Some compositional parameters such as the Ti/Al, Q/Ti and Zr/Ti ratios (Figs.21a-c) also provide support for a relative constancy of source(s). The Ti/Al ratio is relatively uniform, ~ 0·02 - 0·04, in the greater part of the succession. The major variations occur in the sand facies, which, at the base of the succession and in the 'Lower Headon Beds', have higher (~ 0·06 - 0·1) Ti/Al ratios. These sands contain a greater abundance of coarser-grained anatase and rutile. The Ti/Al values of the Barton Sand are, however, similar to those of the marine and non-marine clayey sediments. Closely similar variation is also found for the Q/Ti and Zr/Ti. The muddy deposits are seen to possess uniformly low ratio values, whilst the sands are richer in coarse titanium minerals and zircon. The highest values occur in the basal pebble bed and the non-marine channel sands of the 'Lower Headon Beds'. These parameters also mark out the coarser parts of the Barton Clay; in particular the lower Huntingbridge Clay Member.

In general, the compositional aspects of the sediments are not very variable to suggest significant changes in the nature of the sources. An explanation is thus only required for the differential amounts of mud and sands. The explanation concerns probable relative changes in the regional geomorphology, drainage and tectonics.

b) Detritus variations

The main provenance to the Hampshire Basin has been considered, in previous studies, to be from land areas to the north and west. This is justified by the presence of structural highs, including the Cornubian Massif and, more importantly, the nearer Mid-Dorset Swell (i.e. Drummond, 1970), and several closely related anticlines and horsts of Mesozoic rocks in the southern Midlands, Wiltshire, Hampshire and Sussex (i.e. Stoneley, 1982; Melville & Freshney, 1982). In situ weathering profiles (i.e. Isaac, 1983a) and erosional surfaces of Eocene age (Jones, 1981) also occur on some of the structural highs in Dorset, Devon, Wiltshire and Hampshire. The structural highs are, however, mostly of moderate relief (i.e. $\leq$ 700m O.D; see Fig. 25), and their easterly drainage (West, 1980) would have to traverse wide expanses of well-vegetated lowland (mostly $<$ 200m O.D.) in order to discharge into the Hampshire Basin.

Plint (1983), from work on the Middle Eocene succession, inferred that considerable trapping of detritus within ponds and lakes most probably occurred in the vegetated lowland resulting in low clastic supply to the basinal area. Indeed, kaolinite-rich detritus from the Cornubian Massif was accumulated within inland sag basins of south-western England, i.e. the Late Eocene-Oligocene Bovey Basin (Bristow, 1977). This removal would account for the lack of abundant kaolinitic detritus within the Hampshire Basin. Whilst continuous derivation might be expected from source areas to the north and west, the quantities involved have most probably been low.

The detritus would be expected to comprise both mud and sand, with clay contents richer in illite than smectite. The non-marine 'Lower Headon Beds' sediments are characterised by such illite $>$ smectite clay contents, and would probably typify contributions from the northern and western sources. The marine sedimentation was, however, more diverse. This is characterised by both illite $\lesssim$ smectite and illite $\gtrsim$ smectite clay contents and occurrences of pebbles. Wider and more variable provenance would apply. The most notable of other probable sources would be the 'Chalk horst' to the south in the English Channel. This would have supplied additional smectite and, as well, pebbles in the marine facies.

Plint (op.cit.), however, found little evidence for the existence of extensive surface drainage over the horst structure in the Middle Eocene times. He deduced the presence of a small stream discharging close to the area of Dorset, as well as the presence of a small northerly discharge of coastal fans in Dorset and the western and eastern parts of the Isle of Wight. The implication of the relatively limited extent of surface drainage is that the Chalk exposure was of low relief, perhaps only a few tens of metres. The fact that its detritus contribution appears to be only significant to the marine facies also further suggests that the exposure of the 'Chalk horst' was episodic. This probably results from reverse responses to tectonic movements lowering the Hampshire Basin. With the basin being a passive margin cratonic basin (cf. Reading, 1982), the basin and the horst could have been mirror-image structural features, whereby positive vertical movements on one are complemented by closely equivalent negative movements on the other. The occurrence of a number of somewhat abrupt changes in muds and sands deposited for the marine sedimentation would suggest that the tectonic movements involved were pulsative, occurring rapidly in stages with protracted non-movement intervals. If, as suggested earlier, the Chalk horst mirrored the basin, then the depths of the Palaeogene seas could be close indicators of the emergent reliefs of the horst. Foraminiferal assemblages in the marine Palaeogene sediments (Murray & Wright, 1974) indicate the seas to be of mostly shallow ($<$ 100m) shelf type, although the molluscan fauna indicate (Curry, 1965) probable deeper depths for the London Clay Seas (up to 400m) and the Bracklesham Seas (up to 250m). The emergence of the Chalk horst would probably be to $<$ 400m relief. It will thus be comparable to the lowlands adjoining the basin to the north rather than to the 400-700m relief uplands which Jones (1981) suggested. Higher relief would only be possible if other movements in adjoining basins in the English Channel complemented those of the Hampshire Basin. There is little evidence for this. In fact, Jones' geomorphologic reconstruction, implying emergence throughout the Tertiary times, would be inconsistent with the fact that detritus contribution from the emergent area occurred predominantly in the marine Eocene facies.

On emergence, the Chalk horst, with its axis located in the English Channel could have been drained by active young streams transporting weathering products into the Hampshire Basin. By the nature of Chalk, clastic components would be low, and dominantly comprising smectite clays and few flint pebbles.

In the earliest probable emergence in Lower Eocene times, the weathering and drainage would have only been sufficient for the transport of clays. Hence a largely flint pebble-free London Clay Formation was found. At the onset of subsequent emergences, the earlier weathered-out flint pebbles and coarse clastics would be liable to strong tidal transportation. The pebbles would then be deposited as basal transgressive material in the Hampshire Basin. The emerged Chalk would further be eroded to give smectite clays, and dissolved $CaCO_3$. These would be in addition to those derived from northern and western provenances, as well as that derived from possible submarine re-working of altered ash-bearing sediments.

In addition to the weathered Chalk material, there would also be re-working of Eocene sediments that were deposited over the 'Chalk-horst' during its submergence. Given that the non-marine Palaeogene Hampshire Basin consisted largely of coastal flood plains, it is unlikely that the horst structure would have been submerged deeply. Hence, with strong currents prevailing, the Eocene age sediment cover would most probably have been sandy and of the same northern/western provenances which continuously supplied material to the Hampshire Basin. Such sandy sediments might, on the emergence of the Chalk horst, have been subjected to moderate-intense weathering, probably with the development of acid soils found as palaeosols in the Upper Eocene succession (see Fig.6b). The re-working of such weathered sandy materials would provide kaolinite-rich sandy detritus. However, if the sediment cover was water-logged, leaching and hence authigenesis of kaolinite and goethite would be low. As such, it would provide a dominantly illite - plus smectite - bearing assemblage.

From the distribution of smectite in the Palaeogene succession (Gilkes, 1966), the importance of the English Channel as a sediment source area appears to be insignificant after the deposition of the Barton Sand Formation. Probably the area became submerged after the Barton Sea ceased to exist. Thus, either the tectonic movements were reversed or insufficient to cause re-emergence of the horst structure. Hence late Upper Eocene and Oligocene sedimentation in the Hampshire Basin became dependent, largely, on the northern and western Mesozoic rocks provenance.

The above suggested derivation of detritus from horst structures in areas of the English Channel raises questions as to the position of the

Isle of Wight monoclinal southern margin to the Hampshire Basin. At Whitecliff Bay, the Eocene sedimentation was predominantly of shelf, estuarine and tidal marsh origin (i.e. Murray & Wright, 1974). This locality would have been submerged for most of the time, the shoreline being expected further south. The Palaeogene succession at this locality is, however, adjoined to the south by Upper Cretaceous and Lower Cretaceous sediments. Hence, with no evidence of Palaeogene sedimentation occurring directly to the south, it could only be inferred that the interface of the Palaeogene water bodies (seas) and the monoclinal Cretaceous sediments was steeply dipping. Changes in sedimentation at Whitecliff Bay would thus very probably be due to variations in the rates of basinal subsidence and eustatic sea-level fluctuations (cf. Plint, 1983).

In fact, many authors (i.e. Melville & Freshney, 1982; Plint, op.cit.) have highlighted the finer-grained nature of the Eocene sediments at Whitecliff Bay compared with other localities to the west. It is suggested that little or no direct supply of clastic material to the locality occurs from the horst structure to the south. Plint (1983) has suggested that some derivation of material as fan deposits occurred in the Bracklesham Group. There is, however, no real evidence for such derivation during the Lower and Upper Eocene sedimentation. In all probability, sedimentation at Whitecliff Bay would mostly have been of clastic materials transported from areas to the west by tides and longshore waves.

Alum Bay, in contrast to Whitecliff Bay, is characterised by more coarse clastic and goethitic Upper Eocene sediments that suggest shallower water sedimentation with an adjacent shoreline and drainage outlet. This complements the deduction made by Plint (1983), on the basis of estuarine sands and swamp palaeosols in the underlying Middle Eocene succession, of the location of the Isle of Wight monocline margin to within a few kilometres south of Alum Bay. One possible explanation of the situation of sedimentation at Alum Bay relative to Whitecliff Bay would be differential local manifestation of tectonic movements in the basin and surrounding areas. In particular, movements along the series of arcuate enchelons that comprise the Purbeck - Isle of Wight monoclinal structure (see Stoneley, 1982) would have varied. Those in the vicinity of Alum Bay may have been of more severe magnitude during Eocene times. The probable cause of this is unclear, but further aspects of the basinal movements and sea-level fluctuation are considered in the following section.

17.4 Synthesis of the Upper Eocene Sedimentation

Upper Eocene sedimentation in the Hampshire Basin has been found to be characterised by several rapid and episodic changes in the nature of sediment deposition. These are coupled with corresponding changes in relative depths and current energies of the depositional waters, and occasions of sediment emergence, attended by sub-surface pedogenic processes. These phenomena cannot satisfactorily be explained in terms of the large time-scale cyclical transgression and regressions on which most theories of Palaeogene sedimentation in the region have previously been based (i.e. Stamp, 1921; Curry, 1965). A more probable explanation may be sought from the concept of factors propounded (i.e. Pitman, 1978) as influencing passive, Atlantic-margin cratonic basins (cf. Reading, 1982). The factors, which are inter-related, are the differential rates of eustatic sea-level rise or fall, subsidence (or platform flexuring and isostatic adjustments), and sedimentation.

17.4.1 Eustatic Sea-level Fluctuation

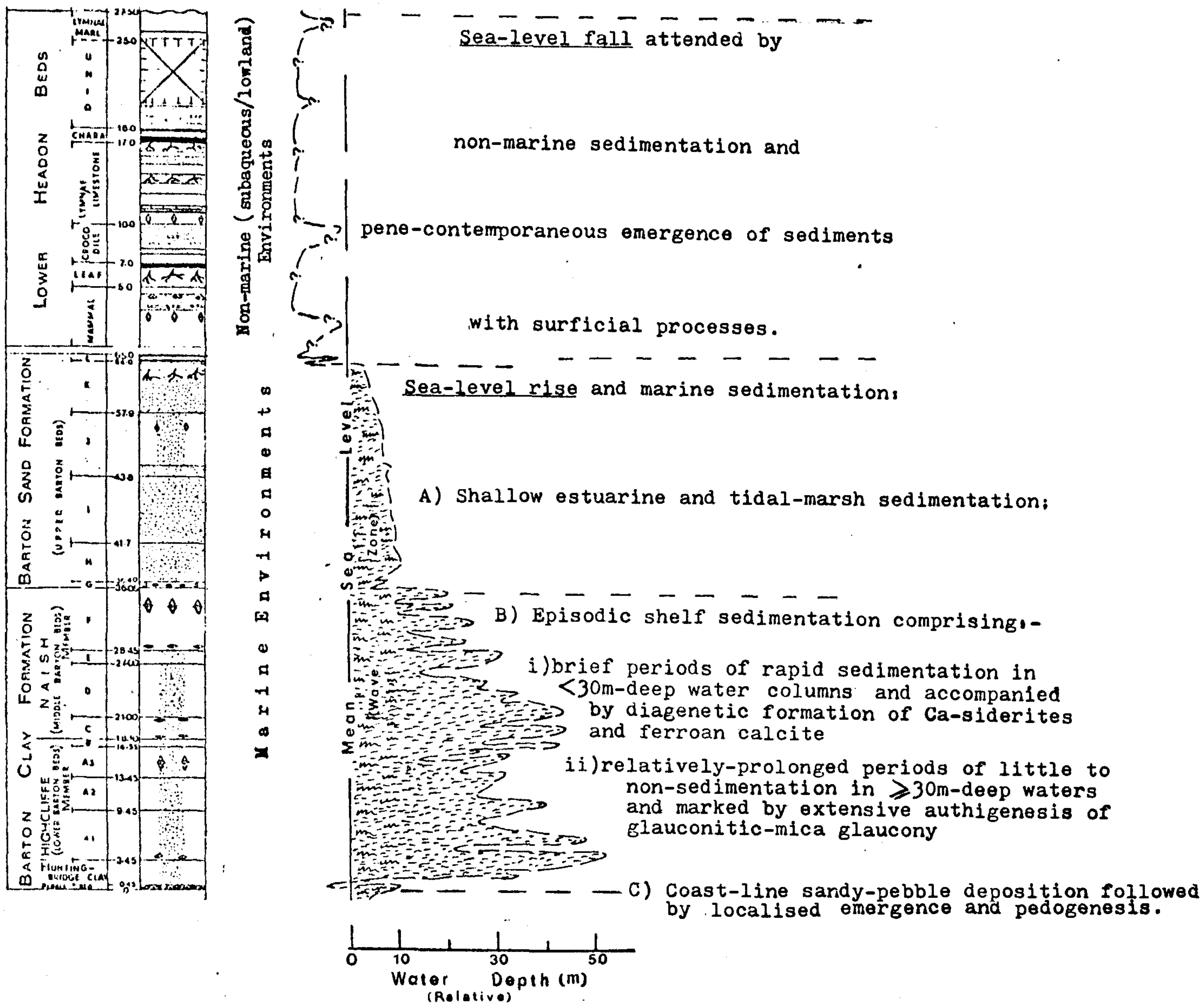
Pitman (1978) has shown that there has been a world-wide sea-level fall since the onset of oceanic crust emplacement during the late Mesozoic times (~ 80 Ma). However, variation in the spreading rates of the ocean floor has caused the eustatic sea-level fall to progress at different rates; with transgressions corresponding to periods of lowered rates, whilst regressions attend periods of more rapid eustatic falls. Pitman and others (i.e. Hallam, 1963; Vail et al., 1977) have also established that world-wide transgressions occurred during Late Cretaceous, Eocene and Miocene times; each separated by regressive phases. The Eocene transgression, however, comprised two major cycles - the earlier being in the Late Palaeocene-Lower Eocene times, whilst the later occurred during Middle Eocene and Upper Eocene times. These coincided, respectively, with the London Clay Sea and the Bracklesham-Barton Sea in the Hampshire Basin. Small scale 'saw-tooth' fluctuations of the sea level (Pitman,1978) or paracycles (Vail et al., op.cit.) have also been recognised from these transgressive cycles. Burnett & Fookes (1974) and King (1981) highlighted four paracycles from the London Clay Formation, each of which appeared to span ~ 4 M.yrs (i.e. Fitch et al., 1978). Plint (1983) showed five paracycles with ~ 1-1·5 M.yrs intervals to occur in the Bracklesham Group and two similar paracycles for the early Upper Eocene Barton Clay and Barton Sand Formations (formerly 'Barton Formation'). This suggestion of two Upper Eocene transgressive paracycles is contrary to the inference of only one transgressive phase by previous authors (Curry, 1965; Murray & Wright, 1974), and from the present study. The most probable Upper Eocene sea-level curve, based on the present study of the successions at Alum Bay on the Isle of Wight and mainland Hampshire, is shown in Figure 51.

The Upper Eocene commenced with a short-lived, small sea-level rise. Locally, the sea-level dropped slightly, causing the emergence of the sandy pebble bed deposited. This emerged deposit developed into a red-yellow podzol, a soil type that would indicate an emergence of about 10^4 years. This was then followed by the only major sea-level rise to occur in Upper Eocene times. Although the sea-level remained fundamentally high as the Barton Sea, for a period of $\sim$ 3 Ma (i.e. $\sim$ 40 → 37 Ma, Odin et al., 1978), there are indications that the sea-level fluctuated very considerably. Foraminiferal assemblage (Murray & Wright, 1974) and molluscan fauna (Burton, 1933; Curry, 1965), supported by mineralogical and geochemical data from the present study, indicate two major water depth ranges. These comprise an early shelf environment with variably shallow (up to 50m) water column, and a much shallower estuarine water body (see also Daley & Edwards, 1973).

The inferred relative magnitudes of the eustatic fluctuation of the Barton Sea (Fig.51) have essentially been based on two primary observations. Firstly, sandy to very sandy and pebbly sedimentations, coupled with re-working of shells into drifts and pockets occurred at shallower depths when the sea bottom lay within the wave zone or close to the wave base level (i.e. $\sim$10m - cf. Davis, 1983). Secondly, glaucony, which occurs in many parts of the Barton Clay, would mainly have formed when the sea-bottom was lowered below the wave base level. Considering that the Barton Sea was cool ($\sim$ 15-18°C - Murray & Wright, 1974), the conducive water depth would have been $\gtrsim$ 30m (cf. Fairbridge, 1967).

Thus, the Huntingbridge Clay Member very probably represents the period of rapid rise of the sea level, and the Barton Sea was being effectively established as a shelf sea. The highest sea-level attained ($\lesssim$ 100m - Murray & Wright, op.cit.) is probably marked by the region-wide diachronous Numulites prestwichianus bed at the base of the Highcliffe Member (cf. Gardner et al., 1888; Stinton, 1975). Thereafter, episodic

Fig.51 :Illustration of Sea-Level Curve and Sedimentation in the Upper Eocene Hampshire Basin.



Sea-level fall attended by

non-marine sedimentation and

pene-contemporaneous emergence of sediments

with surficial processes.

Sea-level rise and marine sedimentation:

A) Shallow estuarine and tidal-marsh sedimentation;

B) Episodic shelf sedimentation comprising:-

i)brief periods of rapid sedimentation in <30m-deep water columns and accompanied by diagenetic formation of Ca-siderites and ferroan calcite

ii)relatively-prolonged periods of little to non-sedimentation in ⩾30m-deep waters and marked by extensive authigenesis of glauconitic-mica glaucony

C) Coast-line sandy-pebble deposition followed by localised emergence and pedogenesis.

lowering of the sea-level occurred, often causing the sea-bottom to be brought briefly within the wave zone. This raising and lowering of the sea-level and corresponding movement of the sea-bottom, below and above the wave base, continued half way up the Naish Member (base of 'Bed D') of Burton (1929) (see Fig.51). After this, the sea bottom appeared to fluctuate only slightly about the wave base levels. These decreased fluctuations heralded the sudden large sea-level fall, and hence the shallowing of the Barton Sea, as marked by 'Shell Bed G'. Thereafter sea-level fluctuations were of very low magnitudes until the top of the Barton Sand Formation, when another large drop of the sea-level resulted in the region-wide emergence of the sand deposits and the development of swamp hydromorphic and acid red-yellow podzol palaeosols (Fig.48). As previously stated in Section 17.2.2D, the virtually 'instantaneous' tidal inundation that followed this emergence was, in turn, followed by another region-wide emergence with the development of palaeosols similar to the earlier ones. Non-marine sedimentation of the 'Lower Headon Beds' then followed in the established coastal plain environments (cf. Keen, 1977; Edwards, 1967). This was then terminated when the sea-level rose again causing the limited transgressive phase of the earliest Oligocene 'Brockenhurst Sea'.

17.4.2 Basinal Subsidence (and Isostatic Adjustments)

The creation of the Hampshire Basin is widely recognised (i.e. Curry, 1965; Ziegler, 1982) to have resulted from tectonic movements related to the opening of the Greenlandic-Norwegian Sea and the Arctic-North Atlantic Ocean in latest Cretaceous-Early Palaeocene times. Its existence was terminated, also by tectonic movements; but by those relating to the Late Oligocene-Miocene Alpine orogeny (i.e. White, 1921; Daley & Edwards, 1971). The tectonic movements are believed to be influenced by deep-seated pre-existing (Hercynian) structures. There is no consensus, however, as to which of the predominating NW-SE and E-W and few NE-SW structures in the region are primary or post-Hercynian (see Stoneley vs. Drummond in Stoneley, 1982). The details of probable tectonic movements in the region in Eocene times have not been clearly established. Jones (1981) inferred, from geomorphological reconstruction of southern England, that low-scale tectonic movements most probably occurred throughout the Palaeogene period. These movements caused the sub-Palaeogene erosional surfaces which have been recognised, in places, over the Upper Cretaceous

Chalk and early Tertiary sediments from Dorset to Sussex. Fisher (1862) and Plint (1982, 1983) have also inferred intrabasinal movements to explain the apparently slow deposition of the pebble bed base of the Upper Eocene succession and the eustatic sea-level fluctuations of the Bracklesham/Barton Sea. Plint (op.cit.) suggested the sea-level fluctuations to be due to periodic oscillatory (vertical) movements of an E-W trending submarine structure located to the east of the Isle of Wight. He could not, however, ascertain the nature of the structure(s) concerned.

In the present study, aspects of the regional tectonics that are particularly important concern probable differential opposite movements of the Hampshire Basin relative to adjoining horst structures to the south of the Isle of Wight monocline. Tectonic movements in the region would, as stated earlier, essentially be posthumous on the extensive Hercynian linear and faulted block structures in the Palaeozoic European craton basement (cf. Anderton et al., 1979). In relatively passive Eocene times of southern England, much of the tectonic movement in the region would have been vertical. Hence, basinal subsidence and isostatic adjustments of the basin, and adjoining structural highs to differential rates of sediment loading, would be expected (cf. Pitman, 1978).

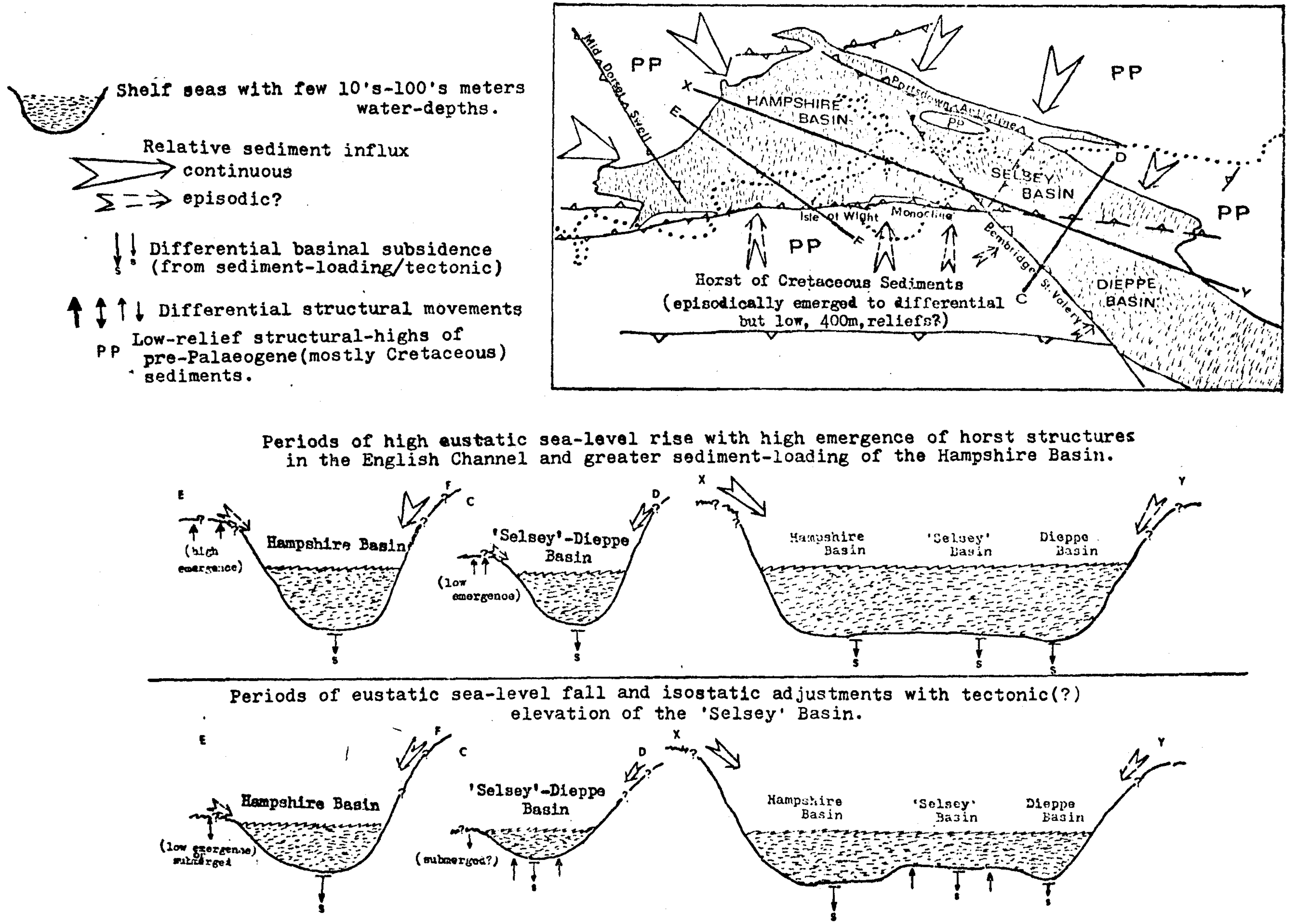
Subsidence, the change of depth which a certain stratigraphic level undergoes during a given time, owing to crustal downwarping of its basement relative to the present sea-level (von Rad & Einsele, 1980), has generally been attributed to the contraction of the cooling lithosphere, and may be inferred from age-depth relationship of basinal basement and present-day seas. Recent works on continental margins (i.e. Watts & Ryan, 1976; von Rad & Einsele, 1980) have indicated that water depths probably never exceeded shelf depths during the past 200 Ma; hence, subsidence rates during a given time may be deduced from the thickness of sediments accumulated over that time. With correction for compaction being insignificant, the subsidence rate of the Hampshire Basin, deduced from the ~ 550-750m thick Palaeogene sediments deposited over 25 M.yrs (i.e. ~ 55 → 30 Ma - Odin et al., 1978), would average 2 to 3 cm/1000 yrs. These are within the 2-4 cm/1000 yrs subsidence rates typifying post-Lower Cretaceous passive Atlantic margin basins (see Pitman, 1978). However, the numerous palaeosols and glauconitic horizons in the Hampshire Basin indicate considerable lengths of time with little or no deposition. This would mean that subsidence proceeded at variable rates. Murray & Wright (1974) suggest that a slowing down of the rate of subsidence relative to the rate of sedimentation might account for the absence of foraminifera from some very sandy and pebble-containing horizons of the Barton Clay at Alum Bay. Burnett & Fookes (1974) also appreciated the variation in the rates of regional subsidence as influencing the distribution of clastic grains in the London Clay Formation from the Hampshire Basin, London Basin, English Channel and north-western France. Fluctuations in the rate of subsidence would have implications for the sea level, a slowing down in the rate of subsidence equating to sea-level fall.

Rates of basinal subsidence have been found to generally decrease with time (Watts & Ryan, 1976; van Rad & Einsele, 1980). Indications of this happening in the Hampshire Basin are probably given by the significant basinward decrease in the magnitude (aerially and thickness) of successive units comprising the Palaeogene succession of the basin (see Fig.1; cf. Melville & Freshney, 1982). The sediments' distribution and facies would further suggest subsidence in the basin to have been centred on the northern half of the Isle of Wight and to have progressed episodically in phase with the eustatic sea-level fluctuations.

Reverse movements complementing the basinal subsidence would be expected on adjoining structural highs. These, in areas to the north and west of the Hampshire Basin, cannot be identified from the present study. It has only been possible to assess the movements of the horst structures adjoining the basin, in particular those to the south in the English Channel and the southern half of the Isle of Wight.

The probable relative movements involved are illustrated in Figure 52. To facilitate the consideration of these movements, a small E-W trending 'Selsey Basin' (after Selsey, Nat.Grid.920850) has been delineated from, and taken to be continuous with, the Hampshire and Dieppe Basins proper (cf. Fig.2). This delineated 'Selsey Basin' is here equated to the inferred submarine structure of Plint (1982, 1983). It is assumed to be separated from the Dieppe Basin to the south by an easterly extension of the E-W trending Isle of Wight monocline. It would also be separated from the Hampshire Basin to the west by the northern end or extension of the NW-SE trending Bembridge-St.Valery monocline, or a SW-NE trending lineation similar to those found over the Mesozoic strata

Fig.52: Illustration of Relative Conditions of the Hampshire-'Selsey'-Dieppe Basins and Adjoining Strutural Highs



in the Central English Channel (cf. Smith & Curry, 1975). In contrast to the greater part of the Hampshire Basin, where large sea-level fluctuations, emergence and submergence occurred, the 'Selsey' and Dieppe Basins were submerged beneath sea waters throughout the Eocene times. These basins are characterised by sandy and calcareous marine sediments (Dingwall & Lott, 1979), which suggest the continuous prevalence of shallow shelf conditions not unlike that of the Hampshire Basin.

The previously discussed mode of sediment derivation (Section 17.3) provides the best indication of probable relative basinal/horst movement. It has been shown that derivation from the horsts was episodic, being substantial during periods of large eustatic sea-level rise, but significantly decreased during periods of large eustatic sea-level falls and the emergence of the Hampshire Basin. It is therefore inferred that the horsts are low-relief emergent structures which periodically become lowered below the regional mean sea-level. However, the geology of the English Channel (Smith & Curry, 1975; Dingwall & Lott, 1979) indicates the horst structures to the south of the Isle of Wight monocline to have been deeply eroded with much of the Upper Cretaceous sediments having been removed. With only a 2-7 km long strip of Upper Cretaceous sediments remaining preserved very close to the Isle of Wight monocline, it could be inferred that the horst submergence was shallow and of limited extent. But further south, out in the English Channel, more extensive (up to 60 km) length of Upper Cretaceous Chalk remains preserved. This constitutes the main horst structure(s) adjoining the Bembridge-St.Valery monoclinal western margin to the Dieppe Basin (Smith & Curry, op.cit.). This Chalk would have been a submarine inversion structure for much of Tertiary times (cf. Ziegler, 1982).

Being strictly continuous, the Hampshire-'Selsey'-Dieppe Basins would most probably have behaved consonantly, although differential magnitude in response to tectonic factors would be expected. The greatest responses would be within and around the more land-locked Hampshire Basin. During periods of rapid basinal subsidence and large eustatic sea-level rise, shelf conditions would prevail in much of the Hampshire Basin, as occurred continuously in the 'Selsey' and Dieppe Basins. The adjoining horst structures would then be raised, with those located close to the Isle of Wight being emergent. Those emerged horsts would then be eroded to provide additional detritus for the marine facies of the Hampshire

Basin. The consequence would be greater sediment-loading of the Hampshire Basin and greater denudation of its adjoined horsts compared to the 'Selsey'-Dieppe Basins. Ensuing isostatic adjustments would probably involve decreases in the basinal subsidence rates with lowering of adjoining horsts. If, as a consequence of its greater sediment loading, the subsidence rate of the Hampshire Basin decreased more slowly, then its sea-bottom would become lowered relative to those of the 'Selsey' Basin and probably of the Dieppe Basin. This would cause a significant reduction in sea water circulation between the Hampshire Basin and the 'Selsey' Basin. Therefore the areal extent and eustatic level of the sea in the Hampshire Basin would become reduced, and shallow sedimentation would occur. When the world-wide sea-level fall occurred, the eustatic fall in the Hampshire Basin would be very rapidly manifested.

Alternative possibilities with regard to possible tectonic movements suggestion have been made by Plint (1983). He envisaged the 'Selsey' Basin to be tectonically raised independently of the Hampshire Basin. Such limited tectonic movement would probably have occurred along structures not common to both the Hampshire and 'Selsey' Basins. The only probable 'different' structure would be the SE-NW trending lineation suggested earlier to separate the two basins. It is most probably a Hercynian structure; and, in fact, movements over such a lineation could account for the inverted Permian-early Upper Cretaceous sediments in the areas of Central English Channel and Western Approaches (cf. Ziegler, 1982). Hence, it is not improbable that in Tertiary times, occasional movements on such lineations differentially affected the 'Selsey' Basin. The consequence of this, when the movement is positive, is the raising of the basin relative to the Hampshire Basin with the attendant restriction of sea-water circulation.

Confirmation of the probable existence of the suggested 'Selsey' Basin and its relative movements would be expected from detailed geophysical studies and investigation of cored material. This is, however, beyond the scope of the present study, and although Curry & Smith (1975) have provided and discussed data from such studies for the English Channel, the areas covered are outside the delineated 'Selsey' Basin.

17.4.3 Variations in Sedimentation

The rates at which sediments accumulate in passive basins are closely related to both the rates of subsidence and eustatic sea-level fluctuations. Pitman (1978) has shown that in such basins the spatial and temporal variations in the rates of sedimentation are such that a constant shelf-coastal plain slope is maintained. Therefore, with sedimentation being positive shelfwards but generally negative landwards, shorelines will be expected to stabilise where the rates of sedimentation equal the rates of sea-level rise and rates of subsidence. In places or periods of non-deposition, the shoreline will occur where rates of subsidence equal the rate of sea-level fall. The implication is thus that the axes of active sedimentation and the shoreline will move landwards during transgression, or shelfwards during regression.

In the Palaeogene Hampshire Basin, the axis of sedimentation shifted to within 5-10 km west and east of Alum Bay (Plint, 1983) or about a hinge now occupied by The Solent (West, 1980) (see Fig.1). There might also have been some small (∼ 2 km?) shoreline shifts to the south of the Isle of Wight monocline, particularly in the vicinity of Alum Bay. From radiometric dating of glaucony, Odin et al. (1978) have shown that the rate of sedimentation in the Hampshire Basin is about 2·5 cm/1000 yrs. Sedimentation has thus been slow, appearing to be in phase with the basinal subsidence. However, the rapid episodic changes in sediment derivation and depositional conditions inferred from the present study would suggest that sedimentation progressed at very variable rates.

The sandy to very sandy nature of the sediments has been regarded as suggesting that sedimentation occurred within shallow water bodies with the prevalence of strong current conditions. However, several horizons show abundant authigenic glaucony. This would only have formed in low energy conditions of periods of high sea-level rise when the sea bottom was lowered below the wave base level (i.e. ∼ 10m). Other significant consequences of such a high sea-level would include the shift of shoreline landwards with attendant extensive inundation of the generally low-lying adjoining land areas and horst structures. Plint (1983) has suggested that, during these periods, drainage to the basin would discharge sediment loads further upstream away from the basin proper. The consequence would be that very little clastic supply and deposition in the shelf area would occur during periods of high sea-level rises. This low or non-existent sedimentation, coupled with the lowering of the sea bottom(to below 30m depth in the cool Barton Sea) was accompanied by extensive glaucony authigenesis. Occasional lowering of the sea level then raised the sea bottom into the wave zone, terminating the glauconitisation processes. Furthermore, the shoreline would move back shelfwards, causing earlier flooded areas to become exposed for erosion. Previous upstream accumulates would thus provide additional detrital materials to the basin. Since the distribution of the glaucony indicates frequent falls and rises of the sea level (Fig.51), then the sedimentation of the large detritus supplies would only have occurred at very rapid rates during periods of substantial falls of the sea levels.

No glaucony occurs higher than half way up the Naish Member (i.e. base of 'Bed D' of Burton, 1929, see Fig.5). Therefore, it could be said that an irreversible fall of the Barton Sea level started at the time of 'Bed D' deposition, the lower part of which is glauconitic, but whose upper part is a mottled, bioturbated very sandy-clay with abundant plant debris and shell masses. The succeeding 'Beds E and F' comprise massive grey and brown clays. These are probably the eroded vast tracts of clays that had built up upstream during the earlier deeper water phase of the Barton Sea. 'Beds E and F', however, also contain several lines of shell drifts, which suggest that the sea-bottom lay close to the wave base level so as to be more affected by storm currents drifting the shells. This explanation of the deposition of 'Beds E and F' conflict with the opinions of Murray & Wright (1974) who regarded them as the only true offshore (deep water, low energy) shelf deposits of the Barton Sea.

A sudden 'large' drop of the sea-level terminated the shelf Barton Clay sedimentation, as represented by 'Bed F' on mainland Hampshire. This sea-level fall was attended by large scale mortality of organisms whose shells then became re-worked by currents and concentrated in the 'Shell Bed G' in the area of Barton-on-Sea, although mottled sandy-clays continued to accumulate elsewhere to the east. After a protracted period of relatively small sea-level fluctuations, the shelfward shift of the shoreline eventually led to coarse-grained sedimentation in the shallowed-up Barton Sea in the area of study. The sea had by now been converted into estuarine-lagoonal water bodies (see Murray & Wright, 1974). The prevalence of strong energy currents facilitated good sorting in the barrier-type quartz-sand accumulation of the Barton Sand. The marine sedimentation was terminated by another sudden large sea-level fall, which would correlate with the world-wide regression of late Upper Eocene-Oligocene times. This was attended by non-marine sedimentation in the coastal plain environments of the 'Lower Headon Beds'.

In summary, the Upper Eocene sedimentation has very probably taken place at variable rates, essentially in shallow water bodies with strong prevalent current energies and fluctuating water levels. The present study has, in particular, allowed deductions of the early Upper Eocene shelf sedimentation as comprising two alternating episodic phases. Firstly, there were relatively protracted periods of high eustatic sea-level rise with little clastic supply and very slow or limited sedimentation. These were attended by extensive glaucony authigenesis. These periods alternated with relatively short periods of substantial sea-level fall with a high supply of clastic material and a rapid sedimentation rate. As discussed later in Section 7.5.3C, it was during these short periods of rapid sedimentation that the early, precompactional diagenetic formations of Ca-siderites and ferroan-calcite occurred in the marine succession.

17.5 Mineral Authigenesis

The mineralogy of the Upper Eocene sediments is characterised by occurrences of authigenic phases comprising:

a) kaolinite, goethite, lepidocrocite, jarosite and gypsum formed from surficial alteration and pedogenous processes on penecontemporaneously emerged sediments;

b) lime mud calcite precipitated, microflorally-induced, from ponded hard, Chalk waters in the late Upper Eocene times;

c) glauconitic-mica glauconies formed at or close to the sediment surface in the early Upper Eocene Barton Sea;

d) pyrite, calcian-siderites and ferroan calcite formed from diagenetic processes at sediment-water interface and within very shallow burial depths.

The significance of these minerals is that they are primary and hence provide information on the various prevailing conditions that led to their formation. The fact that the Upper Eocene sediments have had a shallow ($<$ 200m) burial history means that the effect of elevated temperatures and overburden pressure have been insignificant. The sediments remain poorly compacted and unlithified. In addition, there is no indication of significant diagenetic alteration or transformation of the original sediment constituents.

In earlier discussions of the authigenic minerals, four main environmental/sedimentological factors were deduced to have probably influenced their formation. These are:

i) the prevailing warm, humid palaeoclimatic condition of the Eocene southern England and the characterising moderate-intense weathering.

ii) the derivation of abundant iron-oxides and dissolved $CaCO_3$ from highly calcareous Upper Cretaceous Chalk, and glauconitic or ferruginous earlier Cretaceous and pre-Upper Eocene sediments in low lands and structural highs adjoining the Hampshire Basin;

iii) the alternating short periods of rapid sedimentation and protracted periods of little to non-deposition in the Barton Sea;

iv) penecontemporaneous emergence of sediments to differential geomorphological (reliefs and drainages) conditions.

Factors (iii) and (iv) are, in fact, manifestations of variations in the basin conditions (i.e. eustatic sea-level fluctuations) and low scale tectonic movements (see Section 17.4).

Compositional aspects and the importance of the authigenic minerals are considered further below.

17.5.1 The Pedogenous/Exogenous Phases

Two assemblages of authigenic minerals were formed from sediments emerged and subjected to surface processes. Assemblage A consists of kaolinite and goethite; whilst Assemblage B comprises one of, or combinations of, kaolinite, goethite, lepidocrocite, jarosite and gypsum.

Assemblage A was found characterising the well-evolved acid palaeosols - the red-yellow podzols (arenosol/rossosol) and red-earths (gleysol) in the succession at Alum Bay. The kaolinite consists of b-axis disordered platy crystals and vermicular books in open textural aggregations (Plate 56). Keller (1982) has shown that this type of kaolinite occurs as a primary alteration product of residual weathering profiles. However, unlike many weathering mantles, no associated halloysite or topotaxial continuity of the kaolinite with altered feldspars and other silicate phases were observed (cf. Keller, 1977). Whilst halloysite precursors could not be ruled out, there is convincing evidence for the precipitation of the kaolinite from solution. The lack of topotaxial continuity suggests that the solutions are apparently in equilibrium with the altered silicate phases (cf. Keller, 1977; pp.341 & 342).

Goethite, also precipitated from solution, was found to predominantly consist of disseminated, very fine, crystal laths (i.e. Plate 52d & e), except in the indurated horizons where glaebular and interwoven plates or laths occur (Plates 51, 53). Goethite laths and glaebules are more common in present day soils, particularly in wet and humid tropical-warm temperate regions (i.e. Eswaran & De Connick, 1971; Mackenzie et al., 1971; Chukrov et al., 1972). Intricately interwoven (or boxwork) laths and plates are mostly found in indurated horizons; in particular, the laterite crusts of rainy tropics (i.e. Alexander & Cady, 1962; Schwertmann, 1977). Several authors, including Hsu & Ragone (1972) and Schwertmann (1971-82), have, from synthetic studies, found that the nature and morphology of iron-oxide phases precipitating from solution are influenced by a number of factors, in particular the oxidation rate, the OH^-/Fe^{2+} concentration ratios, and the presence of growth-inhibiting cations such as Al^{3+} and Si^{4+}. The different goethite forms observed in the Upper Eocene palaeosols may thus be interpreted in terms of the prevalence of differential iron abundance, aeration (pO_2) conditions and the level of the water table. The soil horizons below the highest water table have been subjected to 'amphibious aeration conditions' (see Mohr & von Baren, 1954, p.294), and hence variable extents of iron mobilisation and accumulation. In addition, the probable presence of some of the leached silicate cations might have restricted the crystals' growth to lath forms (cf. Taylor & Schwertmann, 1980). The indurated horizons (vesons or IIB2ir) have coincided with the highest water tables; hence their high goethite accumulations (cf. Gidigasu, 1976).

An important topo-induced aspect of the palaeosols was recognised from their substantially high goethite (up to 44%) and kaolinite (35-100%) contents relative to the trace iron-oxides and $< 20\%$ feldspar + 2:1 clay mineral contents of their host parent sandy sediments. The pedogenesis had most certainly involved mobilisation of cations, via sub-surface groundwater drainages, from outside the observed palaeosols. The source of such ion-charged waters would most probably have been exposures of ferruginous sands, swamps rich in pyritic materials, or even glauconitic sediments on the horst structures to the south of Alum Bay. Topo-induced soil features are not uncommon; they have been described from Borneo (Hardon - quoted in Joffee, 1945; p.415) and Central Africa (Maignien, 1966; cf. Gidigasu, 1976).

Assemblage B characterises the lignitic clays and their immediate 'seat-earths' clastic sediments which, together, constitute the poorly-evolved hydromorphic swamp palaeosols (Figs.48, 49). The minerals have most probably formed from the oxidation and/or hydrolysis of pre-existing silicate minerals such as feldspars and detrital clay minerals, and iron-bearing minerals, particularly pyrite and siderite. Ferrous minerals are unstable in oxidising sub-aerial conditions (see Fig.28). When acted upon by atmospheric elements, the unstable iron minerals essentially alter to iron-oxides. The iron-oxides formed may initially be in an amorphous state or directly precipitate out in crystalline forms. Amorphous iron is most common in present-day soil and freshly-laid sediments (i.e. Eswaran & De Connick, 1971). Crystalline iron-oxides, however, comprise several polymorphs in variable crystal forms (i.e. Deer et al., 1962; Schwertmann, 1977; Beutelspacher & van der Marel, 1968). Which crystal phase and form is produced depends on several inter-related factors, including pO_2, pCO_2, pH, concentrations of iron in solution, the presence of other cations and 'seeding materials' (i.e. De Villers, 1969; Schwertmann, 1970-82; Chukrov et al., 1972, 1975). Factors found conducive for goethite and lepidocrocite, the phases found in the present study, have been considered in Chapter 9.

In nature, soil acids or acids produced from altered and hydrolysed iron-minerals would further attack pre-existing silicates and carbonates. Through various intermediary products, varieties of exogenous minerals would form, including kaolinite, jarosite and gypsum (see Deer et al., 1962). Their distribution in the Upper Eocene succession is given in Chapter 10 (see Section 17.2).

The major problem of the exogenous minerals in the present study is the difficulty of ascertaining their age. Whilst penecontemporaneous emergence of sediments in the coastal flood plain environments in the late Upper Eocene times could have been accountable, surficial alteration since the Miocene uplift of the Palaeogene sediments (White, 1915) and the Holocene coastline developments in southern England (West, 1980; Melville & Freshney, 1982) could equally have been accountable. Furthermore, there is no known established criteria that differentiate products of ancient and Recent surficial processes. Gallois and Horton (1981) have highlighted the widespread alteration of minerals on exposed sediment faces in Britain. Indeed, those exogenous minerals, particularly yellowish-flaky jarosites and gypsum of selenitic habit, commonly occur on faces of both the marine and non-marine sediment exposures presently studied (i.e. Plates 7, 39). These surface-coating minerals have certainly formed recently from altered pyrite or glaucony and Fe^{2+}-rich diagenetic carbonates. However, samples of sediments used for detailed laboratory investigations were collected well away ($>$ 30 cm) from the sediment faces and, as much as visibly possible, seen to be fresh, unweathered materials. Samples collected fresh can, nevertheless, also have their unstable mineral contents oxidised to a considerable extent during storage in ordinary laboratory conditions. Taylor & Spears (1981) have highlighted this as a major problem in geochemical studies, whilst Howie (1979) has also shown the serious problem it causes for museum materials.

In the absence of differentiating criteria between ancient and Recent exogenous minerals, perhaps it is only worthwhile considering further the probable stability and preservation of ancient materials.

Reports of jarosite occurrences have mainly been from present-day cat-clays (i.e. Dones & Lynn, 1977) and exposed sediments' surfaces (i.e. Warshaw, 1956; Deeson et al., 1973). Buurman (1980a) has, however, described jarosite from the hydromorphic palaeosols of the Reading Formation at Alum Bay on the Isle of Wight. Reading Formation is the earliest, late Palaeocene - Early Eocene age deposit in the Hampshire Basin (see Table 1). Buurman implies that the jarosite observed is an in situ penecontemporaneous alteration product of pyrite. Jarosite in the Upper Eocene palaeosols occurs intimately admixed with clay minerals, organic matter and similar exogenously formed goethite and gypsum.

Gypsum is a more common constituent of present-day soils. Although most common in soils of areas with hot and/or dry climatic seasons (i.e. Fitzpatrick, 1971), the mineral does also occur in hydromorphic soils of humid, warm climatic regions (i.e. the cat-clays - Dones & Lynn, 1977). The morphology assumed is diverse, varying from disseminated lenticular crystals to aggregated prismatic crystals. Those in the present study are predominantly anhedral/subhedral prismatic crystals occurring in disseminated and in rosette aggregations (Plates 34,35,36). Brewer(1964) has indicated rosette morphology to be common in soils, this being indicative of precipitation from finite solutions within confined micro-spaces. The rosette gypsum may thus be suggestive of primary soil origin. Gypsum will not, however, be expected to survive dissolution in the prevailing humid sub-aerial conditions of the Upper Eocene southern England (see Section 17.1). Nor would it be expected, on burial, to survive dissolution or replacement effects of interstitial waters undersaturated in sulphate ions. In fact, the widespread development of diagenetic carbonates in the succession (discussed later) indicates the existence of HCO_3^- - rich interstitial waters. These should have caused carbonate replacement of the gypsum. Freytet (1971) has described such carbonate pseudomorphs of gypsum from Late Cretaceous - Lower Eocene hydromorphic palaeosols in Languedoc, France. Daley (1967, 1973) has also described pseudomorphs after gypsum from the Oligocene Bembridge Formation occurring higher up the Palaeogene succession on the Isle of Wight. Similar pseudomorphs on gypsum were not observed in the present study. Further investigation, particularly of borehole samples, is required.

Reported occurrences of lepidocrocite were very few compared with goethite, which occurs more often in soils of warm, humid climatic regions (i.e. Chukrov <u>et al.</u>, 1972). Lepidocrocite mainly forms in high water-table (hydromorphic) conditions where abundance of organic accumulates may assist in its stabilisation (i.e. Schwertmann & Taylor, 1979), and the presence of leached-out silica and alumina may inhibit goethite crystallization (i.e. Taylor & Schwertmann, 1982). The disseminated iron-oxides in the Upper Eocene hydromorphic soils were not investigated in detail. Attention was rather paid to two occurrences of iron-oxide crusts and scales formed from sideritic materials. These provided an invaluable opportunity for studying rare natural association of goethite and lepidocrocite. In fact, whilst iron-oxide crusts are commonly reported on altered ironstones (i.e. Gad <u>et al.</u>, 1969, Childs <u>et al.</u>, 1972; Matsumoto & Iijima, 1975), detailed petrographic descriptions of the crusts are rarely given. In one occurrence from Whitecliff Bay, the goethite and lepidocrocite differentiated as alternating steely-goethitic scales and earthy-lepidocrocite crusts (i.e. Plate 25). The goethite scales are the earlier alteration products, and are comprised by stacks or books of thin, serrated-edged, platy goethite crystals pseudomorphed after the rhomb- and spherulitic aggregations - forms of the altered siderites (Plates 88a-j). The lepidocrocite crusts consist of small, anhedral, clay-sized platy crystals often in silt-sized aggregations, but in places appear to have transformed to boxwork of thin platy goethite crystals (Plates 89a-j). In another case studied, only layers of scales occur, and it consisted of a flowery mass of interwoven subhedral platy lepidocrocite with pyramidal terminations and euhedral and subhedral elongated laths, prismatic goethite crystals (Plates 9a-j). These crystals, particularly the lepidocrocite, are seen, in places, to be differentiating(?) from masses of vuggy, crypto-crystalline iron-oxide crust (Plates 90c,h). The alternating scale-crust is thought to be a manifestation of surficial alteration in a fluctuating dry - wet, warm sub-aerial condition; whilst, the flowery admixed phases probably resulted from differential aeration (rate of oxidation) in a water-logged condition (cf. Schwertmann & Taylor, 1972; Taylor & Schwertmann, 1978).

In general, the exogenous phases in the Upper Eocene palaeosols are enigmatic. Satisfactory explanation of their occurrence as to whether penecontemporaneous or Recent can best be given by further investigations of fresh borehole samples. These were not available for the present study.

5.2.2 Sub-aqueous Authigenesis of Micritic Calcite

The only sub-aqueous authigenic phase to be formed in the late Upper Eocene Hampshire Basin comprises the freshwater micritic mud calcites. These constitute the bulk (up to 90%) of the freshwater biomicritic limestones occurring in the non-marine 'Lower Headon Beds' sections at Alum Bay on the Isle of Wight, and on mainland Hampshire. The calcite mostly occurs as anhedral, < 5 µm-sized, low-magnesian variety (Plates 62a-d), although, in places, it appears slightly ferroan (cf. Plate 63). An important textural aspect of the calcite is its lack of significant diagenetic recrystallization or cementation (see Plate 62). In fact, the freshwater limestones are themselves only poorly compacted, and with the associated aragonitic fossil gastropodal shells remaining preserved in an unaltered form (i.e. Plates 63, 64). The formation of the calcites and the observed state of the limestones (see Chapter 13) are amongst the major manifestations of the prevailing palaeoclimatic conditions and nature of sediment-derivation to the basin.

Precipitation of $CaCO_3$ depends on several factors influencing the solubility constant of $CaCO_3$. Several authors, including Leeder (1980), have highlighted the more important thermodynamic factors to be the concentration abundance of Ca^{2+} and HCO_3^-; the partial pressure of CO_2(pCO_2) and temperature. Other notable factors include the total (hydrostatic) pressure, intensity of evaporation, the presence and abundance of dissolved cations (i.e. Mg^{2+}, Zn^{2+} - see Folk, 1974) and dissolved salts (i.e. NaCl, Na_2SO_4 - see Lippman, 1973).

In freshwater bodies, which are of interest to the present study, the lowering of pCO_2 is most relevant. Terlecky (1974) and many other authors have shown that loss of CO_2 to the atmosphere occurs when water bodies warm up, particularly during 'summer' seasons which, if dry or hot, may be attended by substantial evaporation. Considerable amounts of CO_2 are also extracted from waters by aquatic plants for photosynthesis. The more important plants are the green algae, such as Charophytes, which not only blooms abundantly during warmer 'summer' seasons, but also secretes calcite coatings from materials extracted from the water bodies. Normal fresh-waters are, however, only barely saturated with $CaCO_3$ (i.e. $\sim$ 20 ppm - Rosler & Lange, 1971). $CaCO_3$ precipitation is only likely to occur where there has been surface and/or sub-surface drainage through calcareous rocks (i.e. limestones) and Ca-rich gypsiferous/anhydritic deposits. The drainage waters will be 'hard' and, where ponded or protected from strong current turbulencies and where clastic discharge is small, calcite precipitation may be favoured.

The present study has indicated the late Upper Eocene times in the Hampshire Basin to be characterised by much warm, humid sub-aerial conditions and low-lying non-marine coastal environments with warm depositional water bodies (see Section 17.1). It has also been considered that the attending moderately intense weathering effected considerable dissolution of the Upper Cretaceous Chalk, which occurred extensively in land areas and structural highs adjoining the basin (see 17.3). The consequence was the existence of $CaCO_3$-rich drainages to the basin. Micritic mud accumulation occurred where such hard waters became ponded (cf. Plint, 1983). The significant contribution of aquatic microflora is indicated by abundant occurrence of Charophytes oogonia (i.e. Fiest-Castel, 1977). Petrological evidence of algal influence is also given by occurrences of 10-20 μm-sized calcite pieces (i.e. Plate 62e), which are similar to the broken-up algal calcite coatings that Terlecky (1974) described from a marl lake in New York State, U.S.A.

The lack of textural evidence for alteration does not, however, rule out possible syndepositional recrystallization and compaction. Unlike calcite in caves and caliche soils, which precipitate directly as lithified masses (i.e. Lippman, 1973), sub-aqueous calcite precipitations are generally, initially, as micritic muds. Notable Recent examples include those described by Newell & Rigby (1957) from ponds in Andros

Island, Barbados; from marl lakes in North America (i.e. Murphy & Wilkinson, 1980); Lake Zurich (Kelts & Hsu, 1978); and the Black Sea (Hsu & Kelts, 1981). Recrystallization of the initial micrite mud may occur quite rapidly after the precipitation, prior to burial. Perhaps the little amount of iron ($<$ 1% FeO) observed in the calcite was probably incorporated during the recrystallization; that amount being the utmost possible for thermodynamic stability of calcite on the earth surface (i.e. Richter & Fuchtbauer, 1978). The continued preservation of the lime-mud calcite uncemented and of the associated aragonitic shell unaltered was most likely due to the Ca-saturated nature of the ground- and interstitial-waters. In fact, this - a manifestation of the significance of derivation from the nearby Chalk rocks - is also a very important influence on the formation of Ca-rich diagenetic mineral phases in the Upper Eocene sediments. These are discussed later in Section 17.5.3C.

Micritic calcites also occur in other parts of the Palaeogene succession of the Hampshire Basin. These occur constituting the late Middle Eocene(?) Creechbarrow Limestone Formation (Plint, 1983); and limestones within the Oligocene 'Upper Headon Beds' and Bembridge Formation (Edwards, 1967). However, no detailed compositional studies of these are known, and hence comparison with the presently studied Upper Eocene occurrences could not be made. This is an area for further studies in the basin.

17.5.3 Diagenetic Minerals

The Upper Eocene sediments are characterised by occurrences of glaucony, pyrite, siderite and ferroan calcite. These are manifestations of syndiagenesis (sensu Fairbridge, 1967) in the succession. Considerable attention was paid to the petrology and composition of those minerals in order to establish their probable modes of formation. In comparison with previous diagenetic studies, which are few and limited in scope (i.e. Potter, 1977; Hewitt, 1982), the present study has provided considerable insights into the direction fo diagenesis in the Palaeogene succession of southern England. This study also highlights the significant influence, on early diagenesis, of sedimentological factors such as the nature of source rocks and differential rates of sedimentation.

Both glaucony and pyrite are essentially formed at or close to sediment-water interface. The former is favoured in slightly oxidising (Eh $\sim$ 0) micro-environments within relatively passive, low sedimentation shelf conditions, whilst the latter commonly ensued in more reducing ($Eh < 0{\cdot}1$) conditions within freshly-laid sediments (cf. Irwin & Hurst, 1982). The carbonate phases constitute authigenesis below the sediment surface in the presence of abundant Fe^{2+}, Ca^{2+}, and high pCO_2 ($> 10^{-3}$ atm) but low a_{HS^-} (i.e. $pS^{=} < 10^{-10}$) (i.e. Curtis, 1980). These minerals are considered as follows.

A) Glauconitic-mica Glaucony

Formation of glaucony (glauconitisation) occurred extensively in the shelf environments of the early Upper Eocene Barton Sea. The process has previously been considered (Section 17.1.3 - 17.2.2C) to ensue from the relative passive but shallow (~ 10-50m), cool water (~ 15-18°C) conditions of the Barton Sea, and the high influx of colloidal iron-oxides (see 17.3.2). Other important aspects of the glauconitisation considered further below concern the two propounded theories of glaucony formation, and the relationship between compositions and crystal characteristics of glauconies and their length of period of growth.

The growth theories are the 'layer-lattice alteration' of Burst (1958) and the 'Epigenetic substitution' of Ehlman <u>et al.</u> (1963) or the 'Verdissement mode' of Odin & Matter (1981). The former supposes degraded 2:1 clays gradually adsorbing Fe^{3+} and K^+ respectively into charge-deficient octahedral layers and inter-layer positions. The inadequacy of this theory to account for numerous glauconies with kaolinite or non-clay parent materials, together with the lack of a linear relationship between Fe^{3+} and K^+ contents of glauconies, led to the suggestions of the latter theories. These suppose that any clastic and biogenic material can act as substrate or parent material for glauconies. In these, iron emplacement occurs earlier than the fixation of K^+, whilst growth of the glaucony would be maintained by diffusion of essential cations to the substrate. Some authors, including Velde & Odin (1975) and Kohler and Koster (1976), have also shown that glaucony growth commences with crystallization of iron-rich but potassium-poor smectitic-type platy crystallites - the glauconitic smectite. As growth progresses, these would recrystallize into high iron-containing, potassium-rich illitic-type filamentous crystallites - the glauconitic mica (cf. Kohler, 1980; Odin & Matter, 1981). Odin and Matter (<u>op.cit.</u>) further worked out an evolution scheme in which growth over a period of 10^4-10^6 yrs is considered essential for well-evolved glauconitic-mica; lesser period would produce glauconitic-smectite.

Glaucony in the Upper Eocene sediments studied grades from clay ($< 2\ \mu m$) to medium-sand grains (~ 500 um). The granular glauconies were studied in detail. They are morphologically mainly of moulds of foraminifera tests, although few appear to be sub-rounded broken-up pieces (Plates 59, 60, 61a-c). They consist of high iron ($\sim 23\%\ Fe_2O_3$), moderate potassium ($\sim 7\%\ K_2O$) - containing 1 Md glauconitic mica (Table 12, Fig.26). The crystallites are mostly filamentous (Plates 61d-i), these being flattened in the thin ($< 5\ \mu m$) outer wall but in randomly oriented aggregations in the bulk inner mass. In the absence of impurities that may be considered as relic parent materials, the micro-fossil test morphology would suggest a 'Verdissement mode' of formation. Growth of glauconies in tests of micro-organism are very common in literature (i.e. Triplehorn, 1966). The tests provide a semi-confined voidal environment where decay of organic tissues could help establish slightly reducing conditions (Eh ~ 0) conducive to the formation and stability of glaucony (i.e. Takashashi & Yagi, 1929; McRae, 1972). The test walls also act as an interface between the essential ions diffusing from sea-water or accumulated detritus and the developing glaucony.

Alternatively, the glaucony growth might have involved pre-existing mineral(s), but that the glauconitisation processes effected complete transformation of such parent material(s) involved. Such a growth mode (or 'epigenetic substitution') would very probably have involved the clay minerals. These can occur dispersed on the sea-floor, coat surfaces of mineral grains and, in addition, fill skeletal chambers. Any, or a combination of the derived degraded kaolinite, illitic and smectitic phases could have been utilised. Kaolinite is, in fact, the most common clay phase found associated with glauconies (i.e. Odin & Matter, 1981). The abundance of kaolinite in the Upper Eocene succession is, however, uniformly small ($\lesssim 15\%$, Fig. 23a-c). Such derived quantities are insufficient to account for the extensive glauconitisation observed. Even if kaolinite has been involved, a systematic variation in its abundance will be expected, at least in the marine Barton Clay. This is not observed (cf. Figs. 23a, b & c). The utilisation of kaolinite could not have been significant, if at all.

In the case of the smectites, reconstitution in marine environment could be expected. This, however, normally involves Mg^{2+} adsorption (i.e. Whitehouse & McCarter, 1959). In the presence of abundant iron-oxides and a conducive passive shelf condition, the reconstitution might proceed further, resulting in the formation of glauconies (cf. Burst, 1958; Odin & Matter, 1981). Whether the smectites derived for the Barton Clay underwent such transformation is difficult to ascertain from the data obtained at present. If smectites' reconstruction had occurred, it would be expected that smectites left in association with the glauconies will possess good crystallinities. This is not so found; the smectites' crystallinities are poor to fairly good (i.e. indices of 0·4 - 0·7; cf. Biscaye, 1965), variation of these being independent of the presence or absence of glaucony. Besides, no systematic differences of smectite abundance is observed in the glauconitic and non-glauconitic Barton Clay sediments. Whereas, had there been transformation of the derived smectites in the glauconitic horizons, significant differences should be observed.

Illite is generally the more abundant clay phase in the succession. The illite estimates from the glauconitic Barton Clay sediments are, however, inclusive of the structurally similar glauconitic mica of clay-sized glauconies. The glaucony contributions are, however, not manifested into differential illite estimates in the glauconitic and non-glauconitic sediments. This raises two questions. Firstly, could it be that illite derived for the glauconitic horizons was of small amounts but later topped-up with syndepositional glauconies formed from non-illite-involving modes? Secondly, could it be that the derived illite was in amounts as now estimated, but that a substantial portion of it was reconstituted to glauconies in situ? Both are probable, but none can be satisfactorily assessed.

Petrologically the clay matrix of the glauconitic sediments comprises intimately-admixed glauconies and the detrital clay phases (i.e. Plates 30, 31). It would be thought that the illite phase would be low in abundance in the glauconitic sediments compared to the adjoining non-glauconitic sediments. The confirmation of this by differential separation, possibly magnetically, could not be performed during the course of the present study. Whatever amounts were deposited, anyway, illite reconstitution in sea-water would normally only be expected to involve K^+-adsorption (i.e. Nicholls & Loring, 1960). Then there is also the absence of an established mineralogical or chemical transition between illites and glauconies (cf. Velde & Odin, 1975; Odin & Matter, 1981).

Illite reconstitution will thus not be expected from normal sea conditions. Nevertheless, being a potential parent material for glauconies, degraded illites might transform to glauconies where slightly reducing conditions and high amounts of mobilisable colloidal Fe^{3+} are available.

Probable involvement of illitic parent material, along with the presence of high amounts of influxed iron-oxide, would significantly help acoount for the apparent short growth periods of the Barton Clay glauconies. With illite and glauconitic mica being structurally similar (cf. Gruner, 1935; Brindley, 1980a), illitic parent material should not require to transform via the glauconitic smectite phase. This might considerably shorten the 10^4-10^6 growth periods that Odin & Matter (1951) suggested for glauconitic mica. The apparent short growth periods in the Barton Sea were realised from the fact that Odin et al. (1978) have shown the Palaeogene sedimentation rate in the Hampshire Basin to be $\sim 2{\cdot}5$ cm/100 yrs; and that the $\sim$ 25m glauconitic sediments in the Barton Clay Formation could thus have taken only $\sim 10^6$ yrs to accumulate. Such a length of time would, on the basis of Odin & Matter's scheme, be only sufficient for glauconitisation in one, or a very few, horizon(s). Even when the previously suggested differential rates of clastic supply and sedimentation (Fig.51, Section 17.4) are taken into account, the glauconitisation process would still appear to have proceeded rather rapidly.

The evolution time scheme of Odin & Matter (1981) for glauconies needs further assessment from other studies to become valid or be modified. The present study would suggest careful considerations of the influence of sedimentological factors as necessary in such assessments. In particular, the differential eustatic sea-levels and the nature of source and compositions of derived materials need attention.

In the Upper Eocene Hampshire Basin, glauconitisation appears to have been influenced by a number of factors. These are the high influx of iron-oxides derived from iron-rich sediments (and soils) located within and/or close to the basin; episodic, but protracted periods of high sea-level rise during which clastic supply is low, sedimentation is slow and bioturbation by benthic organisms was extensive. The bioturbation most probably extended the aeration zone (cf. Berner, 1980) some few centimetres into the sediments, facilitating the maintenance of much of the influxed iron-oxide in an oxidative state suitable for utilisation for glauconies.

Although the glaucony growths appear to be mainly with voids provided by microfossil tests, it is not improbable that some of the derived illitic materials were transformed to glauconitic mica.

B) Pyrite

Pyrite is the only product of bacterial sulphate reduction process in the Upper Eocene succession. The mineral mostly occurs filling skeletal chambers (i.e. Plate 67) and, in places, partially replacing skeletal walls. In addition, pyritised plant materials are common, especially in the non-marine sediments. The mineral consists of masses and disseminated or framboidal aggregations of < 5 µm-sized cubic and pyritohedral crystals (i.e. Plates 30, 72). This mode of occurrence indicates the organic origin of the mineral (i.e. Love & Murray, 1966). Love (1971; cf. Hudson, 1982) has suggested that pyrites in-filling skeletal chambers are 'early', whilst those replacing skeletal walls are 'late'. The skeletal chambers provide semi-confined reducing micro-environments in which bacterial decomposition of tissue remains is attended by reduction, of organic-S and dissolved-SO_4^{2-} from depositional waters to HS^-, and of organo-Fe complexes and derived iron-oxides to Fe^{2+}. These would lead to pyrite formation, most probably via iron-monosulphide precursors (i.e. Berner, 1964, 1971). Replacement of calcareous skeletal walls is believed (Love, 1971) to follow some dissolution caused by the acidity of HS^-.

Pyrite formation (or bacterial sulphare reduction) would be expected to occur at very shallow depths in the non-marine environments where SO_4^{2-} derived from fresh-waters is very small ($\sim$ 11 ppm). In contrast, the 'sulphate reduction zone' (Curtis, 1980) can occur deeper (few cm to $\sim$ 10m) in marine environments where sea-water contains high concentrations, $\sim$ 2600 ppm, of dissolved SO_4^{2-}. Initially trapped seawaters can be replenished further by diffusion until the diffusion path becomes too great (i.e. Berner, 1971).

This study has, however, indicated the sulphate reduction zone to have occurred very shallowly not only in the non-marine freshwater sediments but also in the marine succession. This is highlighted by the occurrence of diagenetic carbonates with near-surface and pre-compactional features. The causes of the establishment of a sulphate reduction zone are significantly relevant to the formation and distribution of the diagenetic carbonates. These are discussed below.

C) Ca-Siderites and Ferroan Calcite

Concretionary, nodular and bedded diagenetic carbonates occur in both the marine and non-marine Upper Eocene sediments. These, however, show facies-related compositional variations. Septarian calcareous concretions, consisting of ferroan calcites, occur within the glauconitic sediments of the marine Barton Clay; whilst ironstones, consisting of low magnesian, dominantly Ca-substituted siderite, occur in non-marine and non-glauconitic marine sediments (cf. Figs. 36, 38). The concretions possess pre-compactional features such as the absence of laminae (see Plates 3, 10), and the preservation of trace fossils (i.e. Plates 9a-c). They also possess carbonate abundances of ~ 30-50% in sandy hosts, and 60-96% in host clayey sediments (i.e. Tables 22 and 23). These features and compositions are indicative of development within very shallow burial depths and, in places, are very close to the sediments' surface (cf. Raiswell, 1971).

The carbonate minerals, unlike pyrite, which they post-date, require the virtual absence of reduceable SO_4^{2-} ($pS^{=} < 10^{-10}$) and high pCO_2 ($\gtrsim 10^{-3}$ atm) to form (i.e. Curtis & Spear, 1968). This is essentially achieved in bacterial fermentation diagenetic conditions (i.e. Curtis, 1980), where CO_2 is mainly produced from fermentation of organic remains and enriched in heavy carbon (i.e. $\delta^{13}C \simeq 15‰$ - Claypool & Kaplan, 1974). The shallowness of both the 'bacterial sulphate reduction zone' and 'bacterial fermentation zone' and, in addition, the petrological and compositional aspects of the diagenetic carbonates are very unusual diagenetic phenomena. Attempts are made in this study to explain them, although the data available is grossly insufficient for assertive reconstruction.

Very shallow 'sulphate reduction' and 'fermentation' zones can, and often do, occur in non-marine environments where the derivation of reduceable SO_4^{2-} is very small. The sulphate reduction process would cease close to the sediment surface, and will be succeeded by fermentation conditions. This commonly occurs in bogs, swamps and freshwater lakes (i.e. Postma, 1977; Pye, 1981) and can be equated with the late Upper Eocene environments in which the 'Lower Headon Beds' mainly accumulated. Similar shallowness deduced for the marine succession is not, however, expected considering that its sedimentation has been grossly slow (~ 2·5 cm/ 1000 yr - Odin et al., 1978) and many of the sediments are even bioturbated.

Several studies (i.e. Lerman, 1979; Berner, 1980) have shown that slow sedimentation and bioturbational irrigation cause deep diffusional path of up to 10m for effective cessation of diffusional replenishment of SO_4^{2-} buried with marine sediments.

A probable sedimentological explanation could be, as previously suggested (Ch.14), an alternating slow (clayey)/fast(sandy) sedimentation in the Barton Sea. This implies that the sulphate reduction zone will occur shallowly in the swiftly accumulated deposits, and hence act as 'seals' to earlier slowly accumulated sediments. Diffusional replenishment from the sea would thus cease within very shallow burial depths of the slowly accumulated sediments. Similar alternating differential rates of sedimentation have been suggested by Sellwood (1971) for some sideritised mudstones from the Lias in Yorkshire, England. As in the present study, sideritisation occurred in the slowly accumulated units.

Alternative explanations may be related to the modes of derivation of the diagenetic reactants, particularly the HCO_3^-. Sub-surface derivation of $CaCO_3$-rich waters from the Chalk has been advanced as one probable factor causing the Ca-rich early diagenetic phases to form very shallowly. The Chalk water would have been poor in SO_4^{2-}, and by being 'discharged' in considerable quantities, SO_4^{2-} from sea-waters would become very diluted, so as to be ineffective for precipitation of sulphide phases. Questions arising from this are:

i) did dilution by influxed HCO_3^- occur within the 'sulphate reduction zone'? or

ii) was it within an already established fermentation zone? or

iii) did the influxed HCO_3^- cause fermentation conditions to be established?

These may be considered from the thermodynamics of iron phases. The stability conditions of common iron phases have been dealt with in detail by several authors, including Garrel & Christ (1965) and Curtis & Spears (1968) (see Fig.28). In conditions of high pCO_2 and low $pS^=$, precipitations and/or co-existence of siderite and iron monosulphides can be expected. This is, in fact, the situation prevailing in a present-day rapidly accreting coastal marsh in Norfolk, eastern England, described by Pye (1981). No monosulphide phase was observed in the Upper Eocene sediments under consideration; the $pS^{=}$ could, as stated above, have been rendered insignificant by the influxed HCO_3^- or very low $pS^{=}$ conditions could have prevailed independently or prior to the HCO_3^- influx. In conditions of high pCO_2 and $pS^{=}$, siderite and/or pyrite could be expected. Co-precipitation of siderite and pyrite is, however, not known to occur in nature. Hallam (1982) thought that the reason was due to an apparent preferential fixation of Fe^{2+} with $S^{=}$ compared to $CO_3^{=}$. Why, and the mechanism involved, has yet to be established. Perhaps the fixation is controlled or influenced by kinetic factors and/or the relative $a CO_3^{=}/pS^{=}$ in the system, in a manner not unlike how relative Mg^{2+}/Ca^{2+} or Ca^{2+}/Fe^{2+} ratios influence which carbonate phases form.

The implication of the above is that precipitation of iron-rich carbonate may not be exclusive to the 'fermentation zone'. Perhaps such phases may precipitate in the sulphate reduction zone; very probably where very high(?) $a HCO_3^-$ or $a CO_3^{=}$ occur, either along with or inducing low $pS^{=}$. The situation in the marine Upper Eocene succession of the Hampshire Basin may be one example of this. Here external derivation of high amounts of HCO_3^- shifted the diagenetic process to favour the precipitation of carbonate phases.

None of the arguments above, however, rule out the possibility that fermentation conditions had not already been established prior to HCO_3^- influx and/or the precipitation of the carbonate phases. The only verification of what diagenetic condition actually prevailed may be from carbon and oxygen isotopic analysis of the phases concerned. This could not be performed during the course of the present work. If future studies show enrichment of light carbon (i.e. $\delta^{13}C \rightarrow -25‰$) this would indicate involvement of CO_2 produced from bacterial sulphate reduction processes. In contrast, if the enrichment is in heavy carbon (i.e. $\delta^{13}C \rightarrow +15‰$) bacterial fermentation processes can be inferred (cf. Irwin, 1980). The isotopic data should also help to establish whether HCO_3^- derivation from the Chalk was significant. Biogenic $CaCO_3$ predominantly constitutes the Chalk, and this is characterised by $\delta^{13}C \simeq 0‰$ (i.e. Hancock, 1975).

The petrological and compositional features of the diagenetic carbonates also provide invaluable information on the modes of formation involved. Significantly, the concretions were each found to be characterised by a relatively uniform composition from core to rim. Their carbonate (cement) contents are also high, being ~ 30-50% in sandy bodies, and often $>70\%$ in the clayey horizons. These are features indicative of relatively rapid growth in an open system prior to compaction of the hosting sediments. They support the pre-compactional features observed in the field. Concretions with similar growth features are not uncommon in the literature. Raiswell (1971) has described such concretions from the Lias in Dorset, southern England, as 'early concretion types'. They are different from the 'late concretion types', which, by developing at deeper depths and/or having protracted growth, are often characterised by cone-in-cone structure, parallel laminae, smaller abundance of cement materials and, even in places, variable abundance, and types of cement material from core to rim.

The rapid growth of the Upper Eocene diagenetic carbonate bodies is particularly illustrated by the microcrystallinity of ferroan calcites comprising the bulk of the calcareous concretions. The microcrystallinity could only have resulted from rapid crystallization. Fine, rapidly crystallized calcites commonly characterise physico-chemically precipitated lime-muds (Cloud, 1955) and these have also been obtained in laboratory conditions (i.e. Pykowitz, 1965). The rapid calcite precipitation and growth of the calcareous concretions had, in fact, led to the development of expansional cracks - the septarian fissures. This significantly supports the 'expansional growth theory' of septarians by Todd (1913) and Davis (1913) in contrast to the 'dehydration-induced shrinkage theory' of Crooks (1913), Richardson (1919) and Lippman (1955).

The late growth phase of the concretions had essentially involved the crystallization of septarian calcites. These, also of ferroan variety, consist of sparry crystals which vary from <20 μm-sized bladed and equant forms by the vein walls to larger sized (up to 2 mm) equant and prismatic forms at the veins' centre (Fig.35; Plates 71a-c). Their crystallization had been slow from interstitial waters trapped within the expansional fissures. These septarian calcites, by their composition and morphological variation,are very different from those documented by Lindholm (1974) as typical of concretions. They are characterised by crystals varying from 'early' fibrous and bladed forms of magnesium calcites by the vein walls to 'late' equant and prismatic low-magnesian and/or ferroan calcites at the vein centres. The peculiarity of the present septarian calcites is just one of the manifestations of the unusual diagenetic phenomena of the Upper Eocene Hampshire Basin. Factors controlling the pore fluids' compositions are considered later.

In the case of the ironstones, the constituting siderites are sparry rhombs in micro-spherulitic aggregations (i.e. Plates 77, 78, 80). There is, however, no consensus of opinions on the mode of formation of spherules. They have been considered to be direct precipitation from honogeneous solutions or diffusional growth in colloidal or viscous media (i.e. Greensmith, 1971; Hodgson, 1968). The siderites of the present study are predominantly sparry crystals and can be regarded as precipitation from solution, albeit ionic diffusion in the aqueous medium would have been involved. Indication of precipitation from solution is, in fact, found in places where crystal growths are parallel against clastic (quartz) grains (i.e. Plates 85d, e). However, in addition, the probable involvement of the colloidal phase is indicated by the occurrence of cryptocrystalline siderite. This is observed (i.e. Plates 78, 83a) to replace fossil shells in some of the non-marine ironstones. The cryptocrystallinity does not, however, necessarily mean a colloidal medium of growth; it might rather have resulted from relatively more rapid crystallization than had been the case for the spherulitic rhombs. Whatever their mode of precipitation, the siderites' distribution and morphology could not be correlated with the various substitutions indicated by the phase composition analyses. Routine petrological methods (optical and S.E.M.) were found inadequate to differentiate between the substituted phases that X-ray diffraction shows as comprising the siderites (i.e. Fig.19). Apparently, the various dominantly Ca-substituted phases have either precipitated congruously or are separate but intimately admixed. Whilst congruous precipitation of similar phases will not be expected, the intimate admixing could also not be ascertained from random spot analysis with EDX (= energy dispersive X-ray) attachment to the scanning electron microscope. Line profile microprobe analysis may probably help solve the problem of the phases distribution; but this could not be performed during the course of the present work.

The diagenetic carbonates were, in general, developed close to bedding planes between similar or different sediment lithologies. This, along with the somewhat regular spacing of the concretions along particular horizons (i.e. Plate 2), are indicative of a stratigraphical control on the diagenetic processes. The mechanism involved is not well understood. Similarly distributed concretions from the Lower Carboniferous of the Isle of Man were considered by Dickson & Barber (1976) to result from differential concretion of fine-sized organic matter into relatively coarser grained and more permeable horizons within lithologically-inhomogeneous sediments, and along which interstitial fluids are channelled. The supersaturation of the interstitial fluids with respect to a particular phase being relieved by precipitation of the phase around or in the vicinity of diagenising organic matter. Many authors, including Shurubor (1967), Curtis et al. (1975) and Pearson (1979) have also emphasised the importance of lithologic inhomogeneity and channelling of pore fluids along the more permeable horizons. In the present succession, however, the concretionary horizons were not observed to possess clastic materials that, petrologically or in abundance, are different from those of the host sediments. The relative (Quartz + Feldspar)/(Quartz + Feldspar + Total Clay) ratios of the concretions matrix (acid insoluble residue) are not significantly different from those of their hosts; the (Q+F)/(Q+F+Cl) ratios being second-rate substitutes for particle size measurements, which were not performed in this study. Channelling of fluids in the Upper Eocene succession can only be ascertained as being along bedding planes rather than along coarser-grained horizons within each of the host sediments.

The nature of the pore fluids had, in fact, varied in the Upper Eocene times, resulting in episodic, differential precipitation of either low magnesian, low manganese but dominantly Ca-substituted siderites, or low magnesian but ferroan calcites. The variation appears to be facies-related, and, very probably, influenced by the nature of derivations to the depositional areas.

The existence of Ca-rich drainage waters from the Chalk, and the influx of detrital iron-oxides from ferruginous and glauconitic Cretaceous and older Tertiary sediments, ensured availability of abundant Ca^{2+} and Fe^{2+} for diagenesis. Mn^{2+} probably accompanied the detrital iron, but in much smaller abundances. The Mg^{2+} derivation was mainly from the depositional waters; and expectedly decrease from the marine to freshwater facies. Apart from the detrital iron-oxides, other potential source materials within the succession include the clastic silicates, glaucony and micritic calcites. There are, however, no petrological indications that these made any significant contributions. They remained, apparently, well preserved. Only in parts of the non-marine sections is probable internal derivation indicated by the observed siderite replacement of fossil shells and lime-mud $CaCO_3$ forms (Plates 78, 83). However, since diagenetically precipitated phases are indicative of the nature of existing pore fluids (Benson et al., 1972), the low-magnesian, low-manganese but Fe-, Ca-rich carbonate phases observed composing the concretions show that the pore fluids involved were apparently rich in Fe^{2+}, rich or saturated with Ca^{2+}, but poor in Mg^{2+} and Mn^{2+}. The unusual precipitation of low-magnesian carbonate phases in the marine succession could only have meant that the potentially high Mg^{2+} derivation from the Barton Sea waters was diluted and rendered less important within the sediments. The only probable cause of this would be the suggested sub-surface inflow of Ca-rich but Mg-poor waters from the porous and cavernous Chalk terrains bordering the Hampshire Basin. The Chalk, as stated earlier, is predominantly composed of low-magnesian microfossil calcites (Hancock, 1975).

The phase resulting at a particular instance will then have depended on the relative Ca/Fe ratio and the relative abundances of the subordinate cations in the generated pore fluids. Theoretical and experimental studies (i.e. Berner, 1971; Richter & Fuchtbauer, 1978) have shown that Ca/Fe ratio < 20 is essential for the precipitation of siderite; otherwise calcite will result. The occurrence of siderite from all parts of the marine and non-marine succession compared with the ferroan calcites, which are only marine, probably means that the pore fluids were primarily saturated with respect to siderite. Then the observed predominant occurrence of the ferroan calcites within the glauconitic sediments, whilst the siderites are mostly outside such sediments, would further suggest that the glauconitisation processes had a controlling influence on the nature of pore fluids generated within the glauconitic sediments. The glauconitisation, as discussed earlier, involved the utilisation of detrital iron-oxides at the sediments' surface for the formation of the glauconitic mica glauconies in the sediments concerned. This then leads to relatively lesser amounts of detrital iron to be buried and made available for diagenesis in the glauconitic sediments. The pore fluids generated were thus relatively poorer in Fe^{2+}, thus leading to the ratio of Ca/Fe to exceed 20 and, hence, become supersaturated with respect to calcite. However, the fact that the calcites are ferroan means that Fe^{2+} was still available in amounts substantially higher than the Mg^{2+}.

The above enumerated trend of early diagenesis in the Upper Eocene succession of the Hampshire Basin probably applies to other parts of the

Palaeogene successions in the basin. Some aspects of the diagenesis have been recognised from the Bracklesham Group (Potter, 1977) and the London Clay Formation (Hewitt, 1982). Potter (op.cit.) described some sideritic ironstones and small pyritic nodules from a road exposure of mottled and carbonaceous clays in Surrey, southern England. The ironstones are characterised by 58-65% total Fe_2O_3, 0·3 - 0·4% Mg and 0·6 - 0·75% CaO composition that suggests their constitution as being by low-magnesian, low-calcian siderites. They appear to be similar to the freshwater ironstones described from the Isle of Wight in the present study. Potter (op.cit.) highlighted their warm, humid palaeo-environmental significance but did not establish their probable mode of formation. Hewitt (op.cit.) petrologically described early diagenetic bodies of various compositions from the early Eocene London Clay Formation exposures around Leigh-on-Sea in Essex, southern England. These comprise ferroan calcite septarian concretion, zoned francolite concretions, and pyrite concretions; predominantly developed within bioturbated marine clay and with the trace fossils preserved. Although Hewitt did not discuss their probable mode of origin, it is apparent that the diagenesis was essentially of the 'sulphate reduction zone'. Fe^{2+}, Ca^{2+}, SO_4^{2-}, HCO_3^- and HPO_4^- had been abundantly available but the phases precipitated had episodically, or with time, varied with changes in the relative Ca^{2+}/Fe^{2+}, $HCO_2^-/pS^=$ and $HPO_4^-/pS^=$ of the pore fluids concerned. This diversity of diagenetic trends is quite important when related to the Upper Eocene succession where siderite and ferroan calcites occur. It would appear that similar diagenetic conditions existed in the Palaeogene of southern England, but differential local conditions had imprinted some variability of phases precipitated. Further systematic mineralogical and geochemical studies of the Palaeogene successions, to ascertain how diagenetic processes had varied in the region, are required. These would allow comparisons with other basins, such as the Japanese Palaeogene, where shallow to deep burial diagenetic phases occur, to be made. Such studies would also help to establish further probable palaeo-environmental and sedimentological controls of diagenesis.

CHAPTER 18

CONCLUSIONS

In Upper Eocene times and very probably throughout the Palaeogene, the Hampshire Basin was under the considerable influence of episodic low-scale tectonic movements, eustatic sea-level fluctuations and deposition of dominantly clastic sediments. There was also an apparent prevalence of tidal dominated shallow-water shelf and coastal plain environments with sediment derivation from relatively constant sources. These factors, along with the prevailing warm, humid sub-tropical climate, had a significant control on mineral authigenesis and pathways of diagenesis.

In the context of north-western European geology, the Hampshire Basin is one of the manifestations of passive tectonic movements attending the opening-up of the North Atlantic Ocean and the separation of Greenland from Norway in latest Cretaceous to late Palaeocene times. Suggestions have been made of probable continuation of the tectonic movements in southern England throughout Tertiary times from the recognition of sub-Palaeogene erosional surfaces (Jones, 1981) and the paracyclical nature of the basinal sedimentation (i.e. Plint, 1982). Support from the Upper Eocene succession for this is provided by the occurrence of in-situ palaeosols, and apparent subtle sea-level fluctuations and differential sedimentation. Support is also given to the previously suggested (Plint, 1982, 1983) influence of a submarine structure separating the Hampshire Basin from its south-easterly extension, the Dieppe Basin, in the English Channel. This structure, presently designated as the 'Selsey Basin' would have behaved consonantly with the Hampshire and Dieppe Basins, but with lesser relative sediment-loading and probable lower magnitude response to tectonics. The effect would be lesser subsidence of the 'Selsey Basin' and hence would influence water depths and sedimentation in the Hampshire Basin, particularly during periods of regional sea-level fall. These would, however, be in addition to relative movements (isostatic inclusive) between the Hampshire Basin and adjoining structural highs. Well-vegetated lowlands and moderate relief highlands have, from several previous stratigraphical and geomorphological studies, been established to occur in areas to the north and west of the basin with exposures of Mesozoic sedimentary rocks, particularly of Upper Cretaceous Chalk,that extensively adjoin the basin. Cretaceous horst structures also occurred in areas of the English Channel to the south, although the emergence and erosion of these were probably episodic, correlating with marine facies sedimentations in the

Hampshire Basin.

The Upper Eocene sedimentation commenced in a transgressing sea. The sea was rather ineffectively established and a lowering of the sea-level occurred, resulting in localised emergence of the basal sand-supported pebble bed. A red-yellow podzol palaeosol developed with the pebble bed constituting its highest water-table and goethite-indurated horizon. A substantial sea-level rise then followed with effective establishment of a shallow water shelf, and deposition of sandy- and very sandy-clays for the Barton Clay Formation. Irregular distribution of glauconitic horizons and bioturbated mottled very sandy-clays suggest the shelf sedimentation to be episodic, comprising periods of low clastic supply and slow sedimentation within $\gtrsim$ 30m water columns, and relatively shorter periods of high clastic supply and more rapid sedimentation in much shallower waters. Significant eustatic sea-level falls commenced during deposition of the upper parts of the Barton Clay. Rapid shallowing to wave-zone depths caused large-scale mortality of earlier shelf fauna, whose shells were re-worked into bands and pockets as a prelude to the establishment of estuarine conditions with dominantly quartz-arenite bar sand deposits of the Barton Sand Formation. Pipe clays and sandy clays also accumulated within shallow hollows and protected waters. A large eustatic sea-level fall, apparently corresponding to the onset of the late Upper Eocene world-wide regression, terminated the sandy estuarine sedimentation. The eustatic fall caused widespread emergence of the Barton Sand. The emergence was to differential topographical and drainage conditions from mainland Hampshire to the Isle of Wight localities. Waterlogged conditions and the development of hydromorphic swamp palaeosols occurred on mainland Hampshire. In comparison, better drainage conditions at Alum Bay facilitated the development of well-evolved red-yellow podzols and gleysols with high abundance of authigenic kaolinite and goethite. There was, however, only a poorly-evolved loamy, goethite horizon, probably related to the red-yellow podzol, at Whitecliff Bay. The development of the palaeosols was succeeded for the whole of the late Upper Eocene times by 'brackish' and freshwater sedimentation. In addition to clastic deposits, lime-mud and lignitic accumulations also occurred with occasional sediment emergence to hydromorphic conditions and surficial processes.

The succession is predominantly composed of quartz with lesser amounts of clays and feldspars; with the clay assemblage consisting of degraded illite, smectite, kaolinite, illite-smectite and traces of chlorite. The feldspars are mostly microcline with few albite and oligoclase varieties. Other detrital constituents include flint pebbles, anatase, heavy minerals such as zircon, tourmaline, staurolite, rutile, and iron-oxides. The iron-oxide is dominantly goethite in disseminated form and, in places, occurs as cement-material in sand moulds of plant material. Mesozoic rocks in western, southern and midland England would be the major provenance, as previous clay and heavy mineralogical studies (Walder, 1964; Gilkes, 1966; Blondeau & Pomerol, 1968) have shown. In addition, there would have been contributions from horsts of Cretaceous sediments in the area of the English Channel, particularly for the marine facies. Earlier deposited Tertiary sediments, exposed intrabasinally in consequence of continuous basinal tectonic movements and sea-level fluctuations, would also have been significant. There might also have been some contribution from submarine sources and via the North Sea. The lack of high abundance of kaolinite suggests little, if any, direct derivation from the Cornubian Massif and its kaolinitised granites in south-western England. The clay assemblage would most probably have been inherited from actively eroded Mesozoic rocks undergoing moderate chemical weathering in a warm, humid sub-tropical climate. Occurrences of high kaolinite contents are very limited and related to intrabasinally developed and/or re-worked palaeosols.

Dissolved $CaCO_3$ would have been derived in substantial quantity from the Chalk. This and the derived iron-oxide considerably facilitated authigenesis of Ca- and Fe-carbonate phases.

There were subaqueous microfloral-induced lime-mud accumulations in ponded hard-waters. Continuous flushing by hard-waters has, along with the < 200m burial history of the succession, probably contributed to the lack of significant diagenetic alteration of the limestones, which remain largely unlithified with loosely aggregated anhedral, micritic low-magnesian calcite contents.

Extensive authigenesis of glauconitic-mica glauconies occurred during periods of slow shelf sedimentation. The apparent rapidity (few 1000 years?) of the glauconies formation questions the validity of the relationship between the length of the growth and evolution stage or the composition of glauconies proposed by Odin & Matter (1981). Very probably, the nature of the parent material and abundance of derived iron-oxide are significant factors in the glauconitisation process. Growth in voids (the 'Verdissement mode' of Odin & Matter, 1981) and/or involvement of illitic parents (i.e. 'epigenetic mode' of Ehlmann et al., 1963) in the presence of high iron-oxide abundance may complement low clastic sedimentation conditions in accelerating glauconitisation compared with growth from non-illitic parent and dissolved-Fe from sea-water.

In addition to pyrite predominantly formed in association with organic remains, dominantly Ca-substituted siderites and ferroan calcite also formed as cement in bedded, nodular and concretionary bodies. The diagenetic carbonates show a weak facies-related distribution. Sideritic ironstones developed in both marine and non-marine sediments; whilst septarian calcareous concretions formed within shelf sandy-clays, particularly in glauconitic horizons. The pre-compactional, very shallow ($<$ 10m?) burial formation of these diagenetic carbonates is particularly unusual for the marine sediments. Early Ca-siderites have not previously been reported in the literature, whilst ferroan calcite is normally reported from $>$ 500m burial depths in contrast to Mg-rich phases at shallow depths (cf. Curtis, 1980; Matsumoto & Iijima, 1981). The peculiarity of the Upper Eocene carbonates raises the question on the extent to which early diagenesis is influenced by the nature of derived materials. Often only clastic material and general rates of sedimentation are considered in the literature. In the Upper Eocene succession, the high influx of detrital iron-oxide lowered the significance of Mg^{2+} largely derived from incorporated surface waters. It is also believed that surface and sub-surface discharge of $CaCO_3$-rich waters from the Chalk caused depression of Mg/Ca (and HS^-/HCO_3^- ?) concentration ratios in the pore fluids. The significance of such $CaCO_3$ contribution, however, requires further isotopic studies. The apparent consequence of abundant iron-oxide and $CaCO_3$ was the generation of pore-fluids conducive for the precipitation of low-magnesian but Ca- and Fe-rich phases. Siderites, whose formation was more widely favoured, show substitution varying from $\sim$ 10 mol% Ca^{2+} + 3-5 mol% Mg^{2+} + $<$ 1 mol% Mn^{2+} in the marine and 'brackish' ironstones to $\lesssim$ 6 mol% Ca^{2+} + $\lesssim$ 2 mol% Mg^{2+} + 1 mol% Mn^{2+} in the freshwater ironstones. An intimate admixing and apparent co-precipitation of two or more substituted siderites cannot, however, be explained. Further investigation by electron microprobe microanalysis may prove useful. The formation of ferroan calcite was limited and significantly appears to be consequent of earlier utilisation, and hence depletion, of detrital iron-oxide for glauconitisation in the shelf sediments. Indeed, diagenesis in the marine sediments was also generally influenced by the prevailing episodic slow, sandy-clay and more rapid, sandy sedimentation, with the carbonates forming within the sandy-clays during periods of rapid sedimentation. This is similar to the slow - rapid depositional conditions with attendant sideritisation described by Sellwood (1971) from the Lias in Yorkshire, England.

By their composition and very shallow depths of formation, the diagenetic carbonates highlight the diversity in early diagenetic pathways, and enable correlation with local geological conditions to be made. Indeed, these and the other compositional aspects of the Upper Eocene succession studied have allowed greater understanding of the geology of the Hampshire Basin. Further advances may come from similar studies of the rest of the Palaeogene succession; whilst satisfactory solutions to many of the problems left unsolved may be sought particularly from isotopic studies and borehole material.

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PLATES

Plate 1. Cliff section comprising the Boscombe Sand (BS) - the uppermost unit of the late Lower Eocene-Middle Eocene Bracklesham Group; the brownish sand-supported pebble bed (PB) base to the Upper Eocene succession; and the glauconitic Huntingbridge Clay (HC) Member of the Barton Clay Formation. The overlying Highcliffe Member is overgrown.

Location: ~200m west of Highcliffe Castle.

Plate 2. Lines of calcareous concretions (C) marking top and base of the glauconitic sandy-clay 'Bed C' lower part of the Naish Member. Note the 'slip plane' base (sp) of the overlying 'Bed D' (see Barton, 1973).

Location: Cliff exposure ~ 100m east of Chewton Bunny, Highcliffe.

Plate 3. As Plate 2; the deformation of host sediments bedding planes round the concretions (C) indicating the pre-compactional time of growth of the calcareous concretions.

Plate 4. Calcareous concretion from the Naish Member, Highcliffe; split to show the characterising fine-grain size, greyish-green matrix (CC) and septarian calcites (SC), whose yellowish and whitish colour indicates their ferroan nature (cf. Lindholm, 1974).

NB. i) Hammer Handle is 50 cm long.

ii) Trowel is 20 cm long.


1


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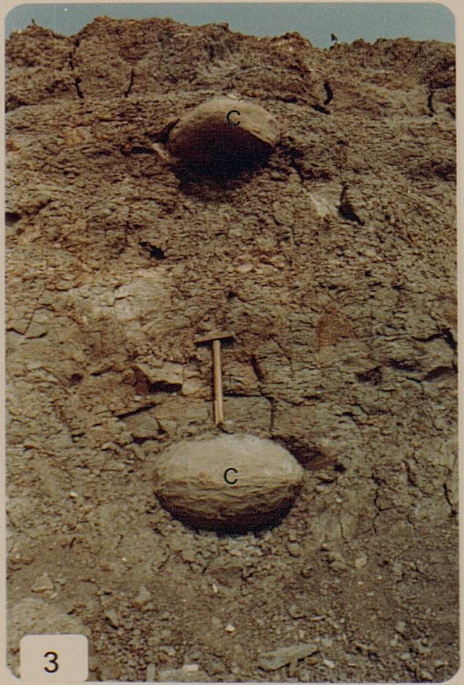
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4

Plate 5. Section of a calcareous concretion showing incorporated greenish glauconitic grains disseminated in the fine-grained matrix (CC), and the yellowish and whitish, septarian ferroan calcites (SC).

Location: Naish Member, Barton-on-Sea.

Plate 6. Fossil shells (FS) encrustation on calcareous concretion (CC), with pyrite fillings (P).

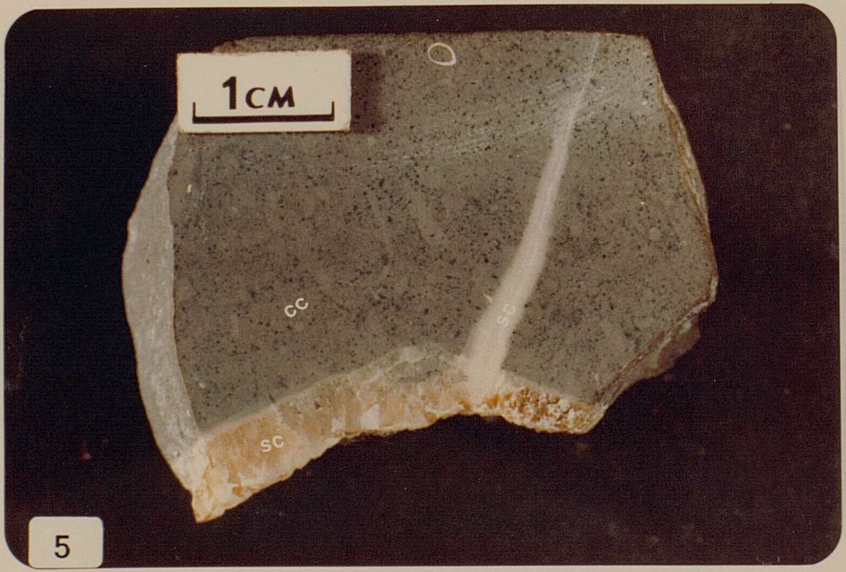
Location: Naish Member, Barton-on-Sea.

Plate 7. Cliff section of the sandy 'Bed K' and lignitic 'Bed L' top of the Barton Sand Formation and the green clays of the Mammal Bed (M) base to the 'Lower Headon Beds'. Note the straw-yellow jarosite coatings (marked by trowel) on the sediment's surface

Location: Beacon Cliff, Long Mead End.

Plate 8. Polished section of a sideritic ironstone with preserved mining-type burrows filled with lighter coloured, non-sideritic silty-clay materials.

Location: 'Shell Bed' base of the Barton Sand Formation, Barton-on-Sea.



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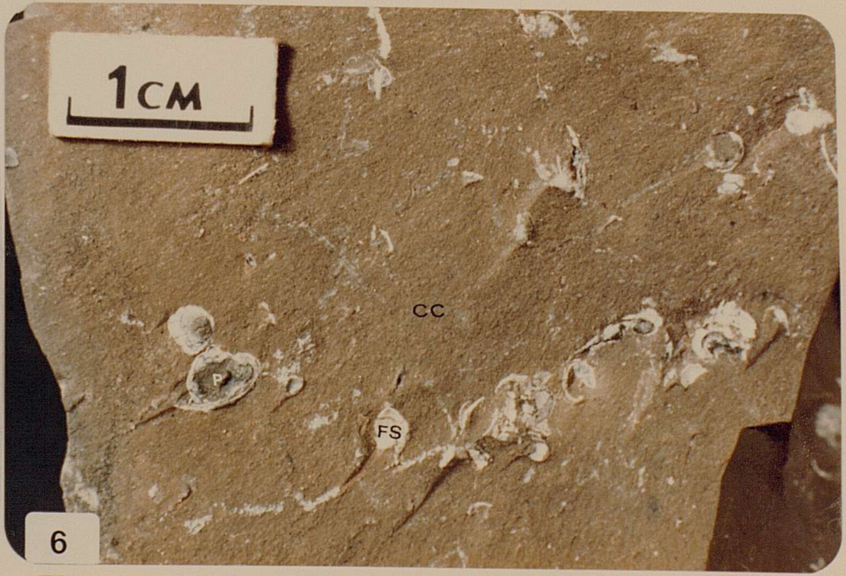


6

7

8

Plate 9.

a. Sample of sideritic clay ironstone with preserved trace fossils indicating very shallow depth of formation.

b. As a, showing surface features of Chondrites (Ch), Thallasnid (O), and current-aligned Turritella shells (T).

c. As a, showing mining-type burrows filled with lighter-coloured, unsideritised fine-grained materials.

Location: 'Shell Band' base of the Barton Sand Formation, Barton-on-Sea.

9a

9b

9c

Plate 10. Sideritic clay ironstone concretion within green clay host immediately above the 'Crocodile Bed' of the 'Lower Headon Beds'. Note the compactional deformation of the host bedding planes round the concretion.

Location: Hordle Cliff, Long Mead End.

Plate 11. Horizon of brownish, goethite-cemented and rootlet-bearing sands at top of the Lymnae Limestone Bed.

Location: 'Lower Headon Beds', Hordle Cliff,
Long Mead End.

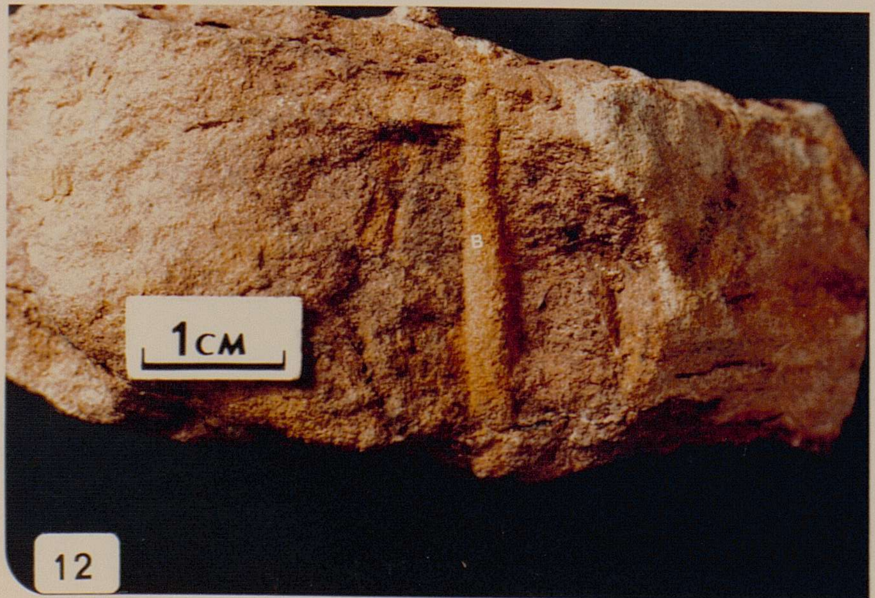
Plate 12. As Plate 11, with sand filled pedotubule (B)

Plate 13. Pedotubule-altered pyritic plant root; with goethite, jarosite and gypsum.

Location: Base of Chara Bed, Hordle Cliff,
~200m east of Long Mead End.

10

11



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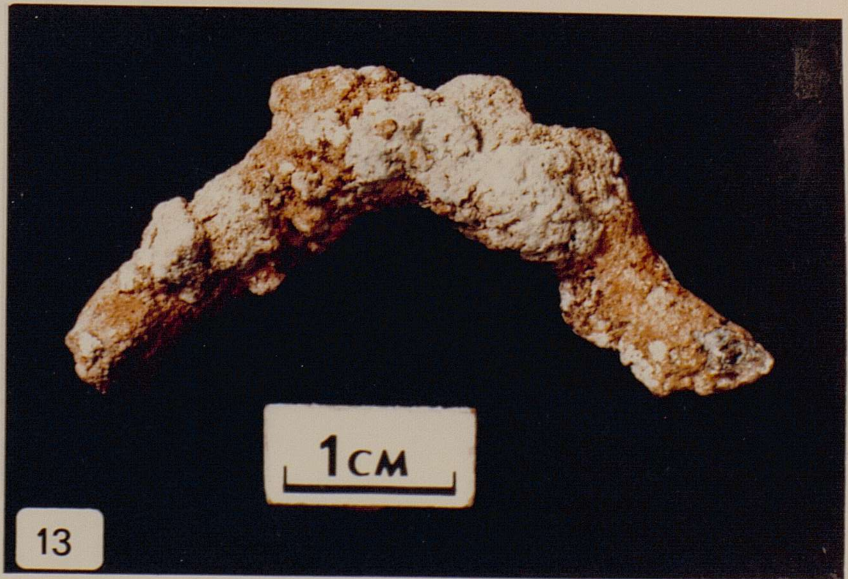


13

Plate 14. Cliff sections of the uppermost brown clay and mottled sandy-clay of the Barton Clay (BC) and the white sand of the Barton Sand (BS). Ironstone band (I) occurs within 1m of top of the Barton Clay.

Location: Alum Bay, north of access to the beach, Isle of Wight.

Plate 15; Cliff section of the basal goethitic pebble bed (PB); the very sandy-clay Huntingbridge Clay - and the often glauconitic and concretion-bearing sandy clay of the Highcliffe and Naish Members of the Barton Clay Formation (BC).

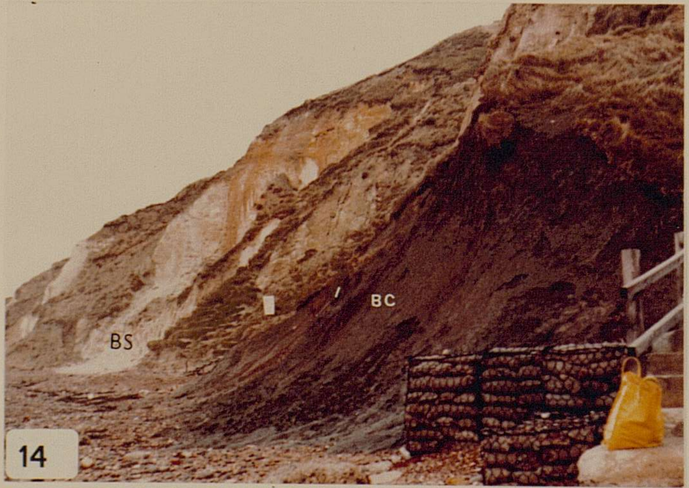
Location: Alum Bay, south of access to the beach, Isle of Wight.

Plate 16. Weakly developed goethitic liesegang rings within ferruginous, yellowish part of the Barton Sand Formation.

Location: Alum Bay, Isle of Wight.

Plate 17. Seams of greenish pipe-clay (PC) with flame structure and thin plant-accumulates within the Barton Sand Formation.

Location: Alum Bay, Isle of Wight.



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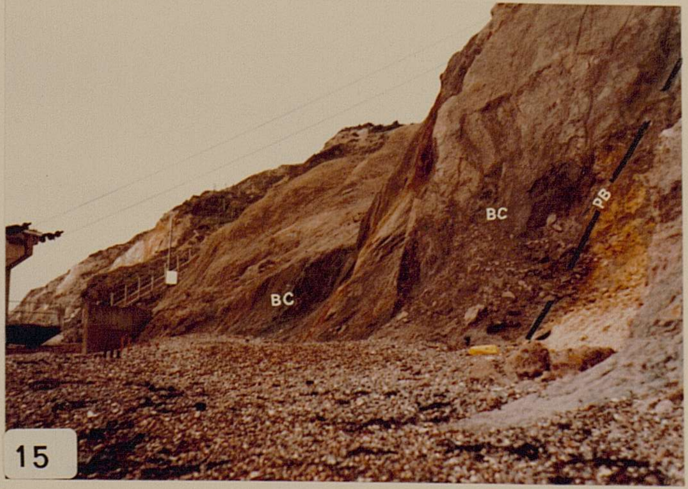


15

16

17

Plate 18.

a. Barton Sand Palaeosols: strongly coloured and comprising two incompletely preserved lower and upper pedounits respectively identified as red-yellow podzol (LP) and gleysol (UP). Below is the Barton Sand (BS), and above is the green clay base to the 'Lower Headon Beds' (LHB).

b. As 18a, showing the palaeosols consisting of arenon (ar), rosal (ro), veson (v) and argillon (ag) horizons (see Fitzpatrick, 1971).

c. Vertical section of the veson, showing high goethite concentration, induration and red mottles; and specks and lenses of greyish-white kaolinite.

d. Horizontal section of the veson, showing reddish goethite concentrations and mottles, and whitish kaolinite.

Location: Heatherwood Point, north of Alum Bay, Isle of Wight.

18a

18b

18c

18d

Plate 19.

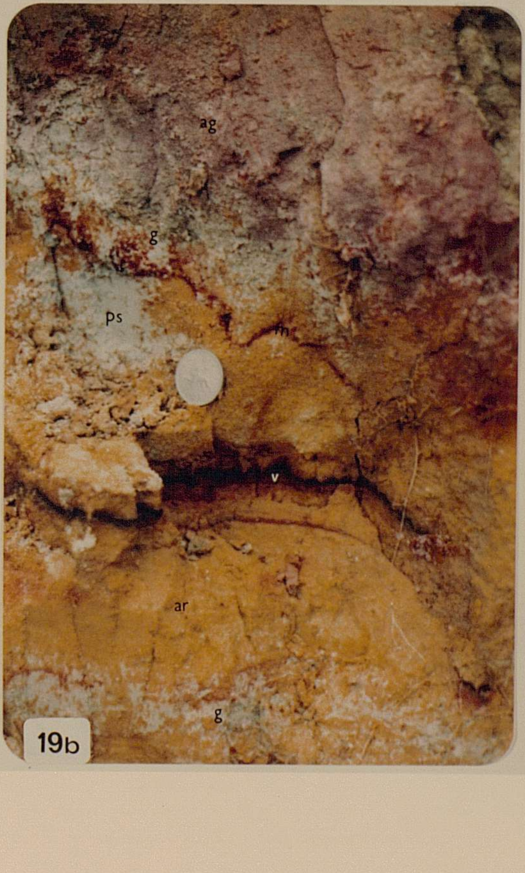
a. Barton Sand Palaeosols, ~ 50m south of Heatherwood Point occurrence of Plate 18. Also made up of a lower pedounit (LP) and an upper pedounit (UP).

b. As Plate 19a, detailing the pedounits' horizons which comprise gleysons (g) with pallid sand (ps) and red mottles (m); loose yellowish-sand arenon (ar); goethite indurated veson (v), and massive purplish clayey-sand argillon (ag).

Location: North of Alum Bay, Isle of Wight.

Plate 20. Part of the arenon and veson of palaeosol in Plate 19, showing red mottles (M) and rootlet pedotubule (R).

19a



19b

20

Plate 22. Specimen of sideritised shelly limestone with preserved gastropodal shells(F) and the primary lime-mud (LM).

Location: 'Lower Headon Beds', Heatherwood Point, Alum Bay, Isle of Wight.

Plate 23. Cliff section of uppermost mottled sandy clays of the Barton Clay (BC) and the lower parts of the white Barton Sand (BS).

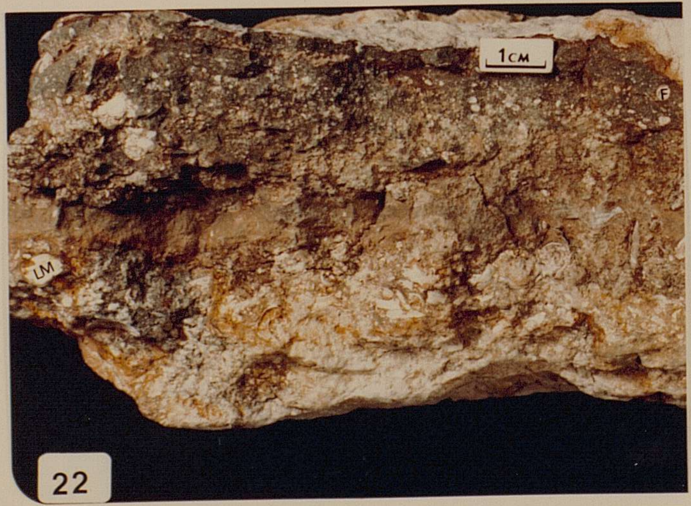
Location: Whitecliff Bay, Isle of Wight.

Plate 24. Section of the ferruginous uppermost part of the Barton Sand (BS), and the lignitic and carbonaceous clays and white sand comprising the greater part of the 'Lower Headon Beds' (LHB).

Location: Path to beach, Whitecliff Bay, Isle of Wight.

Plate 25. Horizon of nodular sideritic ironstones (ir) within the 'Lower Headon Beds' of Plate 24.

Location: Whitecliff Bay, Isle of Wight.


22


23


24


25

Plate 26. Photomicrograph of Barton Sand showing grains of quartz (Q), micaceous clays (M), garnet (G) and zircon (Z).

Sample BBB-7, Barton Sand, Beacon Cliff, Barton-on-Sea.

Plate 27. As Plate 26, showing grains of quartz, zircon, clay flakes and microcline feldspar (MF)

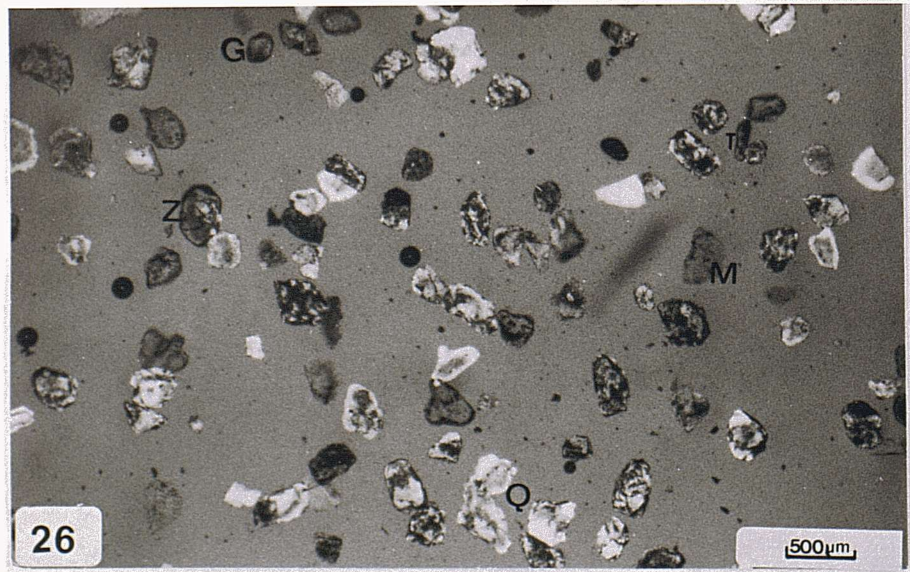
Sample ABBB-16, Barton Sand, Alum Bay, Isle of Wight.

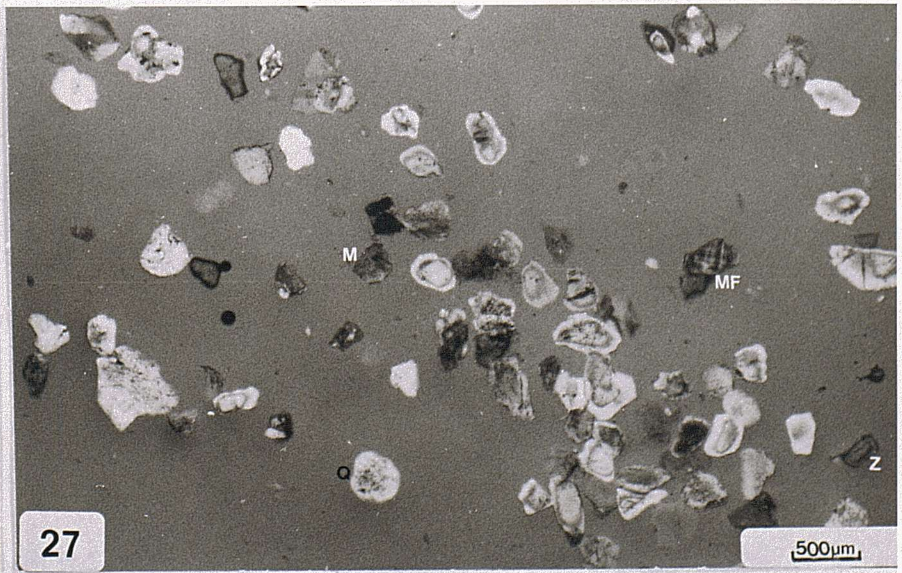
Plate 28. As Plate 26, showing grains of quartz, garnet and albite-oligoclase feldspars (AF).

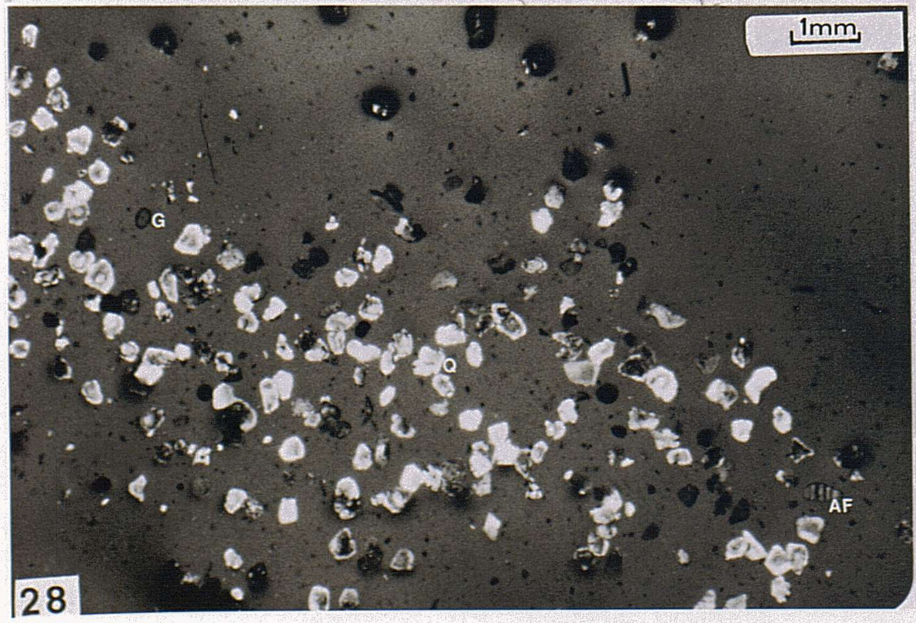
Sample WBBB-7, Barton Sand, Whitecliff Bay, Isle of Wight.

Plate 29. Plant and organic debris in the Barton Sand.

Sample BBB-7, Barton Sand, Beacon Cliff, Barton-on-Sea.


G
T
Z
M
Q
26
500µm


M
MF
Q
Z
27
500µm


1mm
G
Q
AF
28

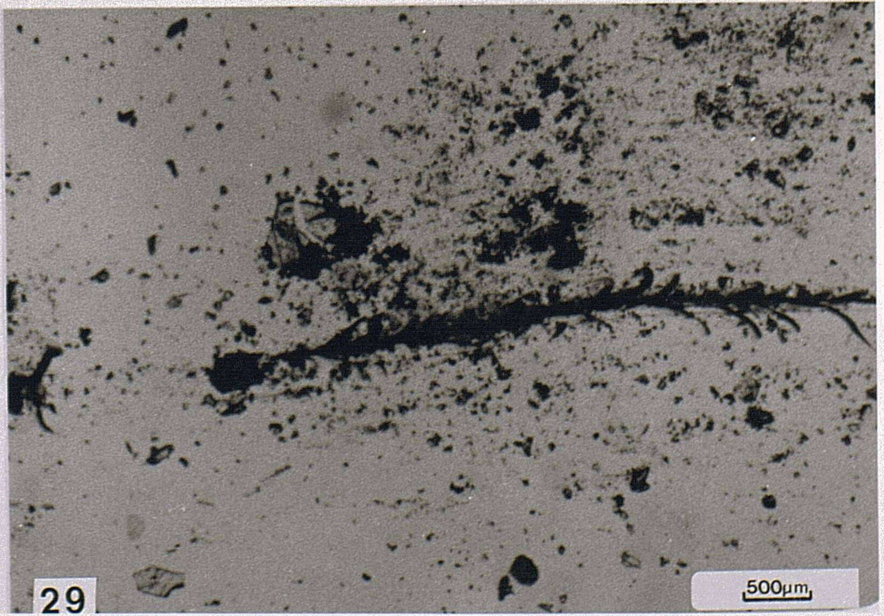

29
500µm

Plate 30. Photomicrograph of glauconitic sandy clay showing quartz (Q), glauconies (G), pyrite (P), staurolite (St) and organic matter (O) in glauconitic clay matrix.

XN. Sample BBB-35, Barton Clay, Highcliffe.

Plate 31. Photomicrograph of glauconitic sandy clay showing quartz, pyrite, glauconies and organic matter.

XL. Sample ABBB-2, Barton Clay, Alum Bay, Isle of Wight.

Plate 32. Photomicrograph of non-marine green clay showing aragonitic fossil shell (AFS), fine quartz grains and organic matter (ON) in clay matrix.

XL. Sample BLH-37, Mammal Bed, 'Lower Headon Beds' Long Mead End.

Plate 33. Photomicrograph of non-marine green clay showing ped/cutanic* aggregation of organic matter (OM), silt sized quartz and clays (cf. Brewer, 1964).

XL. Sample WBLH-13, 'Lower Headon Beds', Whitecliff Bay.

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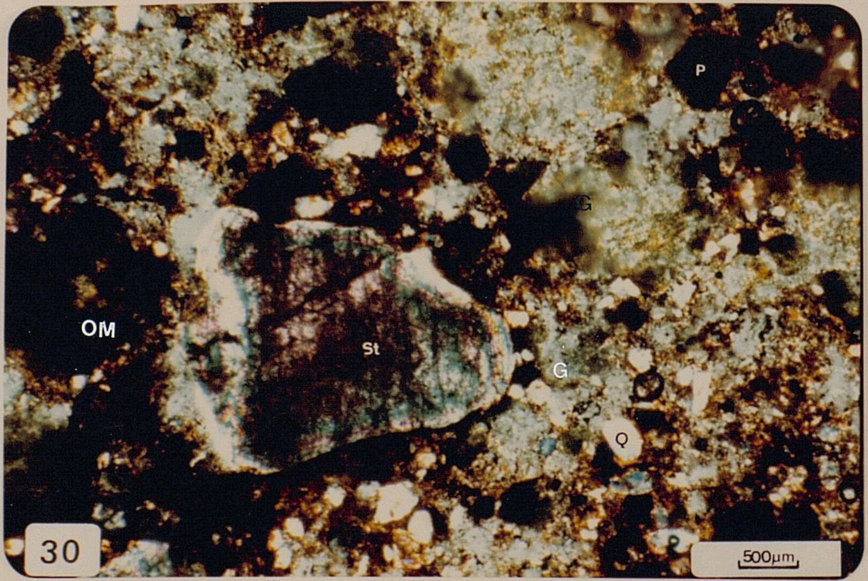
* Pedo-petrological terms, see Brewer (1964).



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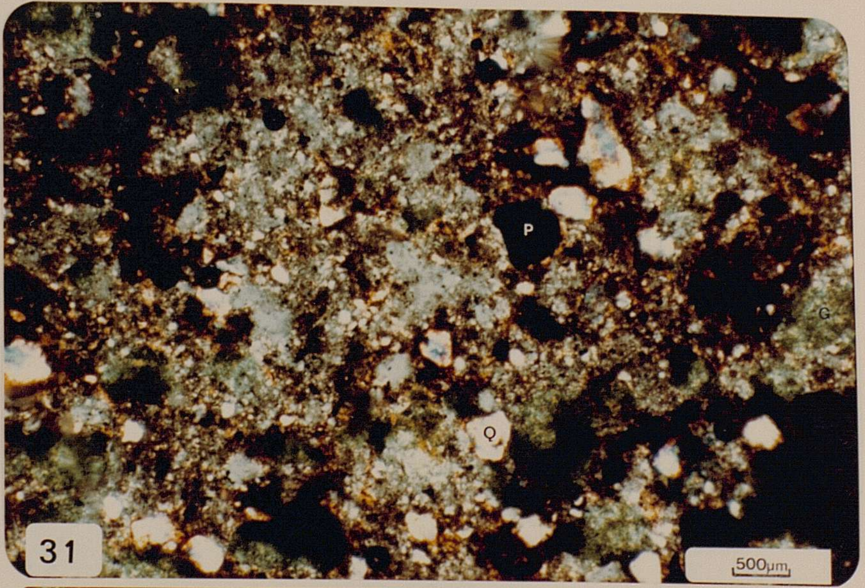

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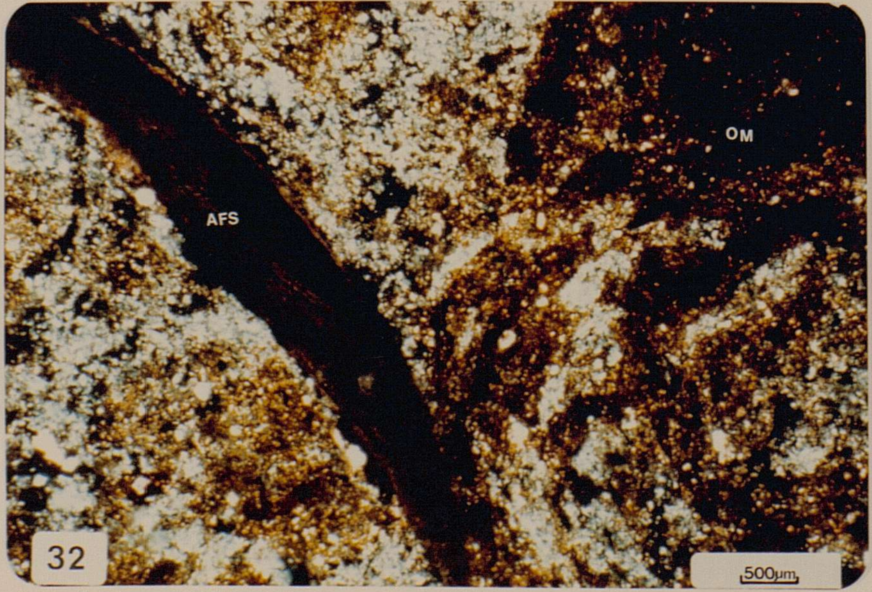

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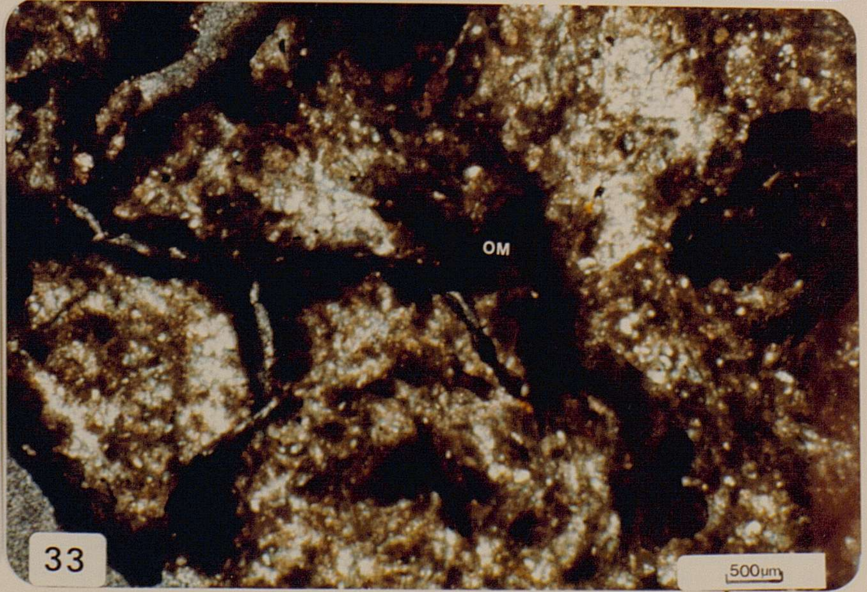


33

Plate 34a. Photomicrograph of a carbonaceous clay showing masses of quartz grains (Q) and gypsum rosettes (Gy) within matrix of clay and organic matter (OM).

Plate 34b. As Plate 34a, showing the gypsum rosettes characterised by radially-arranged prismatic crystals whose sizes decrease to the rosettes centre.

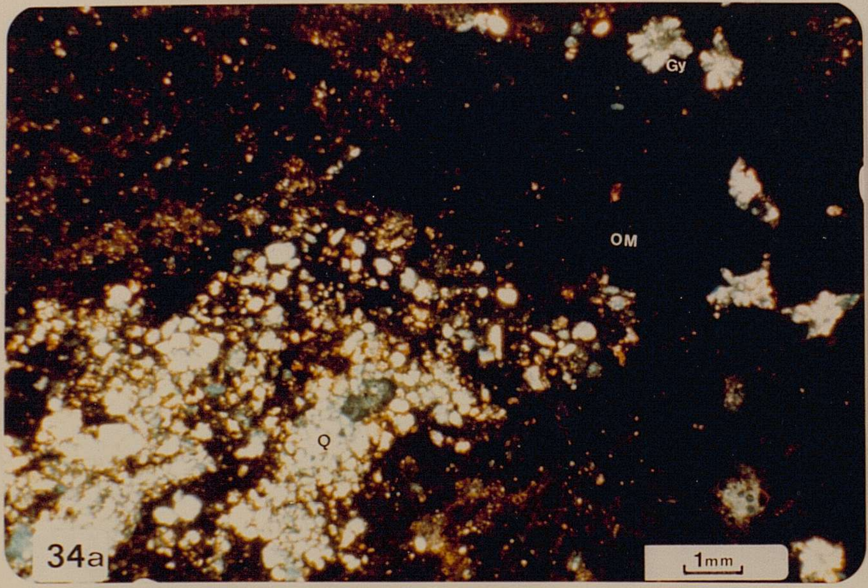
XL. Sample BLH-39, 'Lower Headon Beds', Long Mead End.

Plate 35. Photomicrograph of an altered, pyritised-rootlet pedotubule with goethite (Go) and gypsum (Gy).

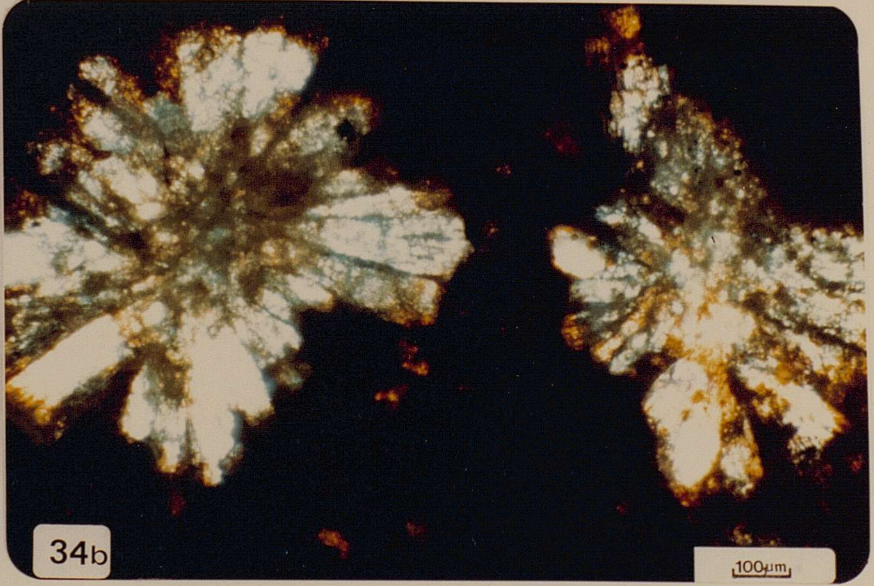
XL. Rootlet from horizon of Sample BLH-11, 'Lower Headon Beds', Hordle Cliff, near Hordle House.

Plate 36. Photomicrograph of a gypsiferous nodular body showing rings of goethite-quartz and gypsum-quartz in jarositic clay matrix (Ja; Gy); in places goethite pseudomorphed pyrite (Go(P)).

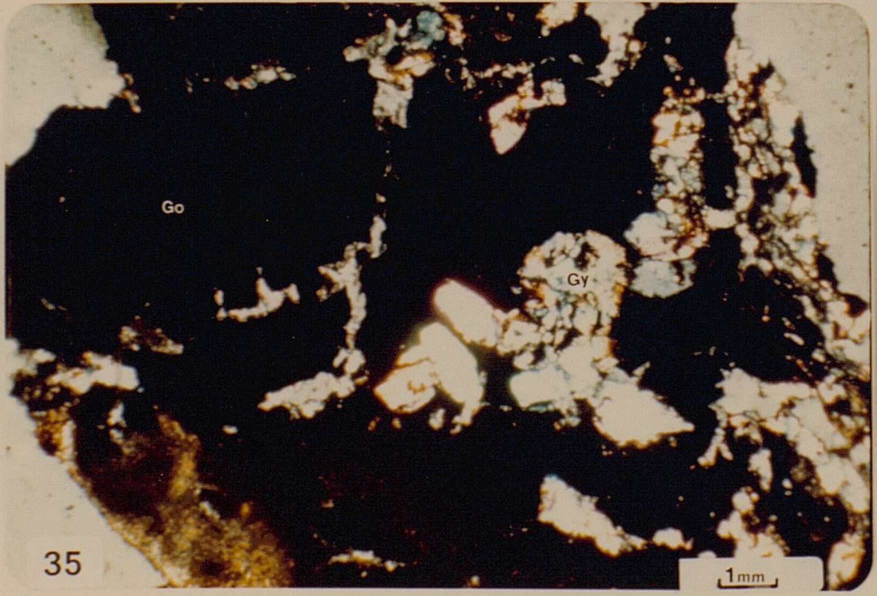
XL. From horizon of BLH-11 at the base of Chara Bed, 'Lower Headon Beds', Hordle Cliff, near Hordle House.



34a



34b



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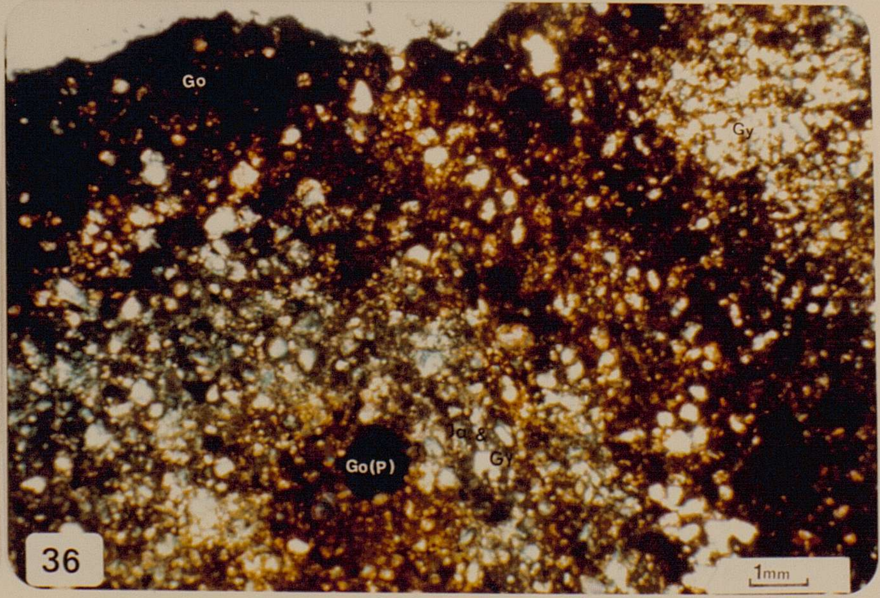


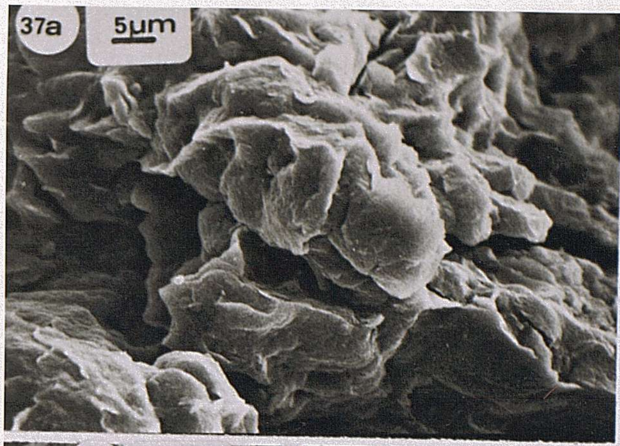
36

Plate 37. Electron micrographs of lignitic clay Sample BLH-18, 'Lower Headon Beds', Hordle Cliff, Long Mead End, showing -

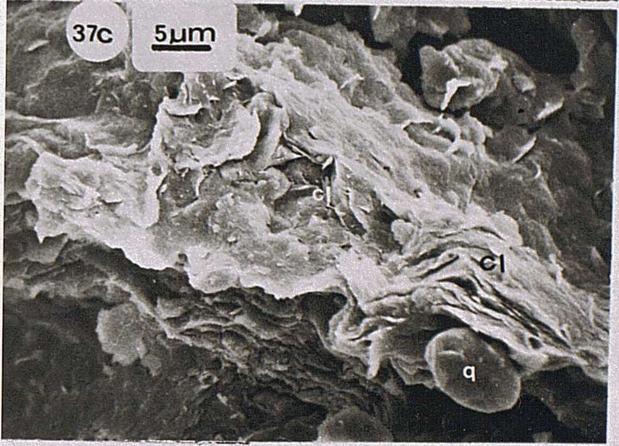
a microfloccules of clays
b micropeds aggregation of clays
c floccules and laminal swirls of clays (cl) and a clay-sized quartz (q).
d laths/platy clays (illitic/halloysite?)
e as d.
f fluffy anhedral platy (kaolinite?) clays.

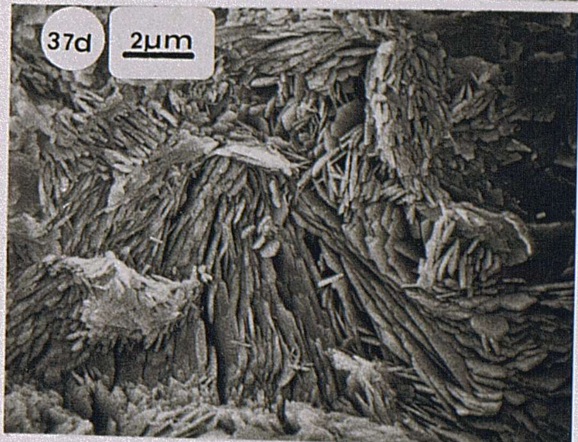
Plate 38. Electron micrograph of gypsiferous nodular bodies (cf. Plate 36) showing predomination of swallow-tail prismatic gypsum crystals.

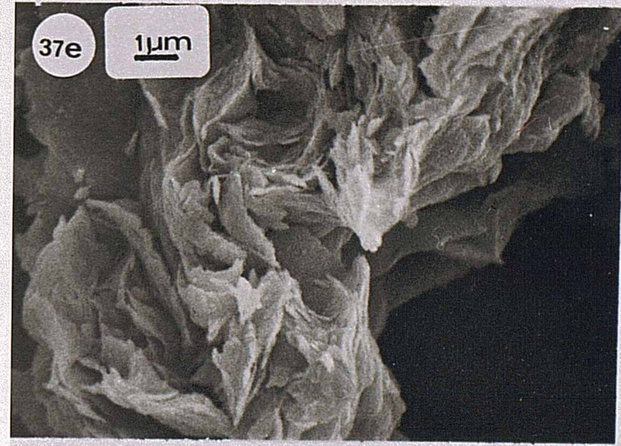
Plate 39. Electron micrograph of a Recent swallow-tail selenite (gypsum) crystal coatings on sediments surface, Barton-on-Sea.

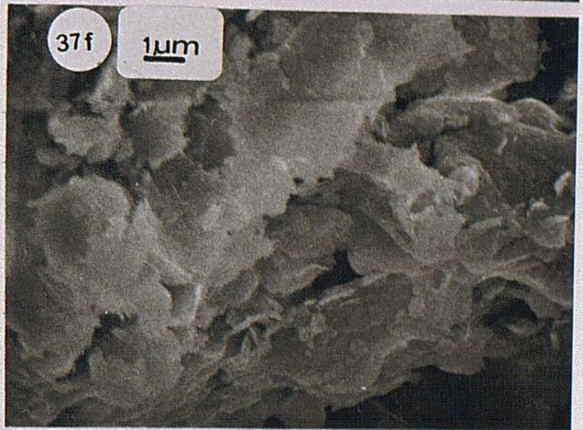

37a


37b


37c


37d


37e


37f


38

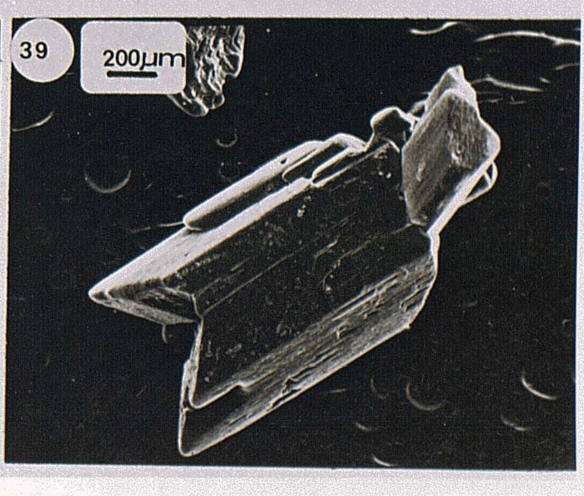

39

Plate 40. Photomicrograph of indurated pebble bed, showing silt to coarse sand-sized quartz grains in a goethitic matrix.

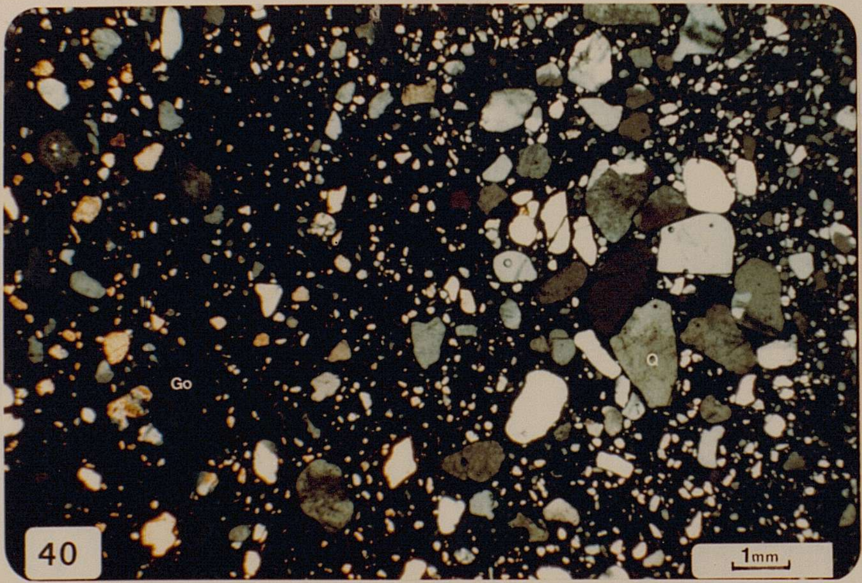
XL. Sample ABPB-1, Pebble Bed, Alum Bay, Isle of Wight.

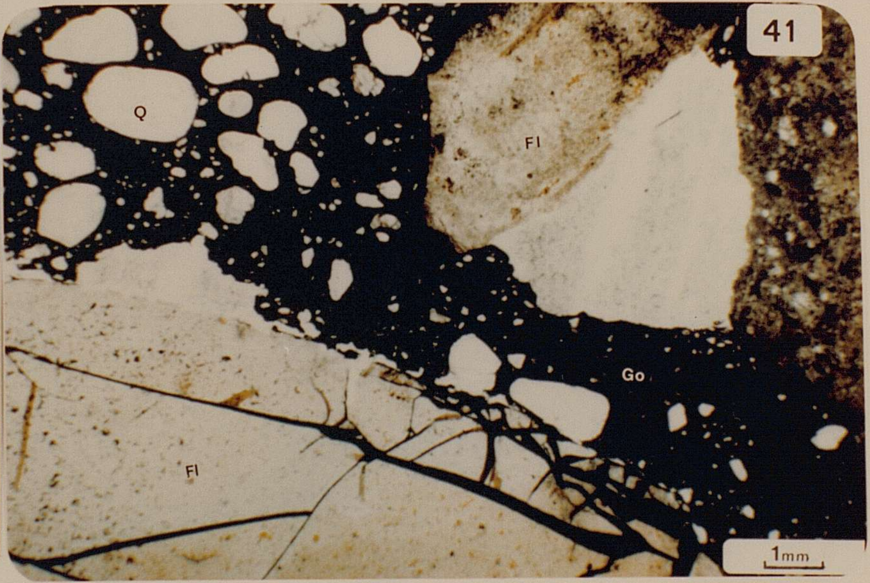
Plate 41. As Plate 40, showing very coarse quartz grains (Q), flint (Fl) grains and pebbles. Note the displacive goethite growths within surface cracks of the pebble.

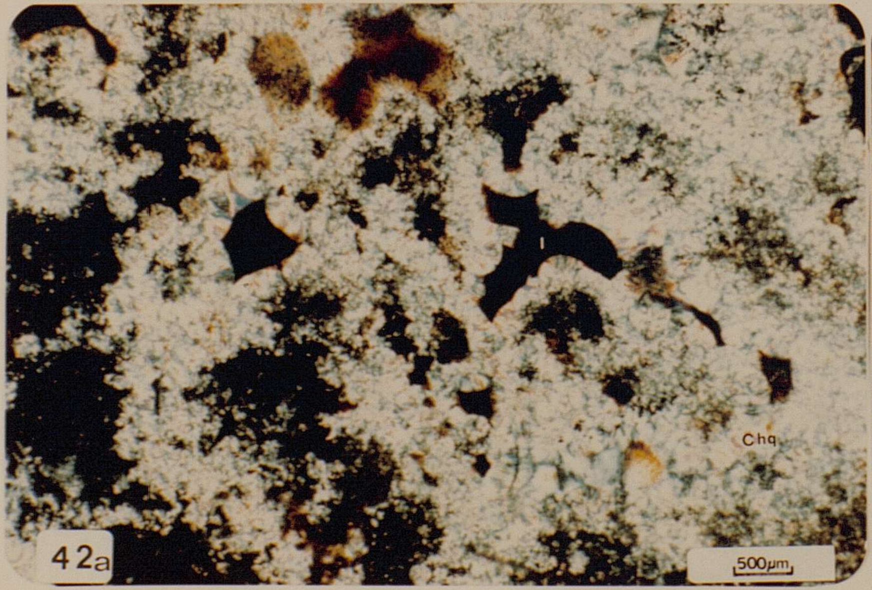
Plate 42a. Photomicrograph of a cryptocrystalline chalcedonic quartz (Chq) in-fills in flint pebbles.

XL. Sample ABPB-1, Sand-supported pebble bed, Highcliffe

Plate 42b. As Plate 42a, showing the length-fast chalcedonic quartz.


Go
Q
40
1mm


41
Q
Fl
Go
Fl
1mm


I
Chq
42a
500µm

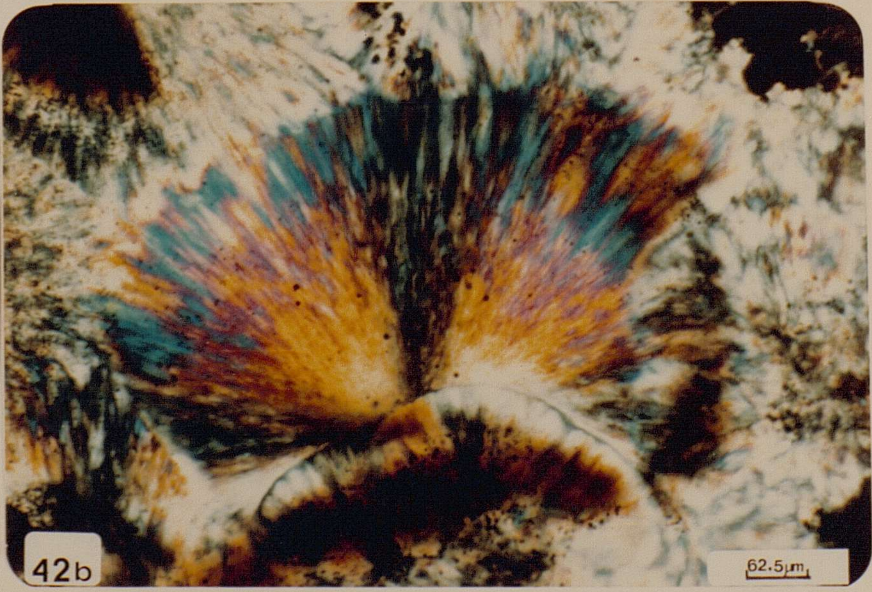

42b
62.5µm

Plate 43. Photomicrograph of flint pebble with microcrystalline quartz and sponge spicules (SP).

XL. From the horizon of Sample BPB-1, sand-supported pebble bed, Highcliffe.

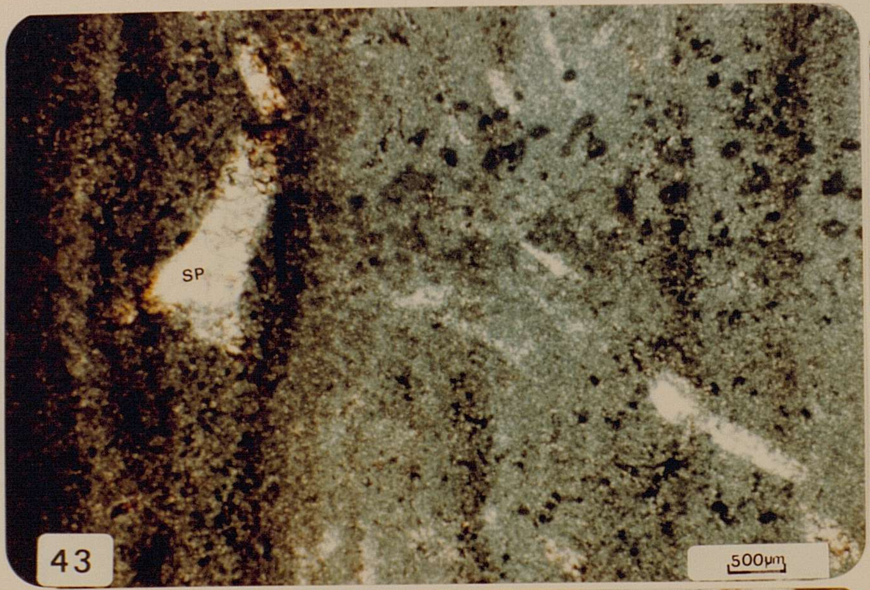
Plate 44. Photomicrograph of a chert pebble predominantly composed of chalcedonic quartz (Chq) and sponge spicules.

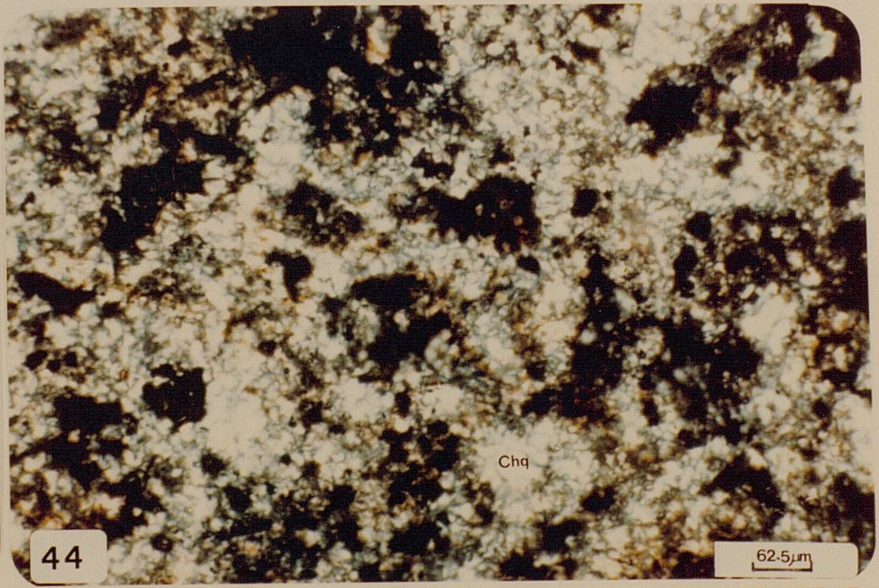
XL. From the horizon of Sample BPB-1, sand-supported pebble bed, Highcliffe.

Plate 45. Photomicrograph of gleysol palaeosol with goethite mottle (GoM) and quartz in goethite-clay matrix.

XL. Sample ABBB/FS-2a. Gleysol palaeosol, Barton Sand, Heatherwood Point, Isle of Wight.

Plate 46. As Plate 45, with goethite mottles, quartz, and goethite-clay matrix.


43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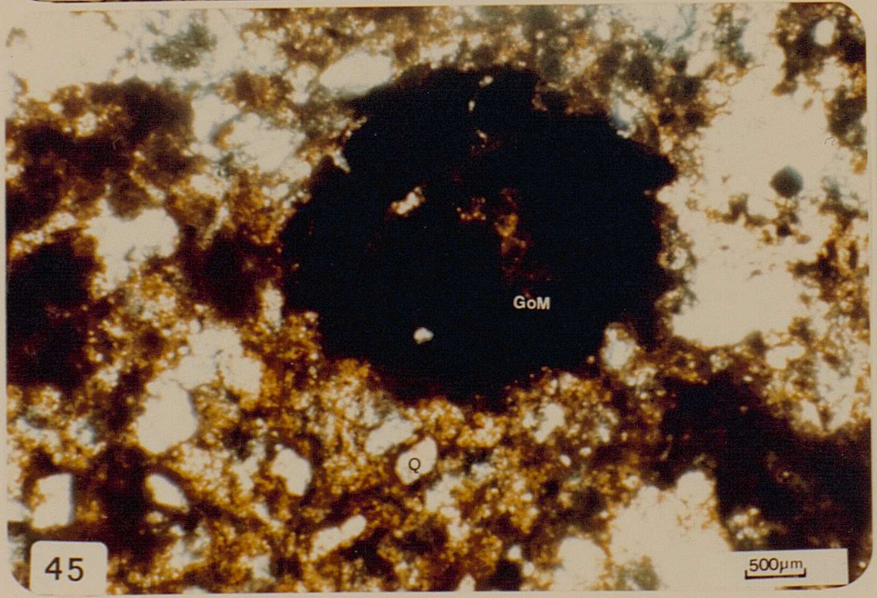
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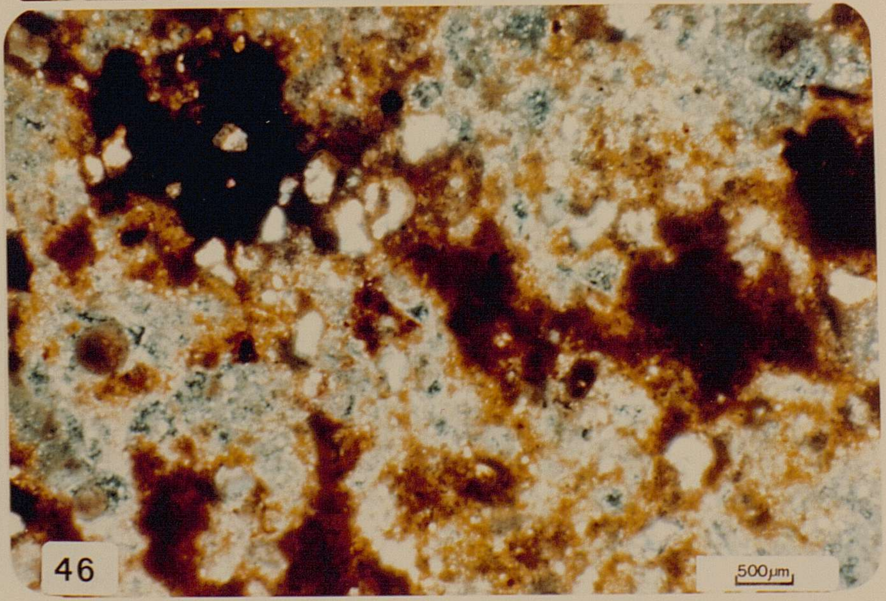

46

Plate 47. Photomicrograph of gleysol palaeosol showing granular fabric with quartz grains set in goethitic matrix.

XL. Sample ABBB/FS-1b. Gleysol palaeosol, Barton Sand, Alum Bay.

Plate 48. Photomicrograph of gleysol palaeosol showing quartz grains in clay-goethite matrix.

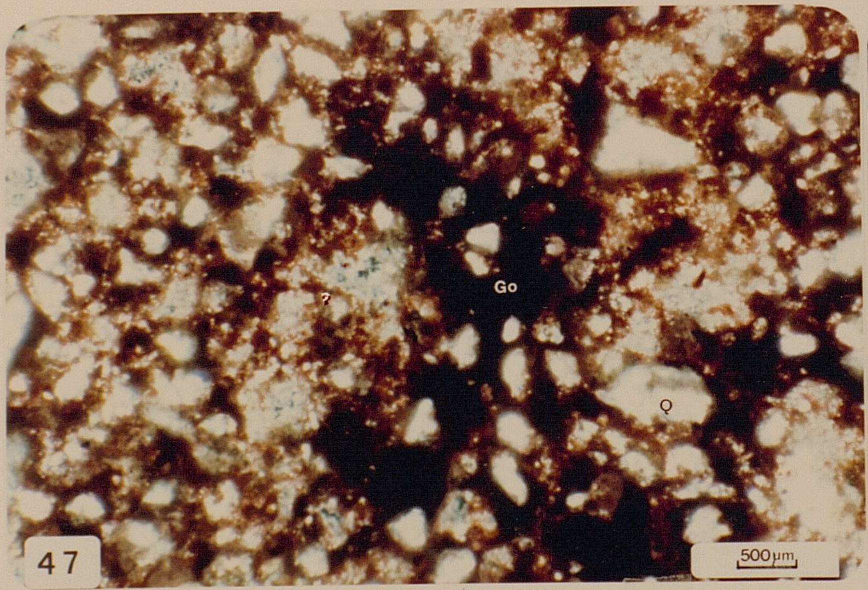
XL. Sample ABBB/FS-2b. Gleysol palaeosol, Barton Sand, Alum Bay.

Plate 49. Photomicrograph of red-yellow podzol palaeosol predominantly composed of quartz (skeletal grains) within goethite cement matrix.

XL. Sample ABBB/FS-4a Red Yellow podzol palaeosol, Barton Sand, Heatherwood Point, Isle of Wight.

Plate 50. Photomicrograph of red-yellow podzol palaeosol with wide goethite voidan and skeletal quartz grains in indurated, veson horizons.

XL. Sample ABBB/FS-3a. Red-yellow podzol palaeosol, Barton Sand, Heatherwood Point, Isle of Wight.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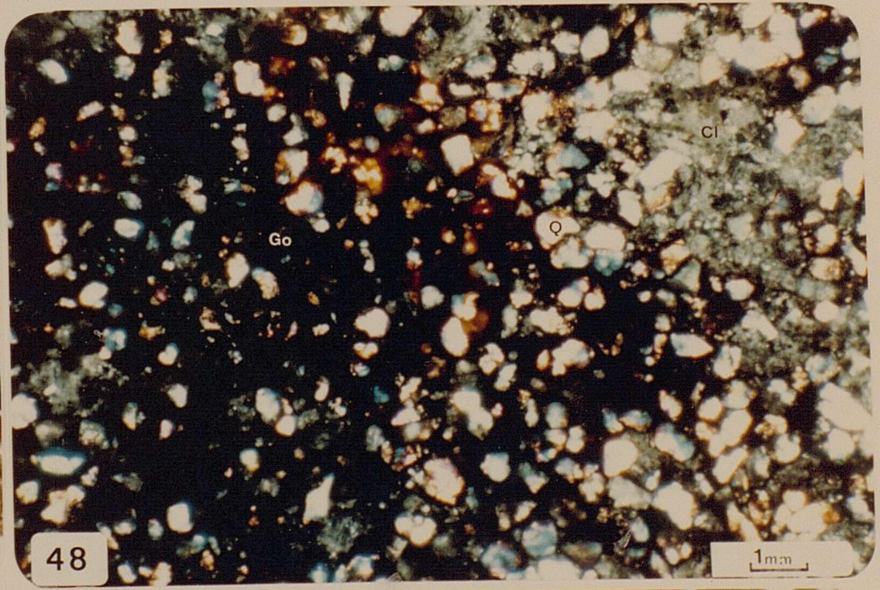
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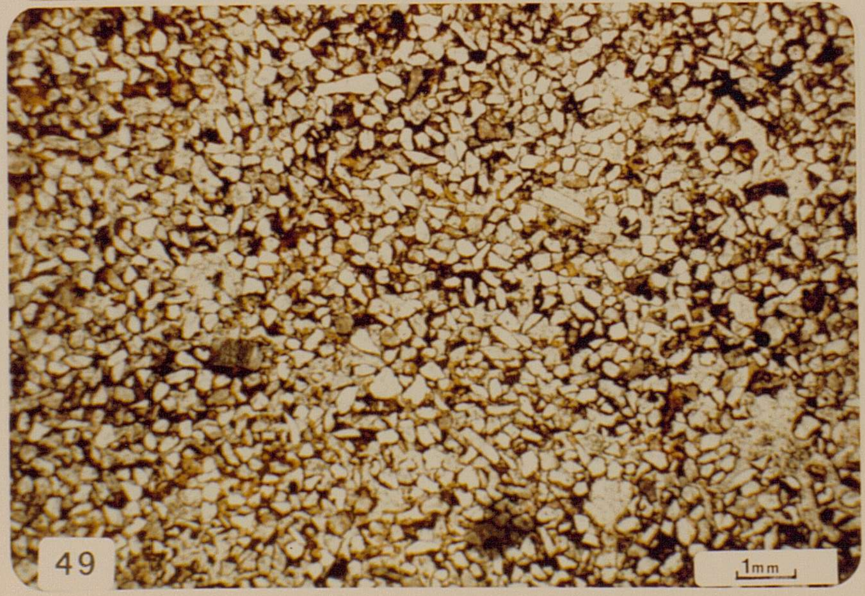
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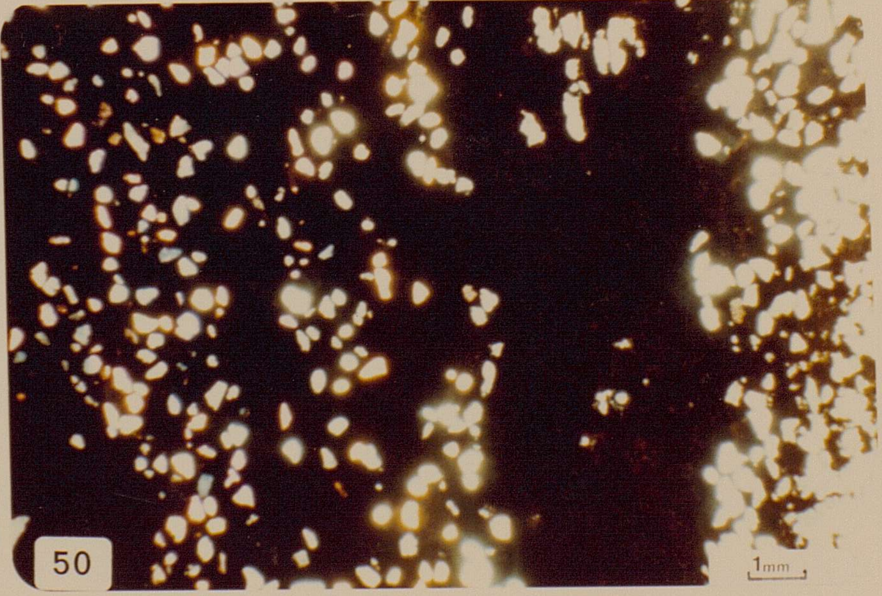

50

Plate 51. Electron micrographs of the indurated pebble bed, Alum Bay, showing -

a. microcrystalline quartz overgrowths in flints.

b. low magnification view of indurating, voidal and coating goethites (h, vm, g) and skeletal quartz grains (q).

c. spherical mounds of goethite(s) in clay matrix.

d. flaky plates of anhedral kaolinite crystals (cl).

e. various forms of the indurating goethite - glaebules (g), honeycombed interlocked plates (h) and cryptocrystalline masses (cg)

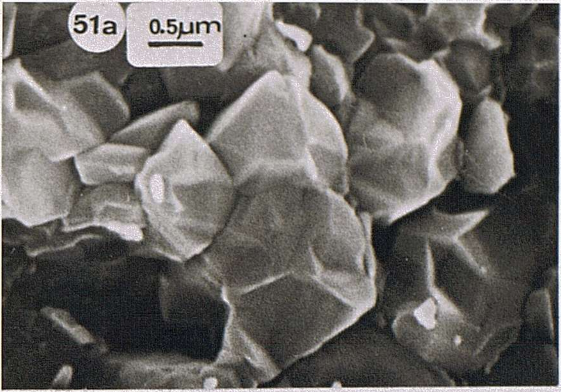
f. glaebular goethites (g)

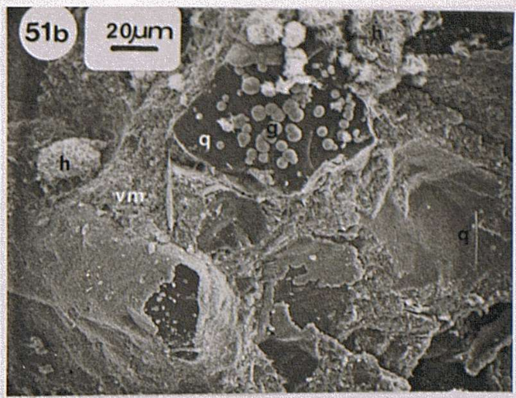
g. poorly-differentiated, cryptocrystalline goethite (cg).

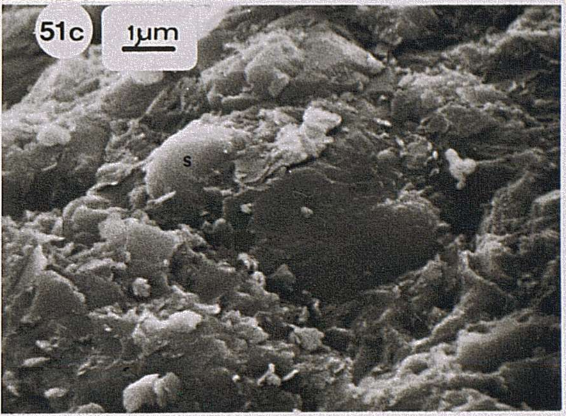
h. radiating goethite laths/plates.

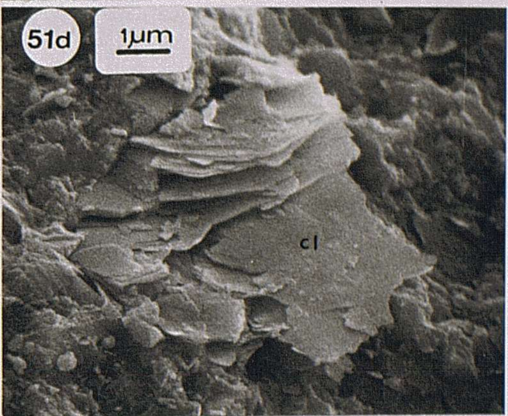
i. spherical, 'bird-nest' or honeycombed goethite laths/plates.

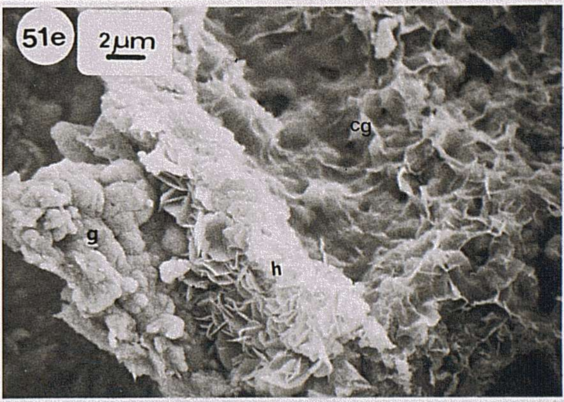
j. As i, showing edge-edge twinning of goethite plates.

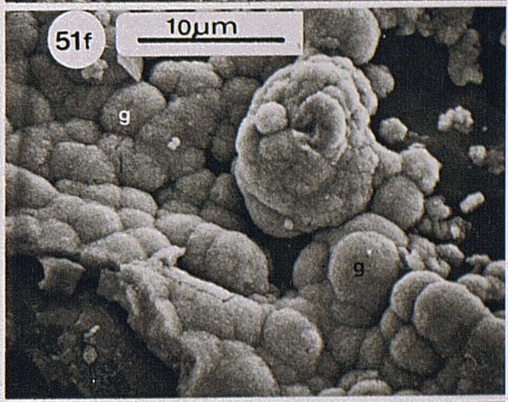

51a
0.5μm

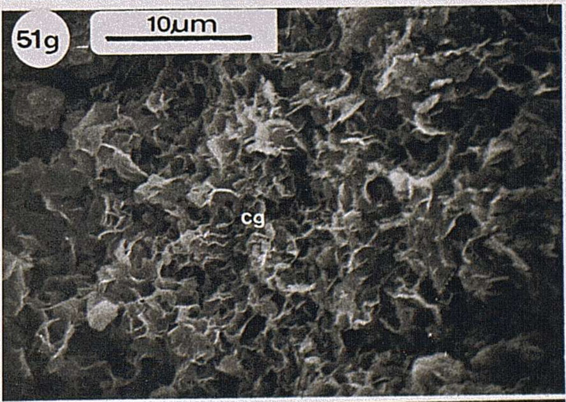

51b
20μm
h
g
q
h
vm
q

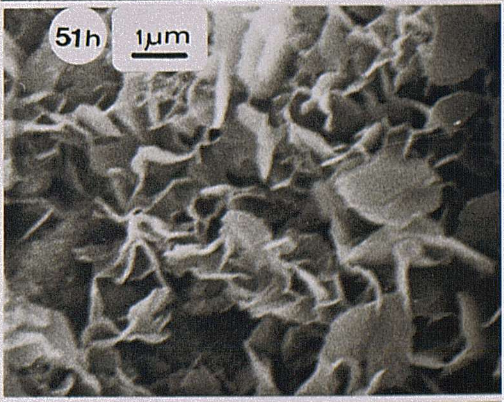

51c
1μm
s

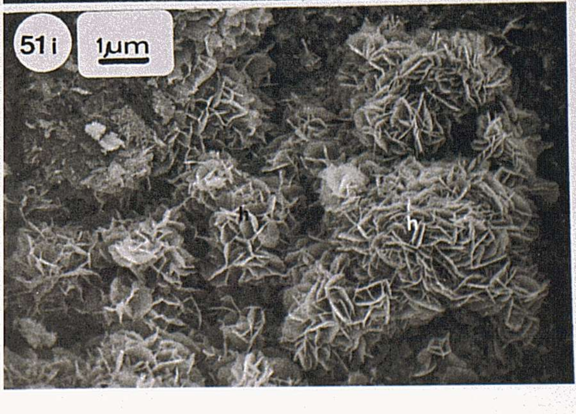

51d
1μm
cl


51e
2μm
cg
g
h


51f
10μm
g
g


51g
10μm
cg


51h
1μm


51i
1μm
h
h

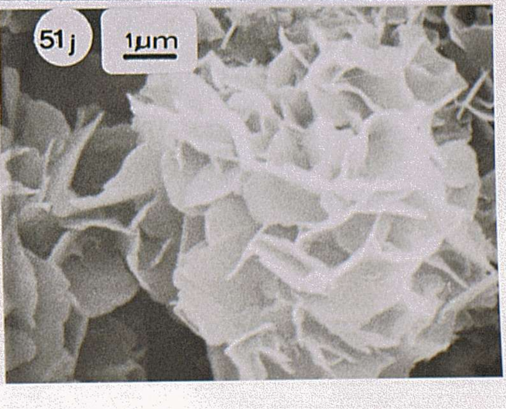

51j
1μm

Plate 52. Electron micrographs of red-yellow podzol palaeosols, Barton Sand, Heatherwood Point/ Alum Bay, showing -

a. skeletal quartz grains(q) and voidal, cementing materials (vm).

b. As a at higher magnification, showing sharp contacts between grains and voidal material.

c. clay floccules (cl) within void.

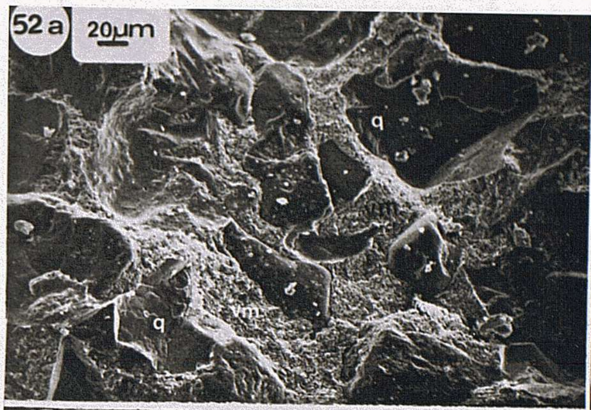
d. clay floccules and goethite laths (lag) within voids.

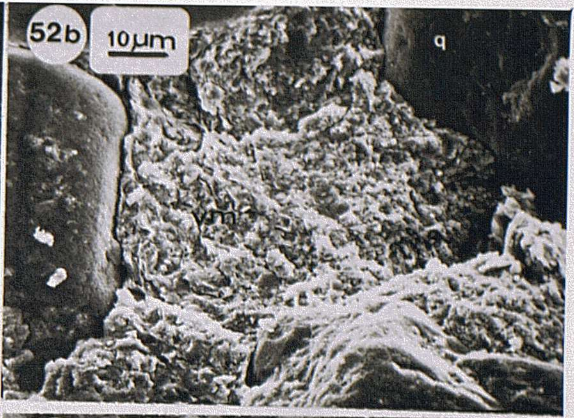
e. as d.

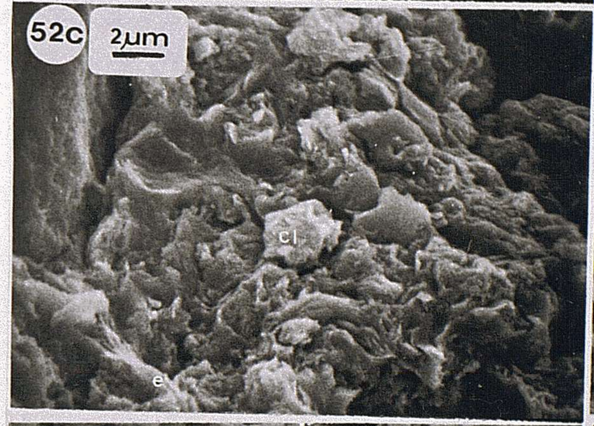
f. glaebular goethite (g) coating quartz and within voids.

g. glaebular goethites(g) and plant debris (p) and rootlets (r).

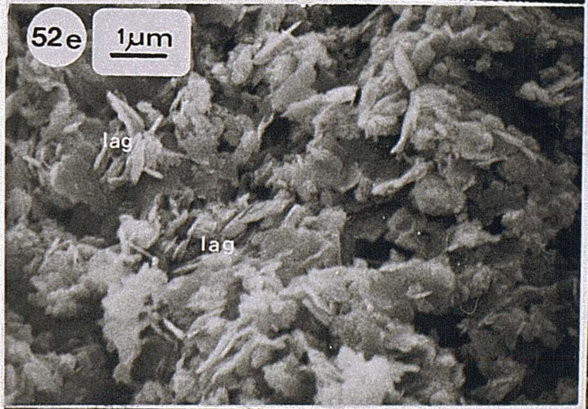
h. as g.

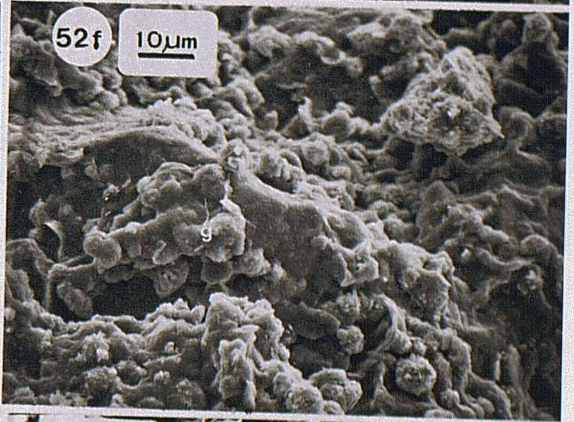

52a
20µm
q
vm
q
vm
q

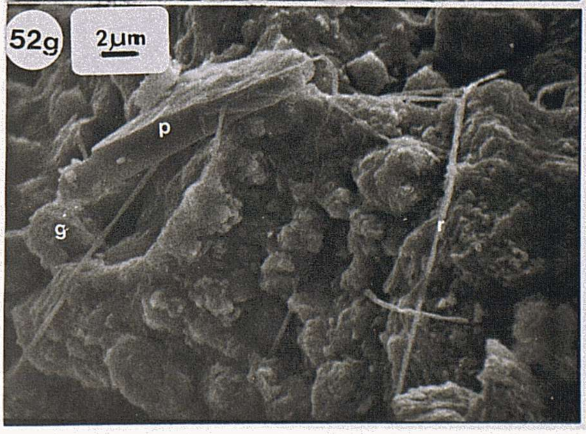

52b
10µm
q
vm


52c
2µm
cl
e


52d
1µm
lag


52e
1µm
lag
lag


52f
10µm
g


52g
2µm
p
g
r

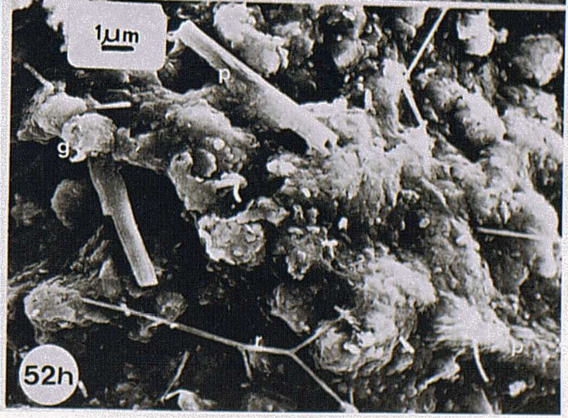

1µm
p
g
r
p
52h

Plate 53. Electron micrographs of red-yellow podzol palaeosols, Heatherwood Point/Alum Bay, showing -

a. voidan and coating glaebular and honeycombed goethites.

b. glaebular goethites coating corroded grains.

c. wool-ball like glaebular aggregation of microcrystalline and lath goethite crystals.

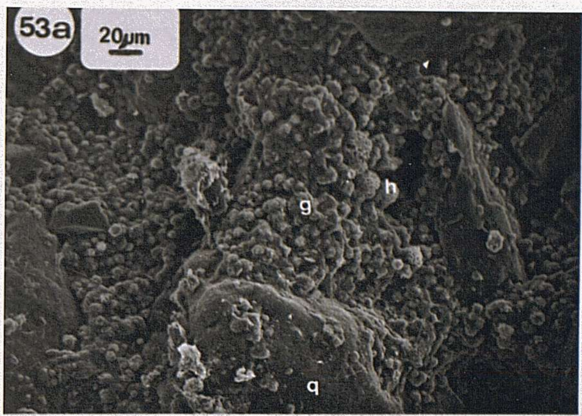
d. 'smooth-surfaced' glaebular goethite.

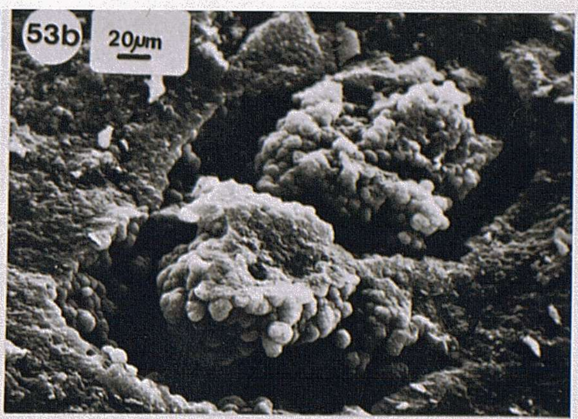
e. puffed glaebular aggregation of goethite.

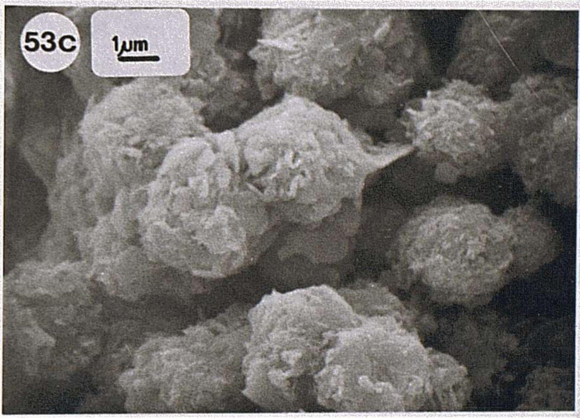
f. spheres of 'honeycombed' goethites.

g. interlocked platy crystals of the 'honeycombed' goethites.

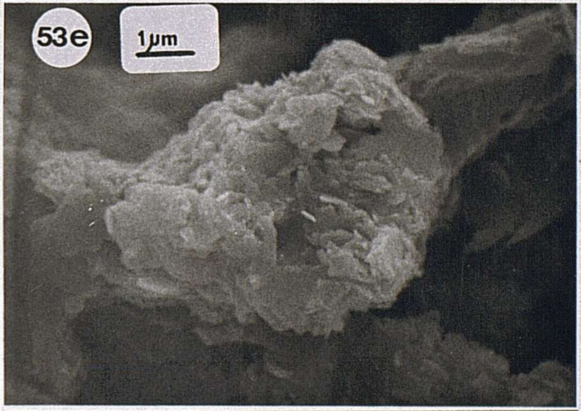
h. radiating laths and flattened goethite crystals.

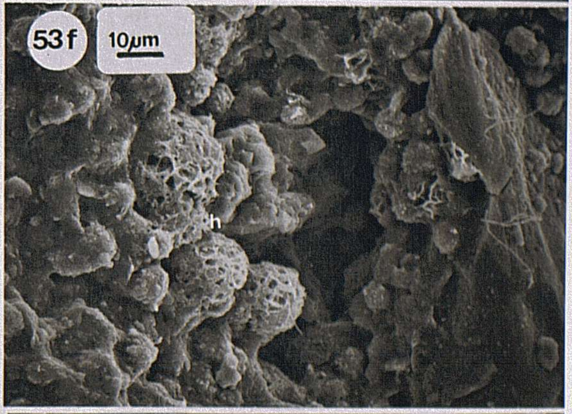

53a
20µm
h
g
q

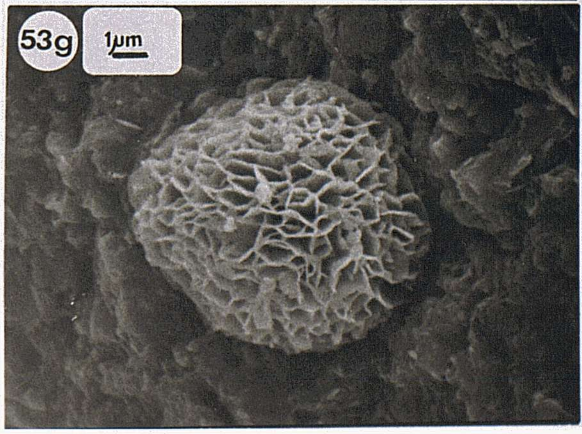

53b
20µm


53c
1µm


53d
0.5µm


53e
1µm


53f
10µm
h


53g
1µm

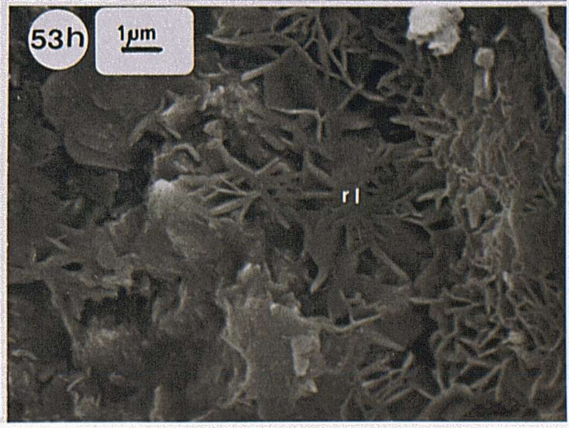

53h
1µm
rl

Plate 54. Electron micrographs of red-yellow podzol palaeosols, Heatherwood Point/Alum Bay, showing -

a. etched or corroded quartz grain (q).

b. heavily corroded and pitted quartz.

c. corroded feldspars broken into $\lesssim$ 10 μm cleaved pieces.

d. corroded feldspars broken into platy pieces.

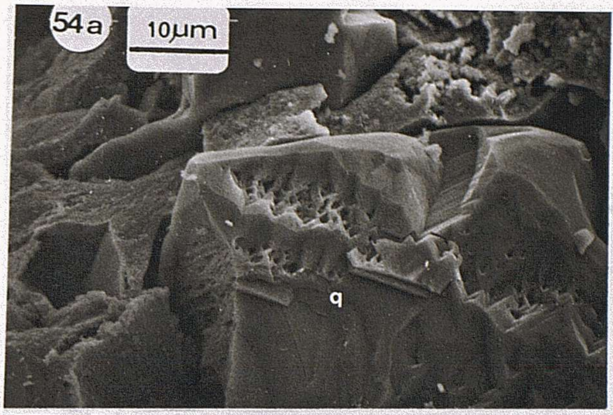
e. voidal materials including broken up feldspar(F).

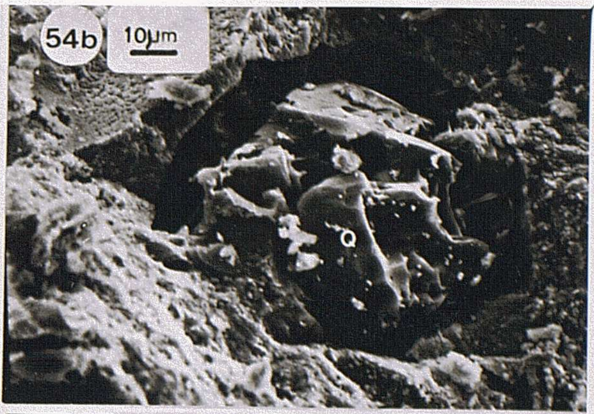
Plate 55. Electron micrographs of indurated sand sample BLH-12, 'Lower Headon Beds', Hordle Cliff, Long Mead End, showing -

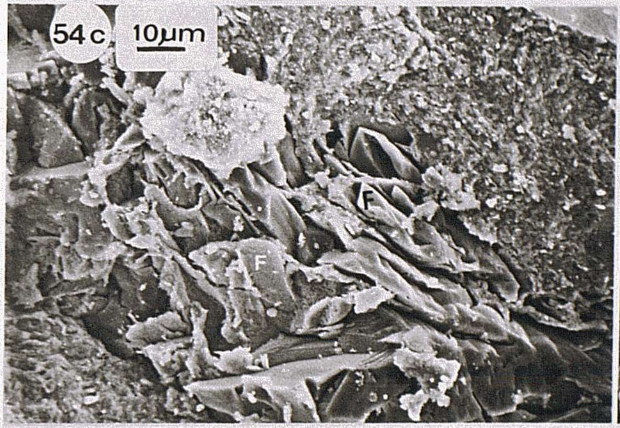
a. voidal materials consisting of clay, quartz and siderite rhombs (sc).

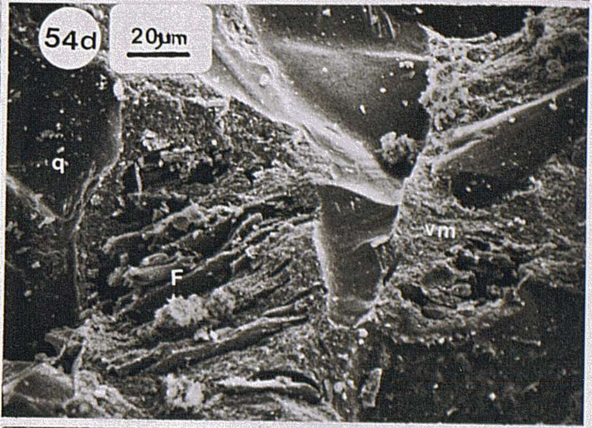
b. plant material (p) with goethite glaebules (g), and clay-sized quartz crystals (q).

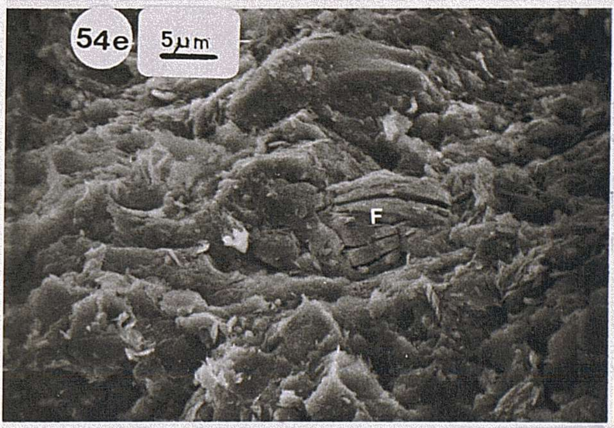
c. cluster of glaebular goethite and clay floccules.

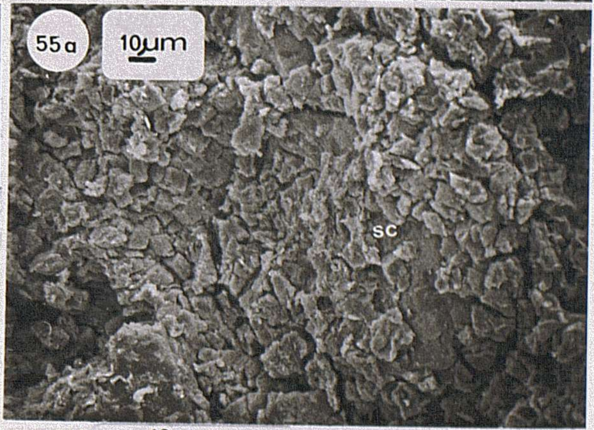

54a
10µm
q

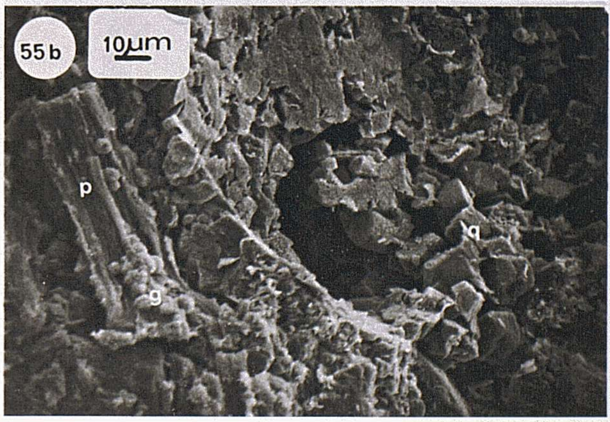

54b
10µm
Q


54c
10µm
F
F


54d
20µm
q
vm
F


54e
5µm
F


55a
10µm
sc


55b
10µm
p
g
q

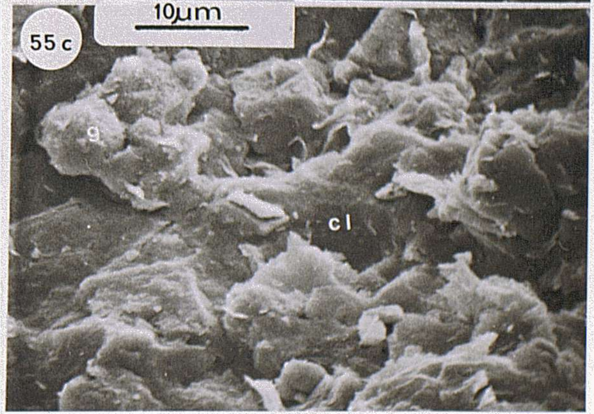

55c
10µm
g
cl

Plate 56. Electron micrographs of kaolinite in the red-yellow podzol palaeosol, Barton Sand, Heatherwood Point, showing -

a. low magnification fine-grained view of the kaolinite (K) within packing voids of quartz grains (Q).

b. as a.

c. anhedral, micro-crystals of kaolinite.

d. flattened (001) faces of kaolinite crystals (p) (in a quartz mould).

e. plates and elongated S shaped vermicular kaolinites (V) in open textural aggregations.

f. wedge-shaped vermicular books of kaolinites.

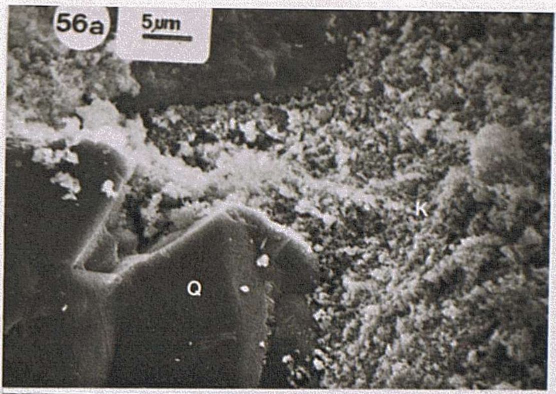
g. vermicular kaolinites.

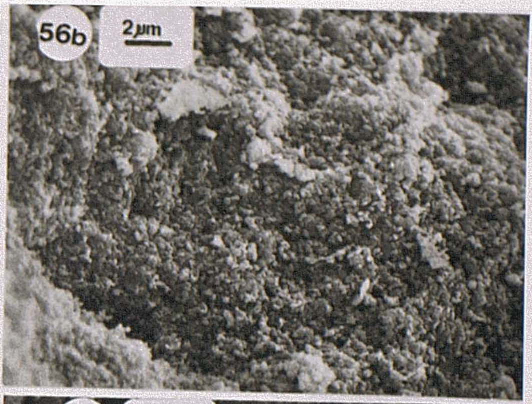
h. large anhedral (pk) and small platy kaolinite crystals.

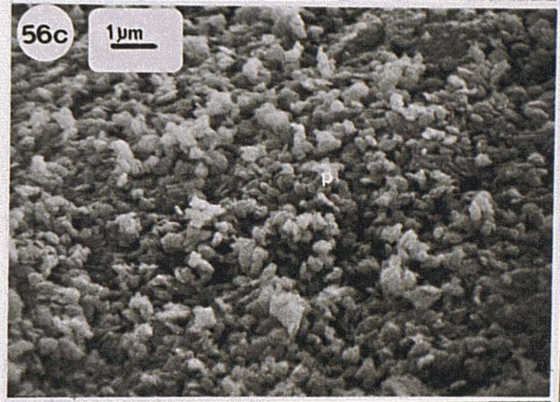
i. delaminated and 'curling-up' platy kaolinite crystals (d).

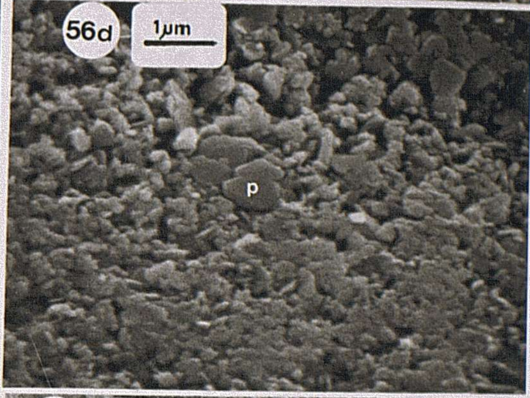
j. fluffy platelets (p) and delaminated platy kaolinites (d).

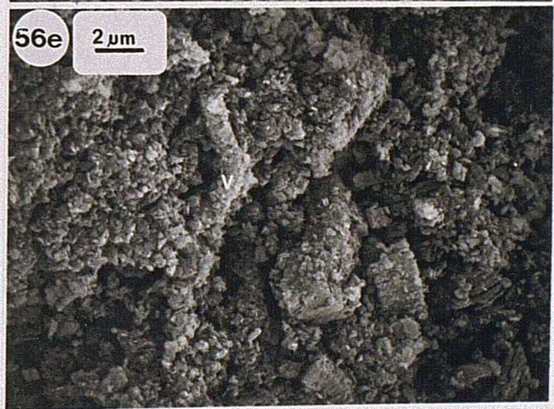
5

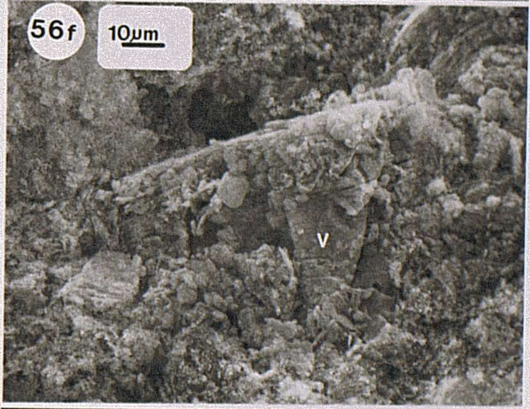

56a

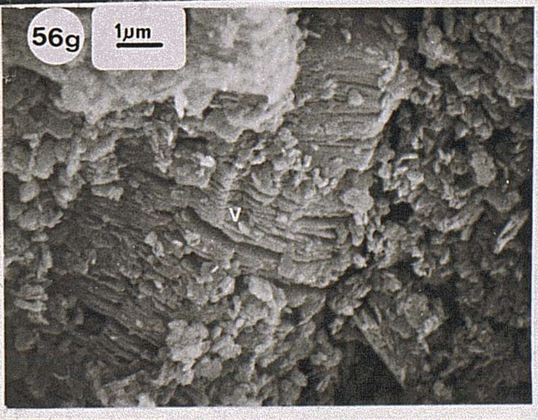

56b

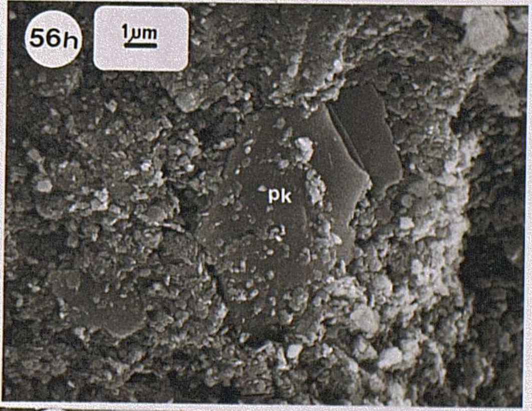

56c

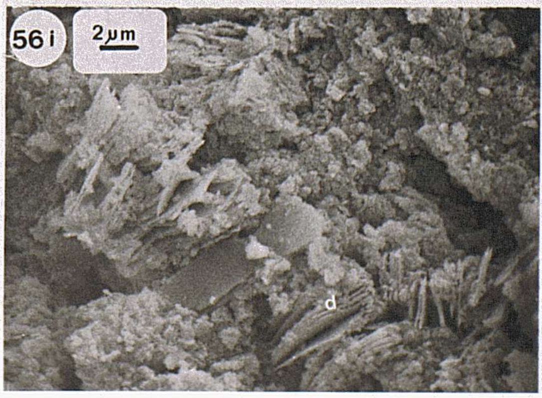

56d


56e


56f


56g


56h


56i

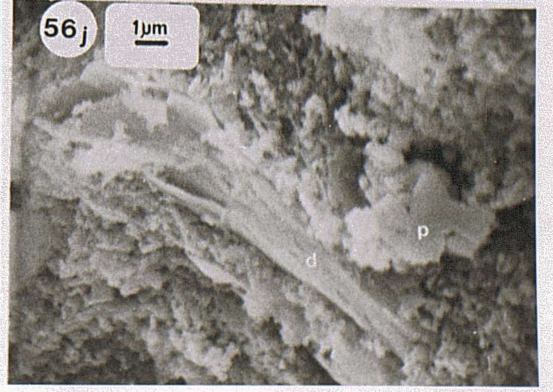

56j

Plate 57. Photomicrograph of chert pebble showing sponge spicules within microcrystalline/ chalcedonic quartz matrix (cf. Plate 44).

PL. Chert pebble from the sandy pebble-bed, Highcliffe.

Plate 58. Photomicrograph of skeletal quartz grains (q) within cementing goethite (cf. Plate 49).

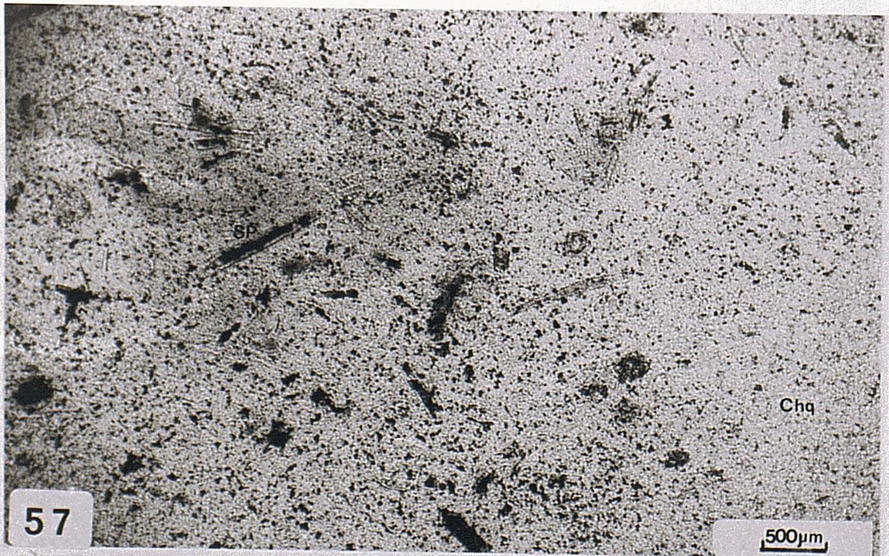
PL. Sample BLH-12, 'Lower Headon Beds', Long Mead End.

Plate 59. Micrograph of 'coarse' glaucony grains; they are predominantly of foraminiferal test moulds.

PL. From Sample BBB-49, Highcliffe Member, Highcliffe.

Plate 60. Micrograph of 'fine' glaucony grains.

PL. From Sample BBB-37, Naish Member, Highcliffe.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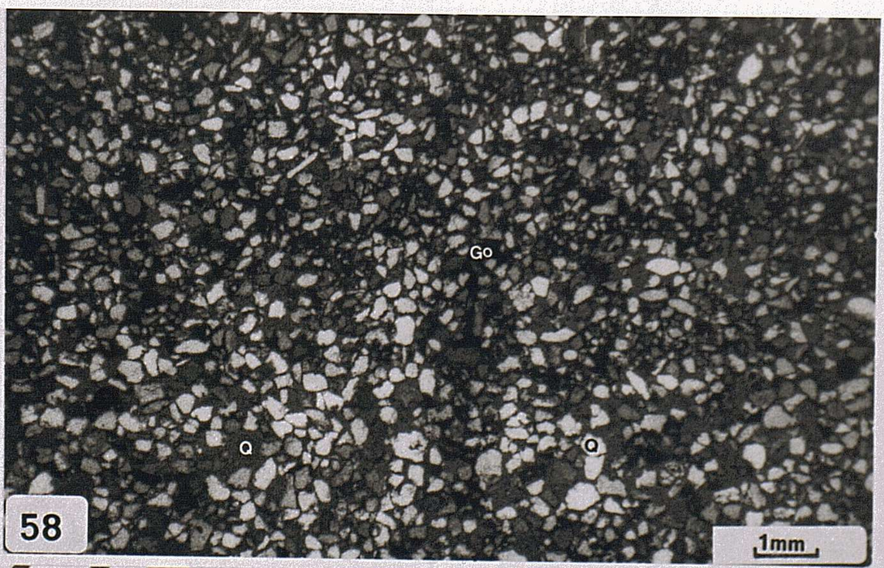

58


59

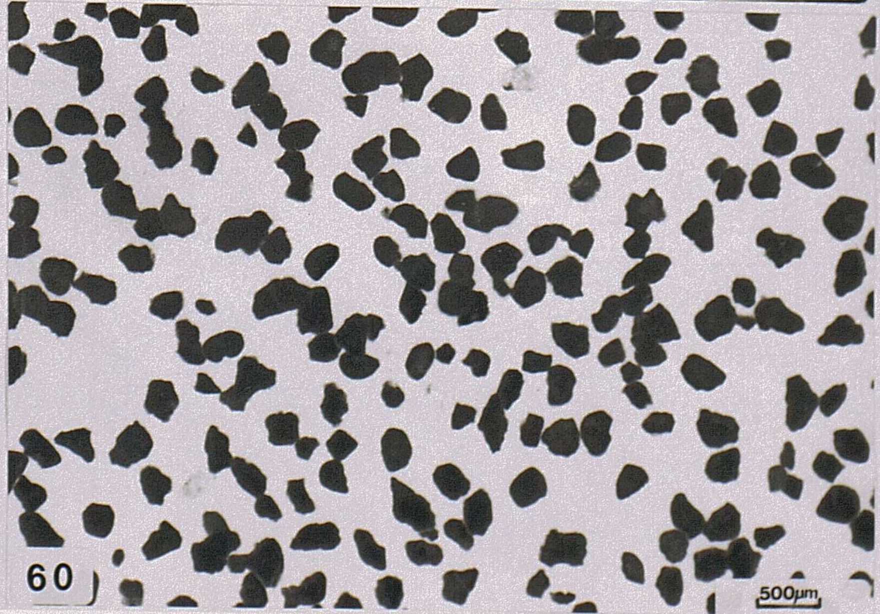

60

Plate 61. Electron micrographs of glaucony grains, showing -

a. 'foram moulds', sub-rounded - sub-spherical morphologies of the grains.

b. a glaucony grain with thin smooth wall and internal aggregated crystallites.

c. a glaucony grain with smooth surface.

d. as b, at higher magnification.

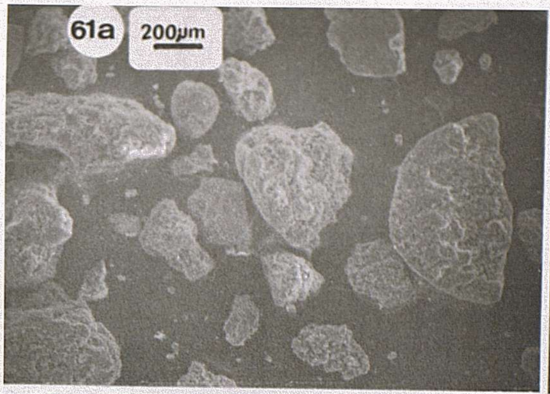
e. aggregated bunch of feather-like crystallites of glauconitic-mica.

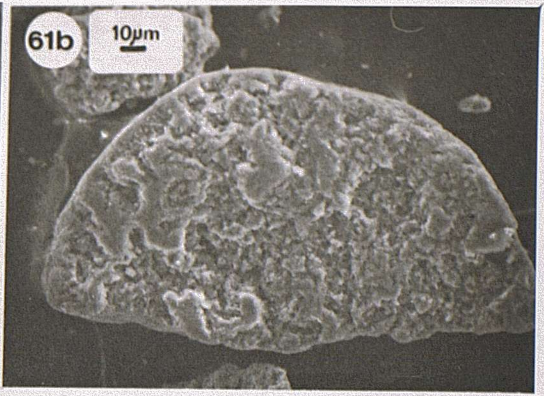
f. as e.

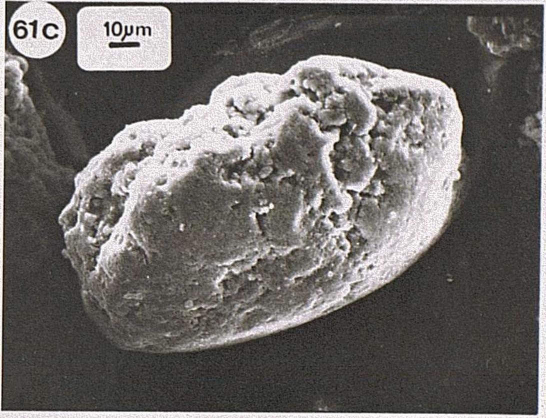
g. mound-like aggregation of crystallites.

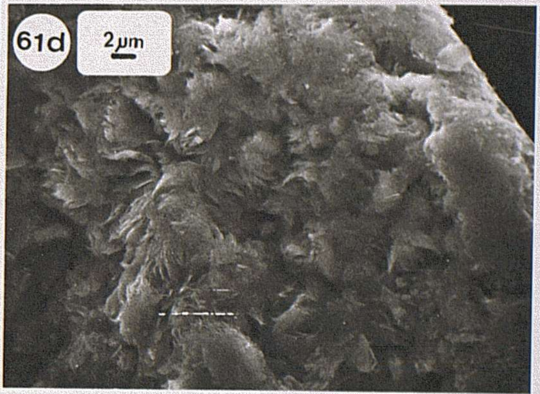
h. aggregations of flattened, serrated crystallites.

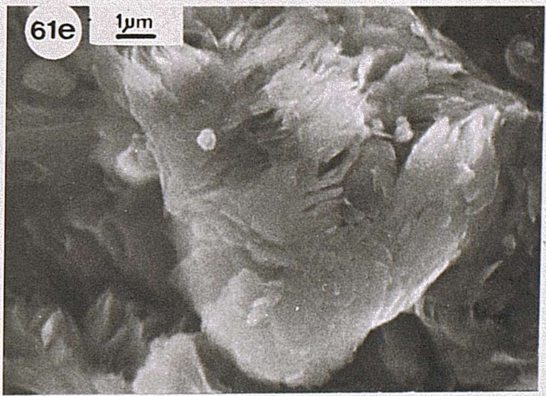
i. as h, at higher magnification.

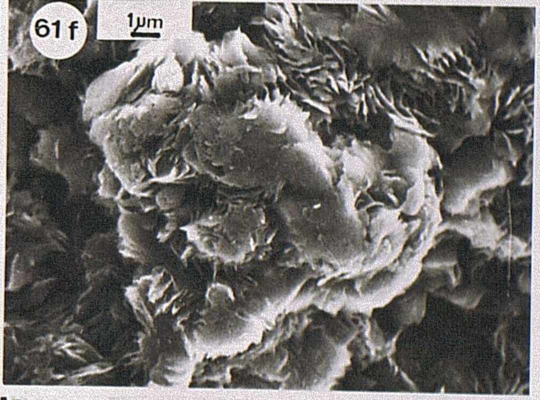

61a
200μm

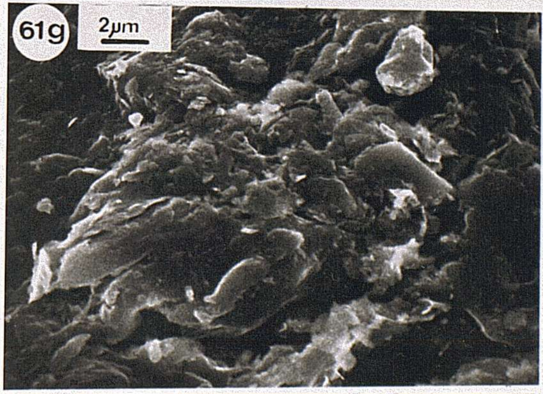

61b
10μm

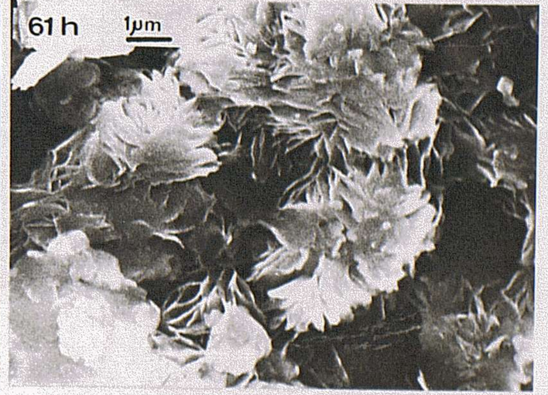

61c
10μm


61d
2μm


61e
1μm


61 f
1μm


61g
2μm


61 h
1μm

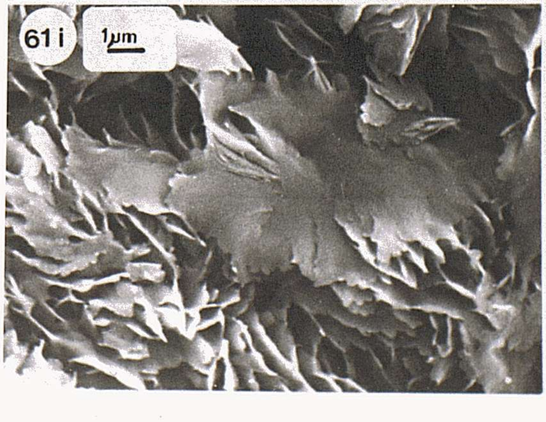

61 i
1μm

Plate 62. Electron micrographs of freshwater limestones, 'Lower Headon Beds', Heatherwood Point, Isle of Wight, showing -

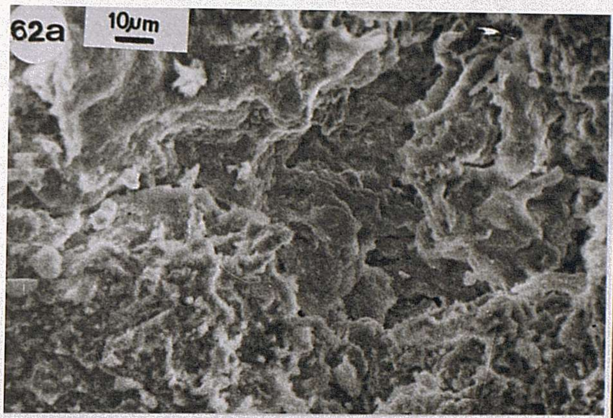
a. poorly differentiated, micritic calcites.

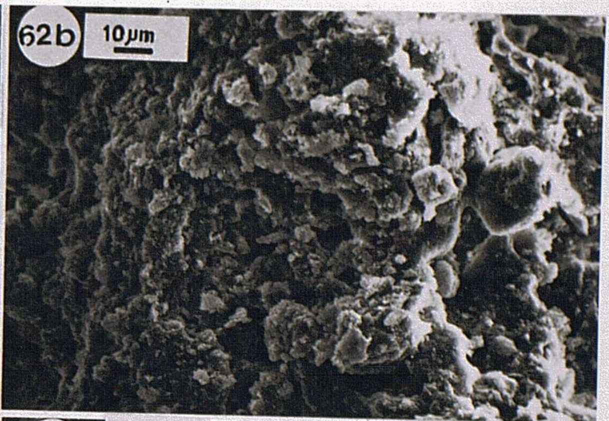
b. aggregation of micritic calcites.

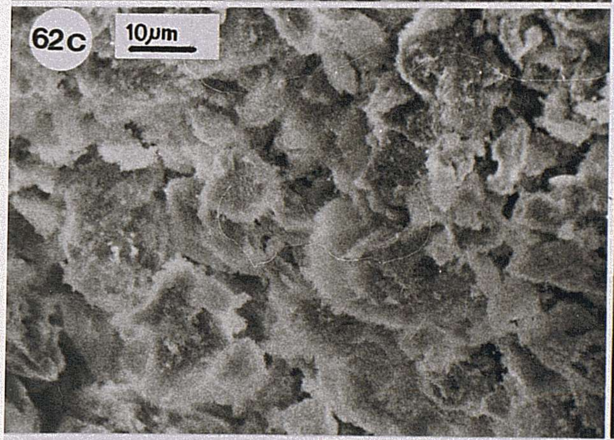
c. fluffy anhedral calcite crystals; poorly intergrown or stacked.

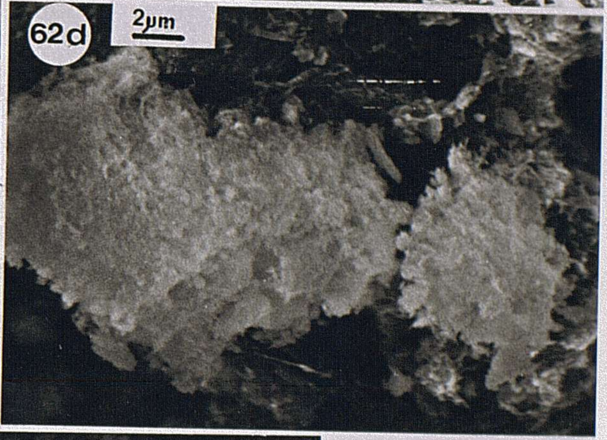
d. as c.

e. piece of broken-up algal-plate calcite(?).


62a


62b


62c


62d


62e

Plate 63. Photomicrograph of stained freshwater limestone, showing non-ferroan aragonitic shells (AFS), quartz (Q) and organic matter (OM) in a slightly ferroan calcitic mud matrix.

Sample ABLH-3, How Ledge Limestone, 'Lower Headon Beds', Heatherwood Point, Isle of Wight.

Plate 64. Photomicrograph of stained freshwater limestone showing mass of quartz grains (Q), organic matter (OM) and aragonitic shell in low ferroan micritic mud.

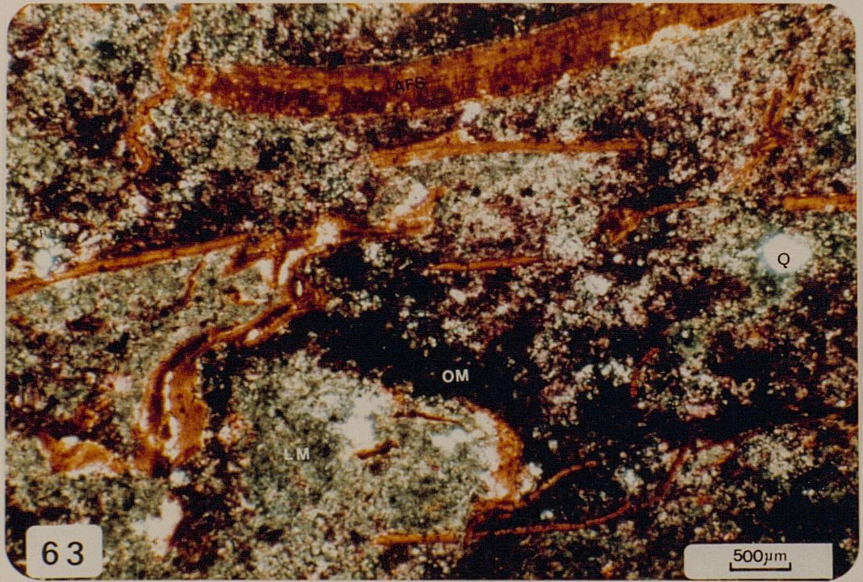
Sample ABLH-6, 'Lower Headon Beds' Heatherwood Point.

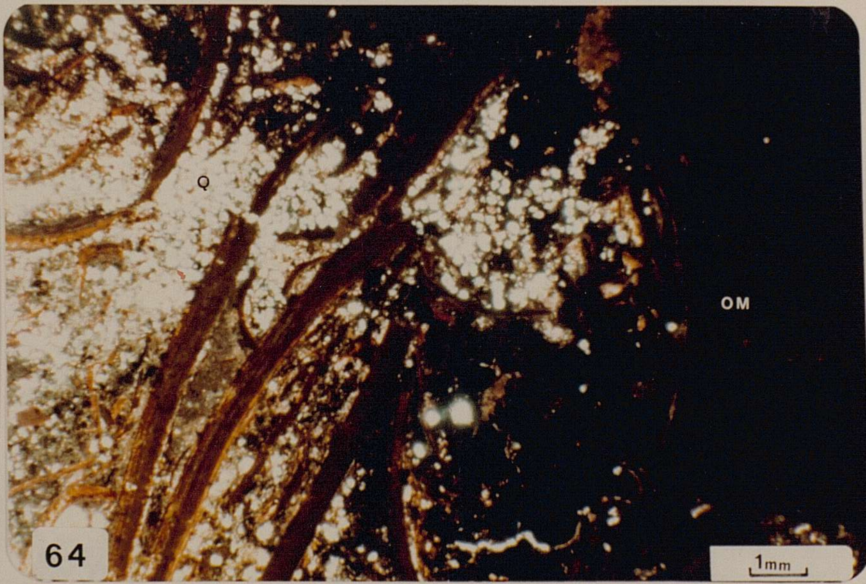
Plate 65. Photomicrograph of stained calcareous concretion showing glaucony grains (Gl) and quartz within microcrystalline ferroan calcite matrix (FC).

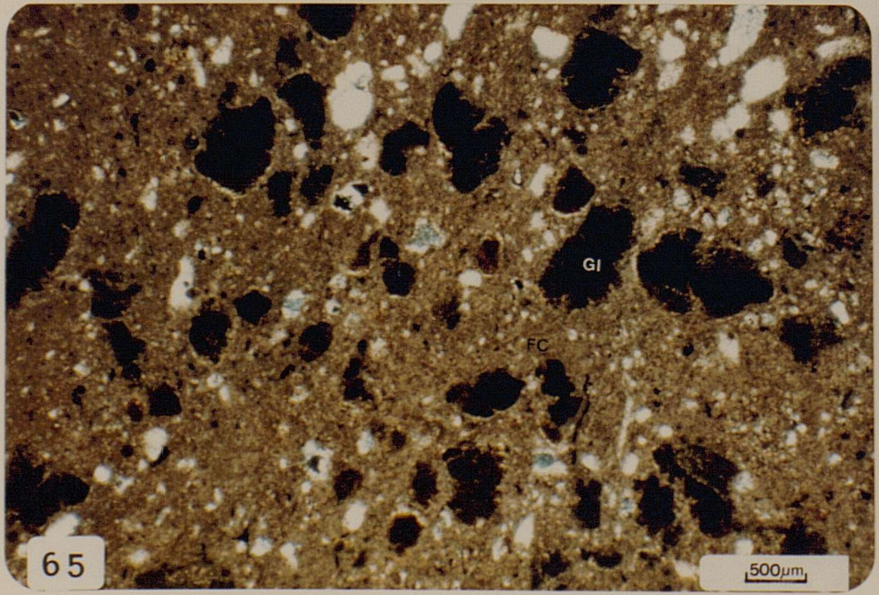
Sample ABBB-5, Barton Clay, Alum Bay.

Plate 66. Photomicrograph of a stained calcareous nodule, showing quartz moulds of microfossils (foraminiferal) within microcrystalline ferroan calcite matrix.

Sample ABBB-4, Barton Clay, Alum Bay.


63


64


65

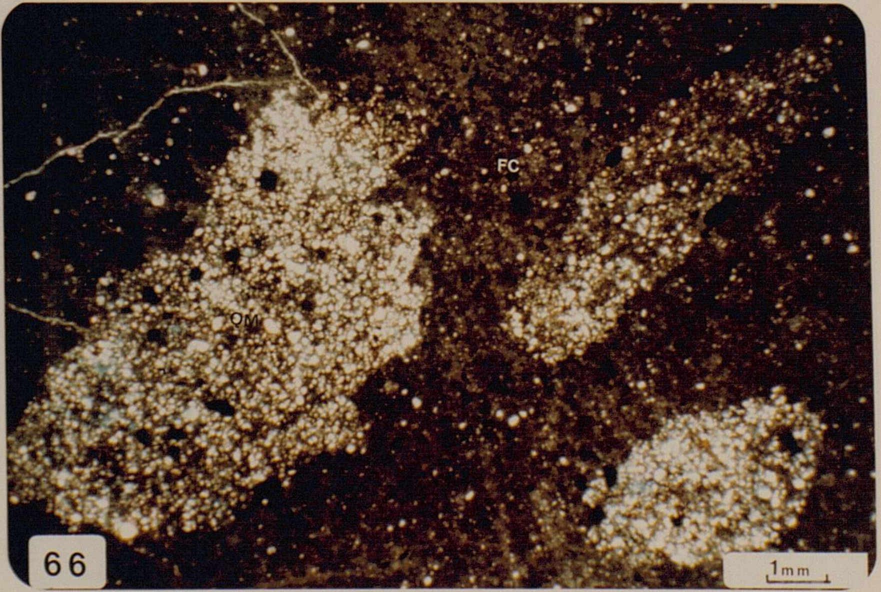

66

Plate 67. Photomicrograph of stained sample of a calcareous band showing infilling (early)* and replacing (late)* pyrites(P) within aragonitic molluscan shell (AFS) set in microcrystalline ferroan calcite matrix (FC). Note ferroan calcite filling septarian fissues in the shell wall.

Sample BBB-25, 'Bed F', Naish Member, Barton-on-Sea.

Plate 68. As Plate 67, showing matrix ferroan calcite (FC), aragonitic shells and ferroan calcite-filled septarian vein and fissures (SFC). Note quartz and glaucony grains in the matrix.

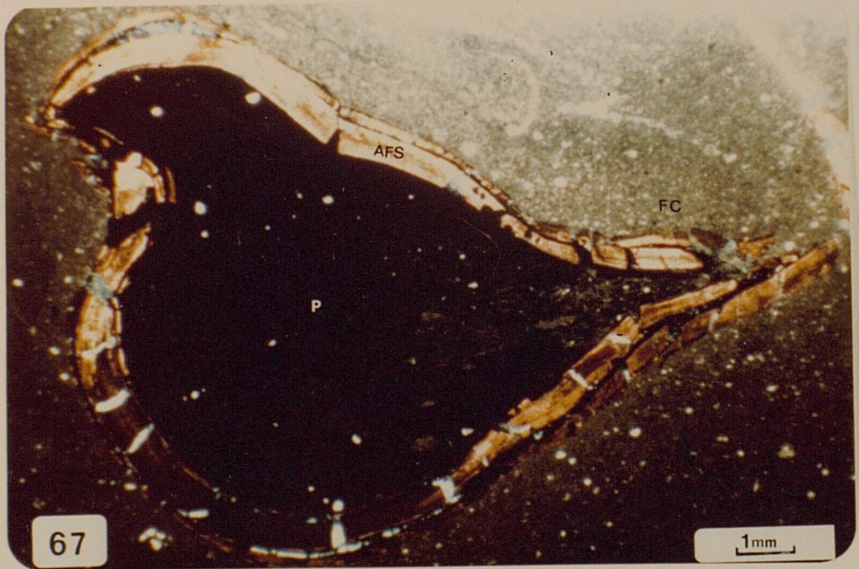
Plate 69. Photomicrograph of stained sample of a calcareous concretion showing the ferroan, septarian calcites to vary from early bladed/ equant micro-crystals to equant/prismatic sparry crystals and, in places, late, slightly ferroan - non-ferroan equant crystals.

Sample BBB-31, Naish Member, Barton-on-Sea.

Plate 70. Photomicrograph showing variation of septarian calcite from early, micro-, bladed and equant crystals to late sparry and anhedral equant/ prismatic and a few bladed crystals.

Sample BBB-36, Naish Member, Highcliffe.

(* see Love, 1971)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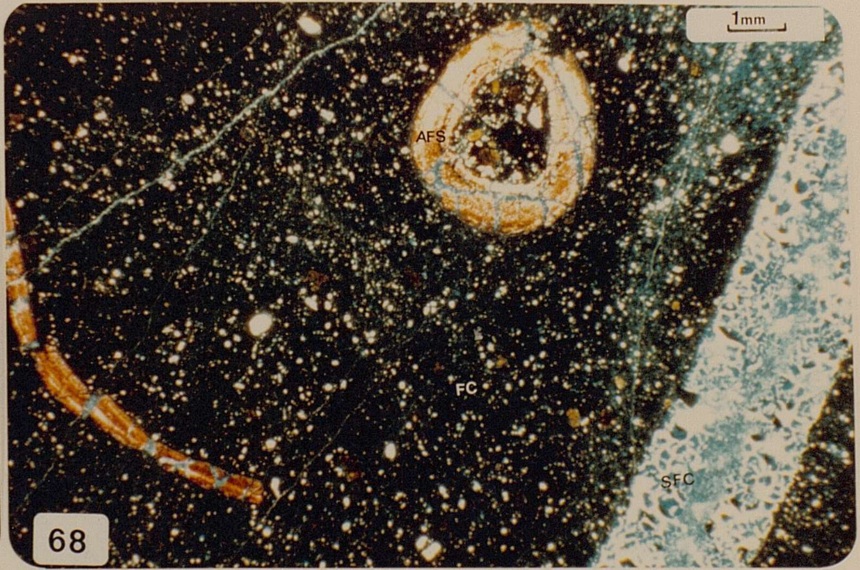
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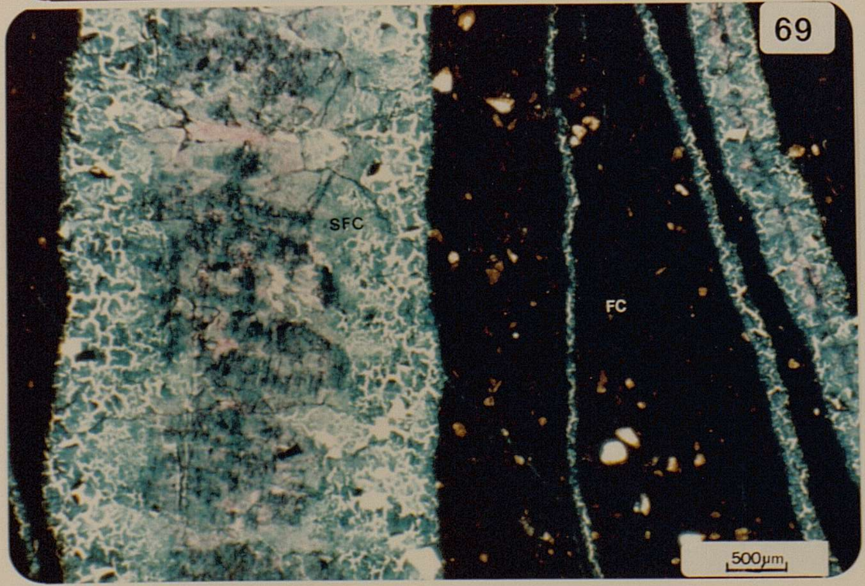
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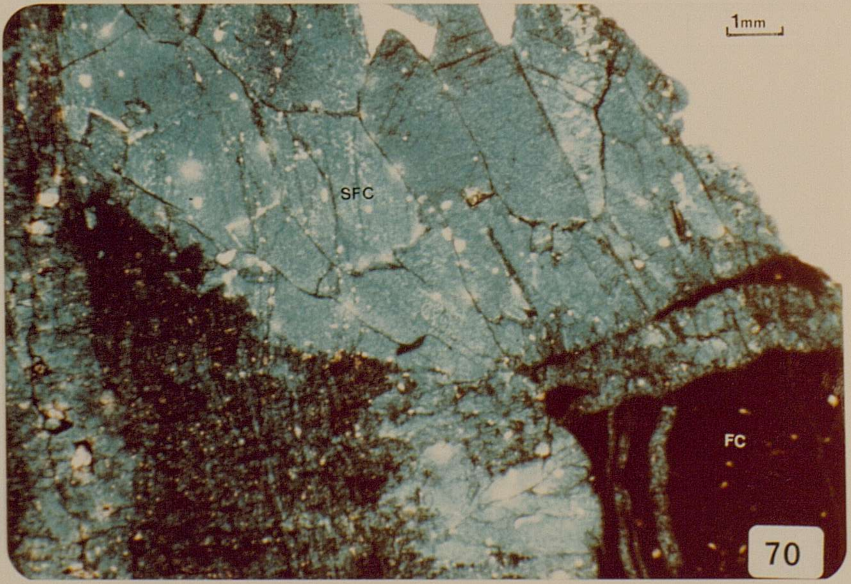

70

Plate 71. Electron micrographs of calcareous concretion, Barton Clay, Barton-on-Sea, showing -

a. equant crystals of septarian calcite increasing in size from the vein wall (lower half of micrograph).

b. sharp contact of septarian calcites (SC) and the microcrystalline matrix of the concretion (MC).

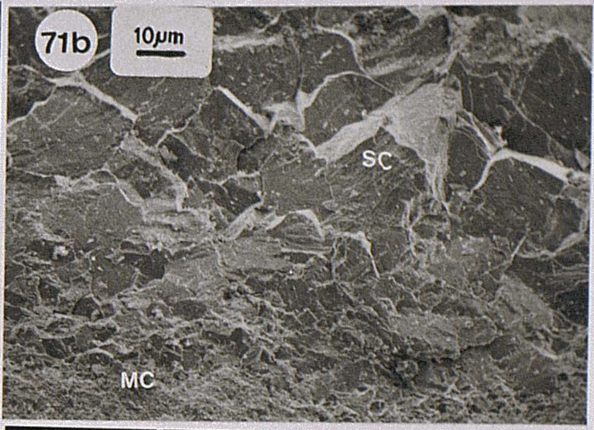
c. as b, emphasizing the flat rhombohedral termination of the septarian calcite crystals.

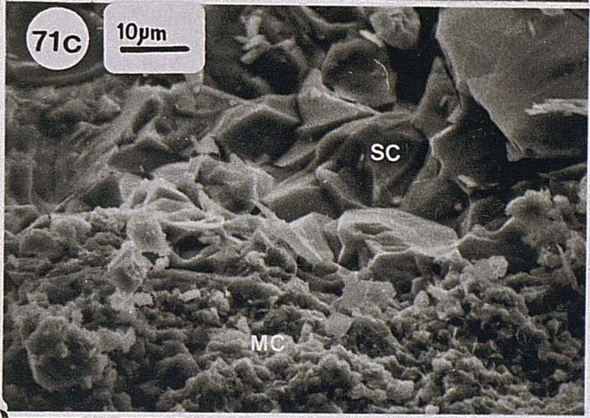
d. the fineness of the matrix with some glauconies (gl).

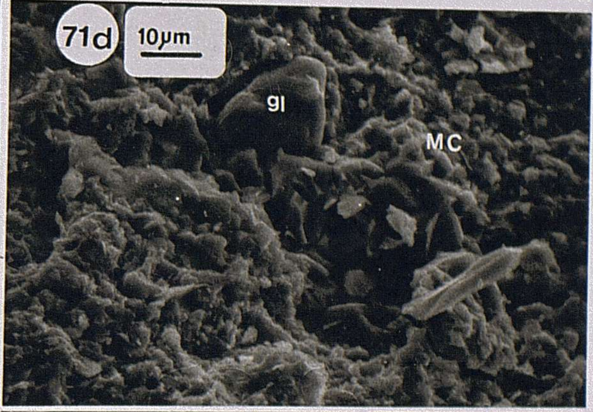
e. as d, with quartz grain (Q).

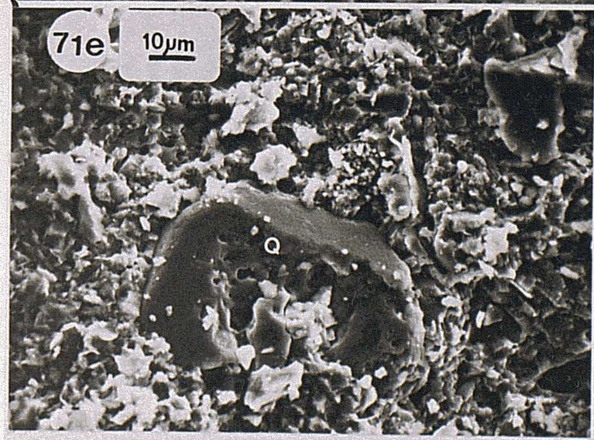
f. part of the concretion matrix with micritic calcites, and clays enclosing framboidal aggregation of octahedral pyrite crystals (py).


71a
100μm
SC


71b
10μm
SC
MC


71c
10μm
SC
MC


71d
10μm
gl
MC


71e
10μm
Q

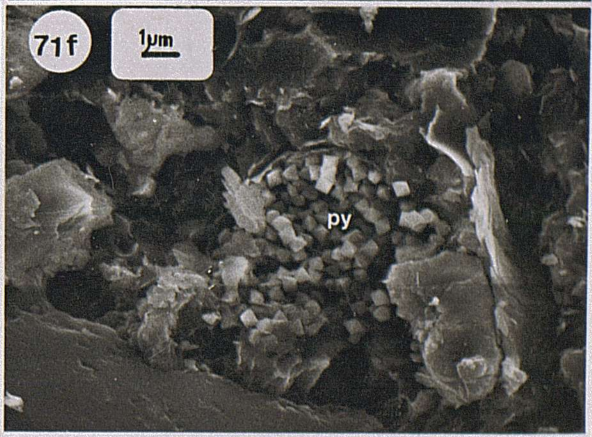

71f
1μm
py

Plate 72. Electron micrographs framboidal aggregation of pyrite crystals in calcareous and sideritic concretions.

a. 'channel-like' framboids and disseminated pyrite crystals (pyf) in a glauconitic sand-clay ironstone.

Sample BBB-50, base of Highcliffe Member,
Highcliffe.

b. as a.

c. as b, emphasizing the octahedral and pyritohedral crystal forms.

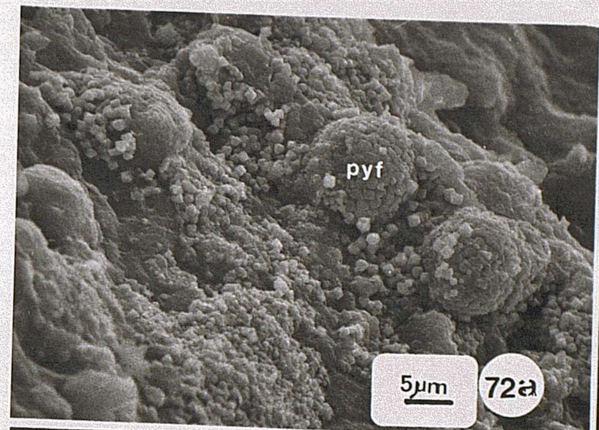
d. octahedral crystals of pyrite framboid (enclosed within a fossil shell) in a calcareous concretion.

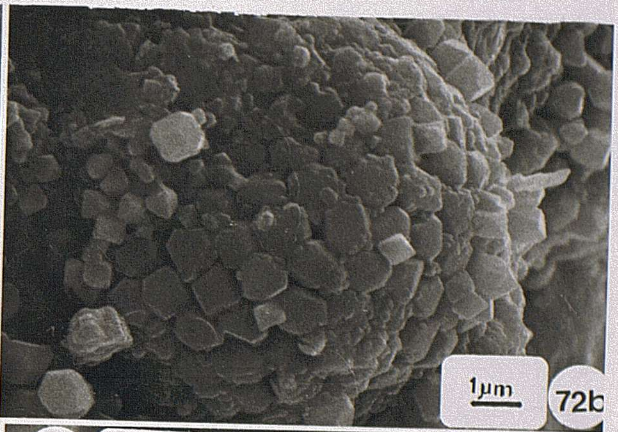
Sample BBB-36, Naish Member, Highcliffe.

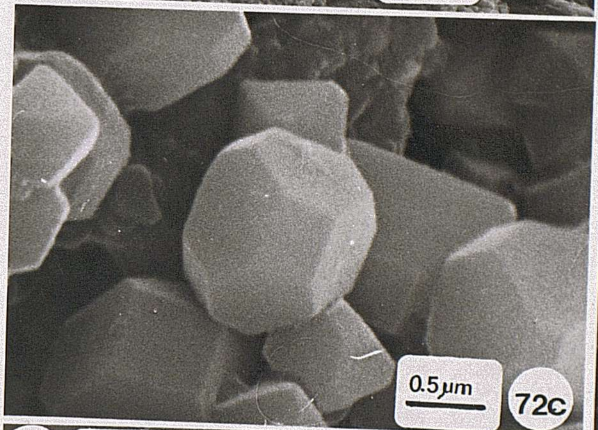
e. clay-coated pyrite framboid within preserved burrows in a sideritic ironstone.

Sample BBB-23, the 'Shell Band' base to the
Barton Sand, Barton-on-Sea.

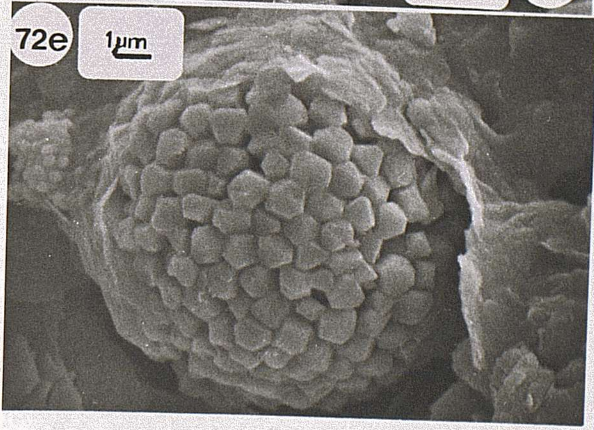
f. disaggregated pyrite crystals from e.


pyf
5µm
72a


1µm
72b


0.5µm
72c


72d
0.5µm


72e
1µm

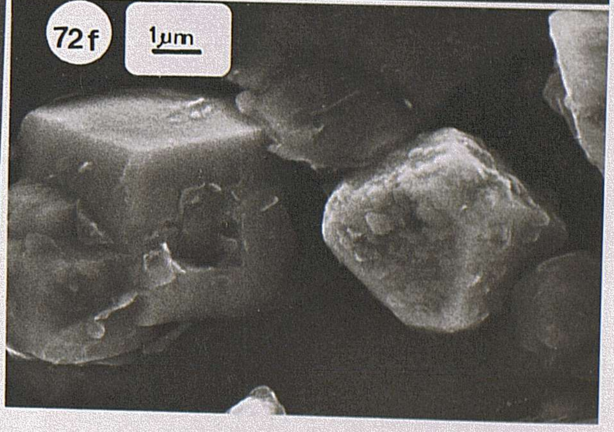

72f
1µm

Plate 73. Photomicrograph of calcareous concretion with septarian calcites. The concretion matrix (MC) consists of densely-aggregated calcite microcrystals, whilst the septarian calcite (SFC) varies from small bladed/equant crystals at vein-wall to sparry equant crystals at vein centre. Note extensional tears in the septarian calcites.

PL. Sample BBB-31, Naish Member, Barton-on-Sea.

Plate 74. Micrograph of pyrite crystals within shell enclosure in a clay ironstone.

PL. Sample BBB-23 in the 'Shell Band' base of Barton Sand, Barton-on-Sea.

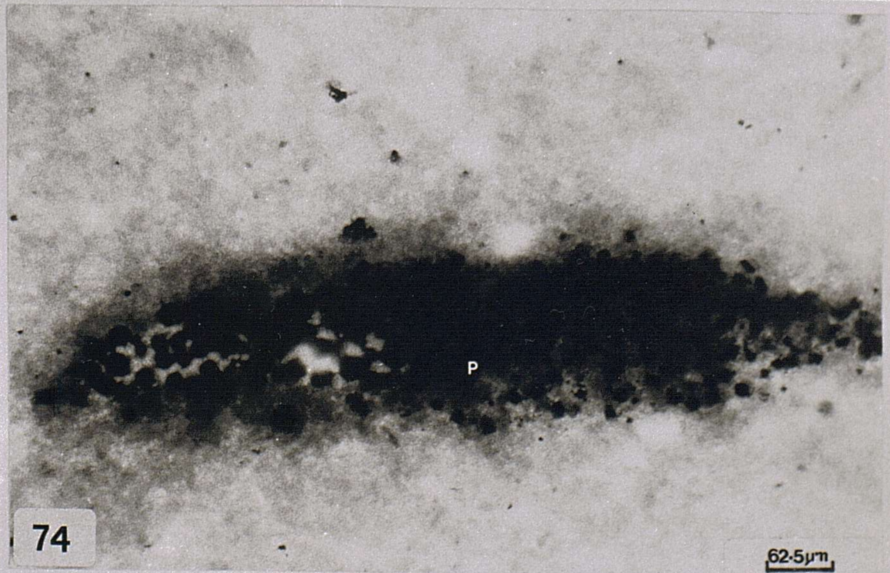
Plate 75. Micrograph showing pyrite mass in a gastropodal shell (G) and disseminated pyrite crystals in dinoflagellate test(D) within a texturally fine-grained friable clay ironstone.

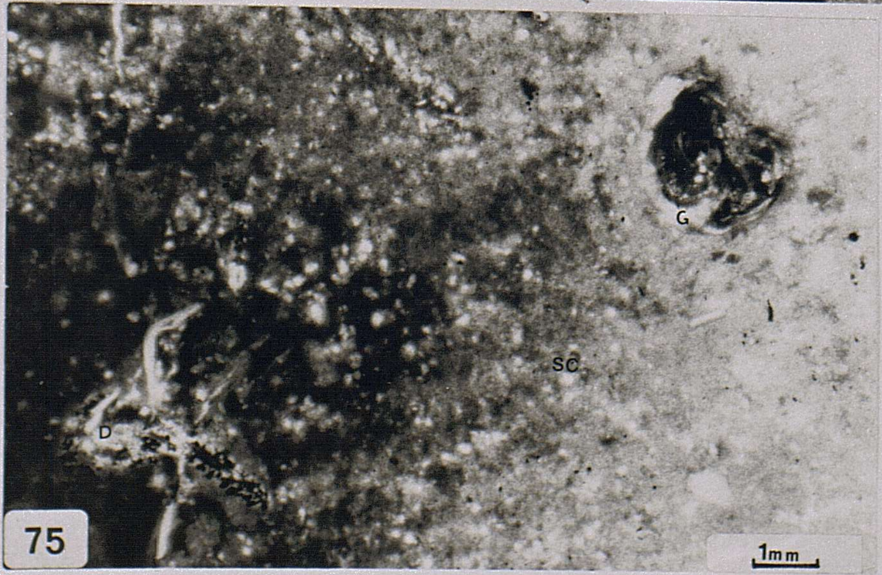
PL. Sample BBB-26, 'Bed F', Naish Member, Barton-on-Sea.

Plate 76. Photomicrograph of a sandy sideritic ironstone showing its fine-grained texture with siderite spherule (SD) and quartz grains.

PL. Sample WBLH-6, 'Lower Headon Beds', Whitecliff Bay.


73


74


75

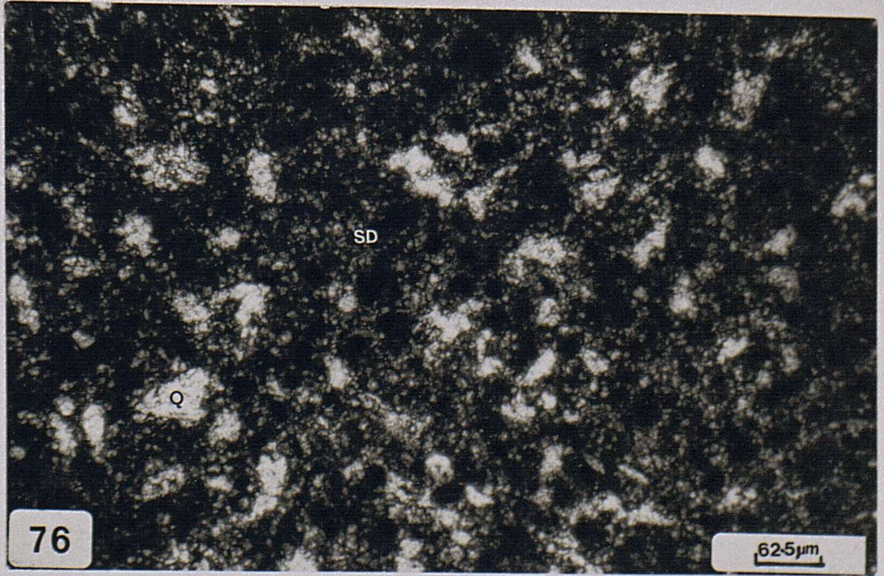

76

Plate 77a. Photomicrograph of a marine clay ironstone showing its fine textured sideritic matrix (SC) and a preserved burrow (B). Note the sharp contact of burrow with the matrix.

PL. Sample BBB-23, the 'Shell Band' base to the Barton Sand, Barton-on-Sea.

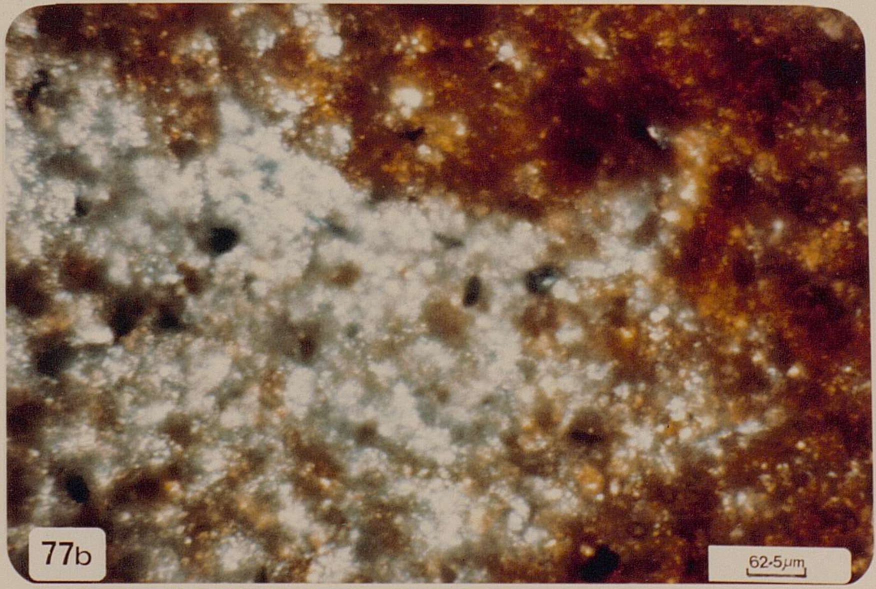
Plate 77b. As 77a at higher magnification, showing microspherulitic siderite of the ironstone matrix and silt-sized quartz, clays, pyrite in the burrow. (Some coccoliths also occur in the burrow, see Appendix 4).

Plate 78a. Photomicrograph of a freshwater clay ironstone showing well developed spherulitic siderite (SD) and cryptocrystalline side (CSD) rimming the spherules and replacing aragonitic gastropod shells (SdFs).

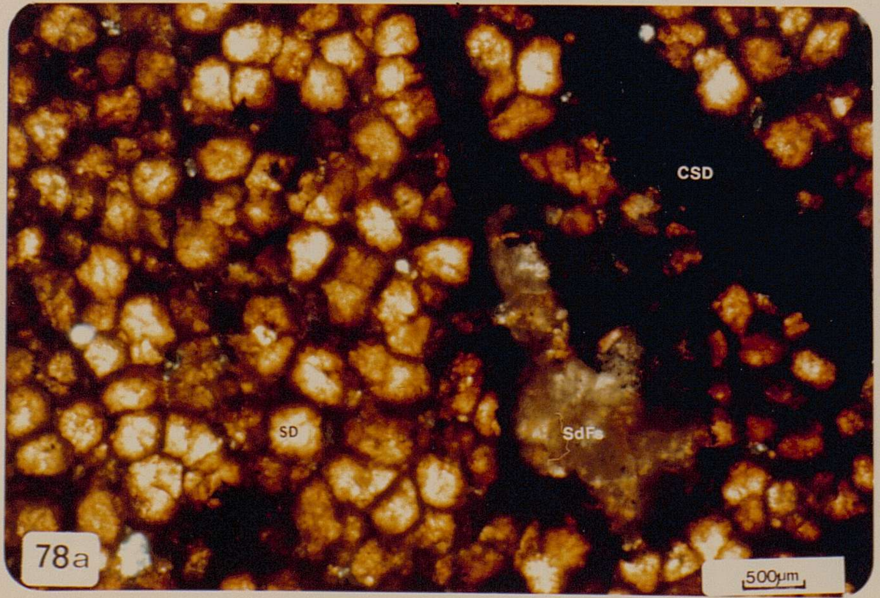
Pl. Sample ABLH-7, 'Lower Headon Beds', Heatherwood Point, Isle of Wight.

Plate 78b. As 78a, but stained.

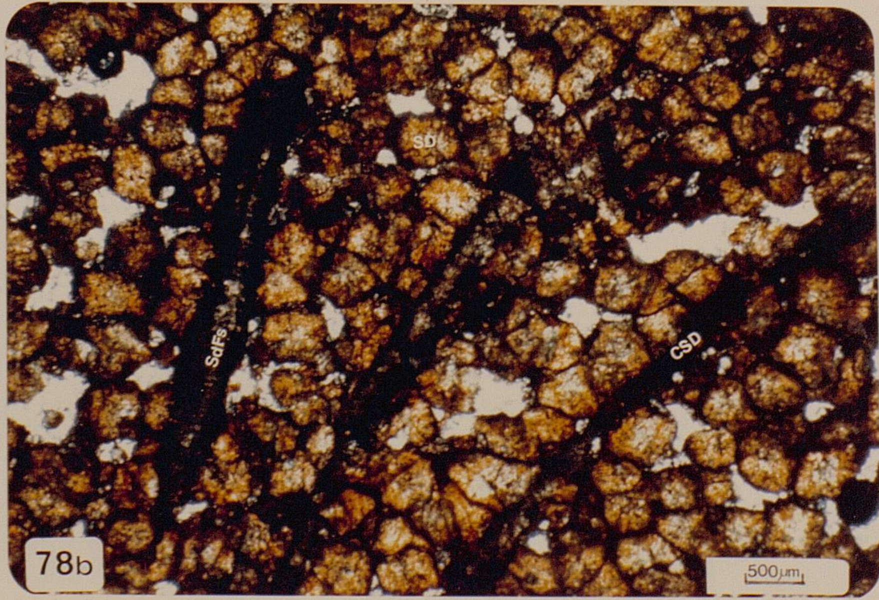
77a



77b



78a



78b

Plates 79, 80 & 81. Electron micrographs of clay ironstones and siderite spherules.

79a & b. Siderite rhombs admixed with clays.

Sample BBB-23, Barton Sand,
Barton-on-Sea.

80a. Fine-sand to silt-sized siderite spherules (SP)

b. A separated spherule, consisting of siderite rhombs.

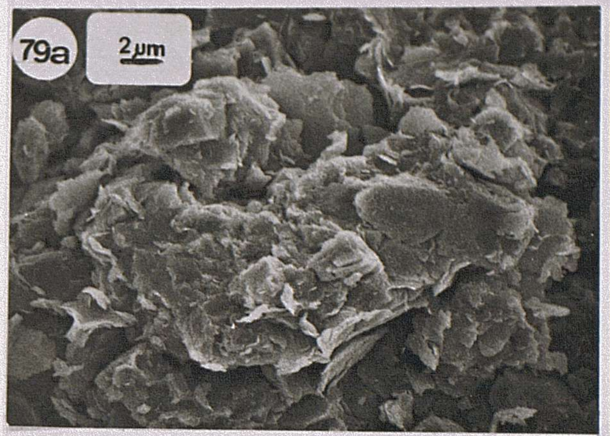
c. As 80b at higher magnification.

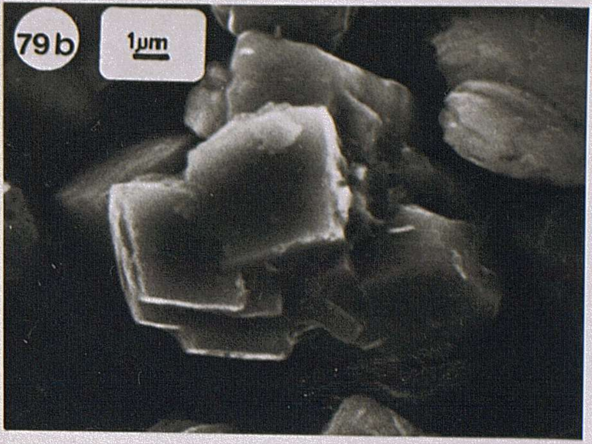
d. 'Channel-like aligned siderite rhombs admixed with clays.

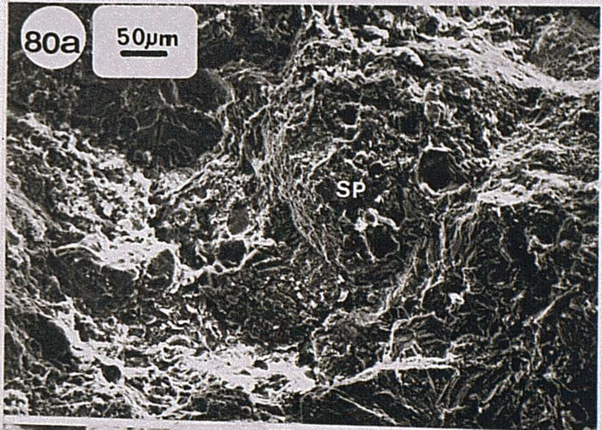
Sample ABLH-7, 'Lower Headon Beds'
Heatherwood Point, Isle of Wight.

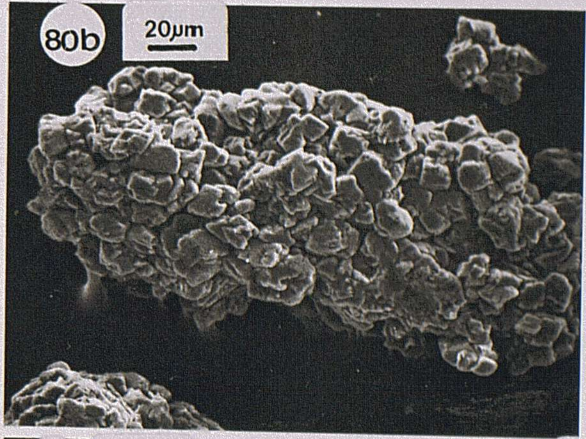
81. Micritic siderite rhombs intimately admixed with clays.

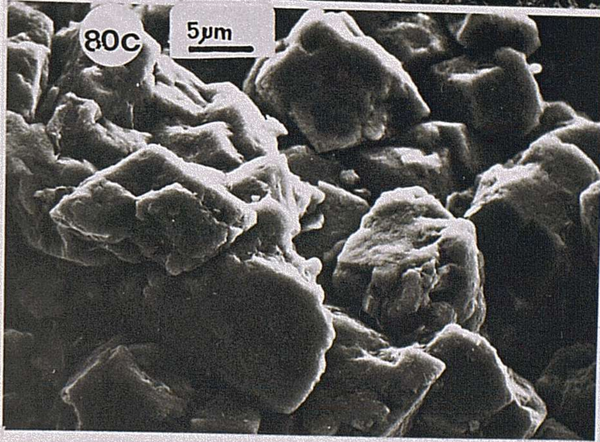
Sample BLH-36, Mammal Bed 'Lower Headon
Beds', Beacon Cliff, Long Mead End.

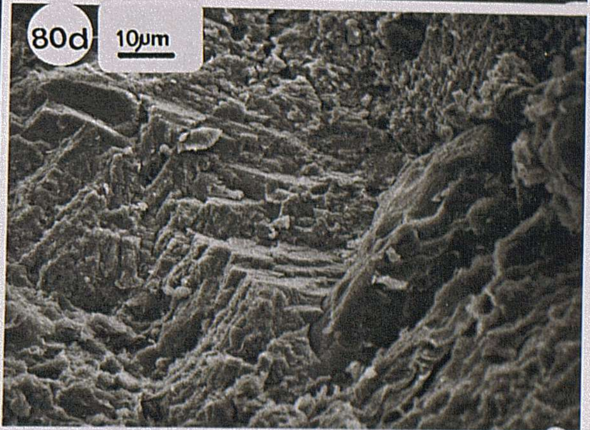

79a


79b


80a


80b


80c


80d

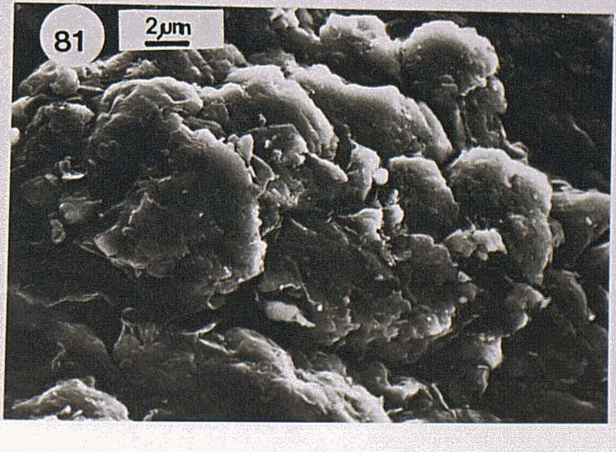
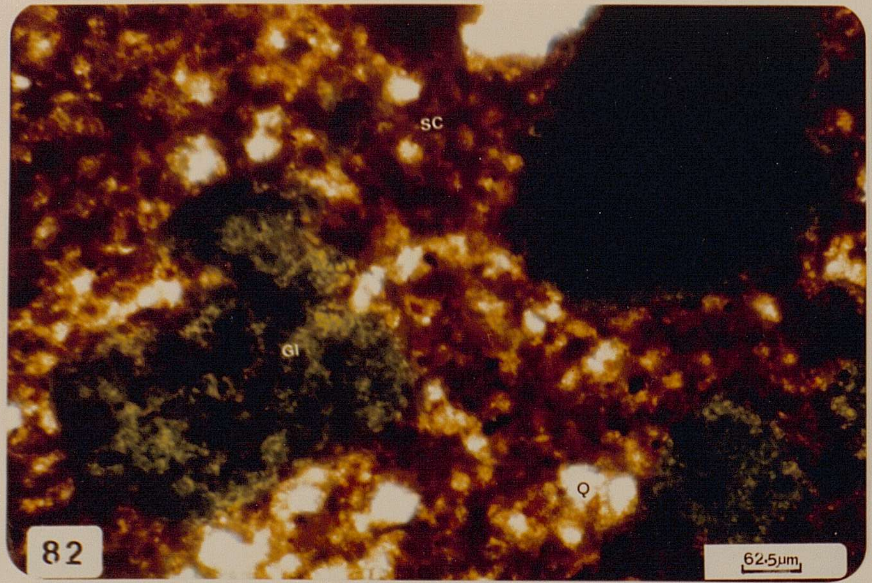

81

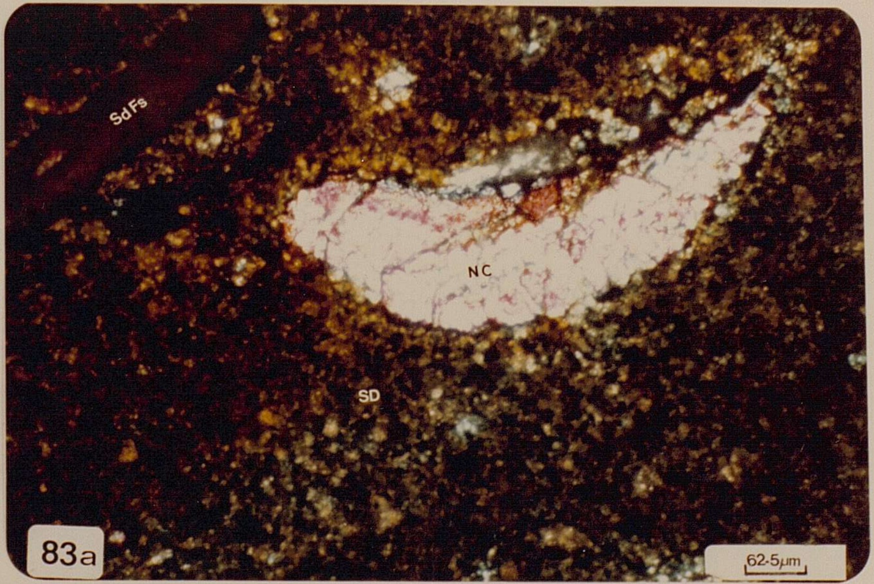
Plate 82. Photomicrograph showing glaucony grains (Gl) and fine quartz grains (Q) in siderite spherule-containing clay matrix of a friable, glauconitic, sandy-clay ironstone.

PL. Sample BBB-50 base to the Highcliffe Member, Highcliffe.

Plate 83a,b & c. Photomicrographs of stained samples of a sideritised shelly limestone, showing siderite spherules (SD) that replaced the primary lime-mud calcite, aragonitic shells pseudomorphed after or replaced by siderite (A, SdFs). In places, the shells or lime-muds have recrystallized into non-ferroan sparry calcite (NC).

Sample ABLH-5, 'Lower Headon Beds', Heatherwood Point, Isle of Wight.


82


83a


83b

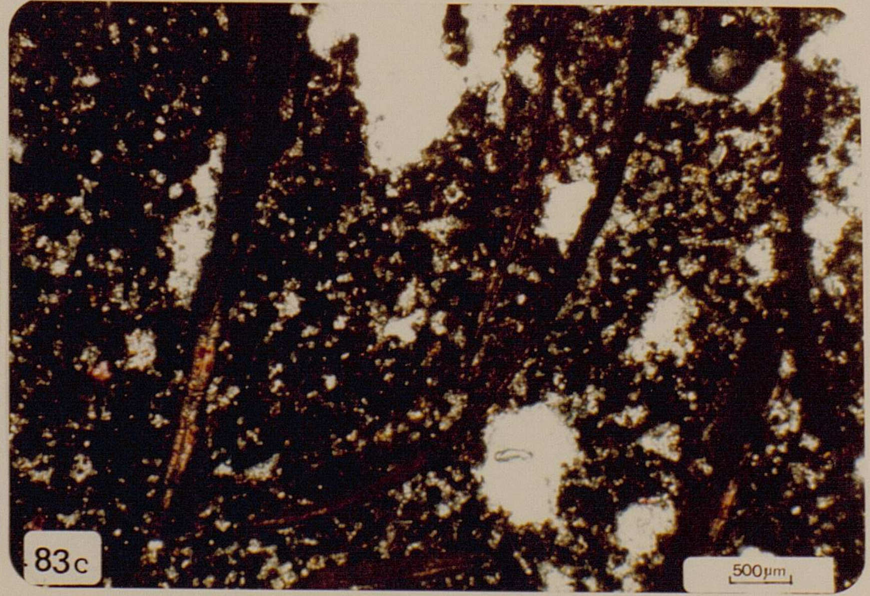

83c

Plate 84. Electron micrographs of sideritised limestone, Sample ABLH-5, 'Lower Headon Beds', Heatherwood Point, Isle of Wight, showing -

a. preserved 'island' of calcitic lime (LM) within sideritised matrix (SD).

b. fibrous aragonitic shell wall (Ar) separating the calcitic lime (LM) and sideritised matrix (SD).

c. as b, showing the aragonitic fibres at higher magnification.

d. the micritic calcite of the preserved lime, compared to the limestones (Plate 62); these are more anhedral but still poorly aggregated and randomly orientated (i.e. uncemented).

e. relatively large siderite rhombs (SD) sharply separating calcitic lime (LM) from the sideritised clay matrix (to the left of the micrograph).

Plate 85. Electron micrographs of an almost pure freshwater sideritic nodule. Sample WBLH-10, 'Lower Headon Beds', Whitecliff Bay, Isle of Wight, showing -

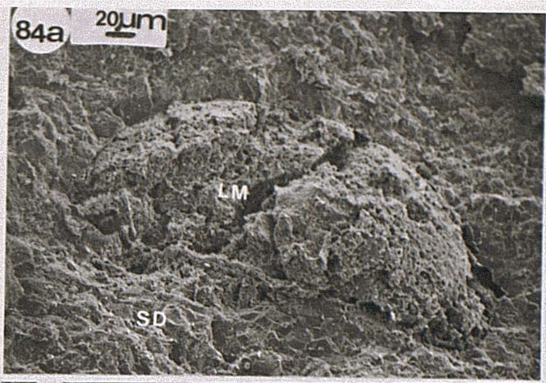
a. fine silt-sized spherules of siderite.

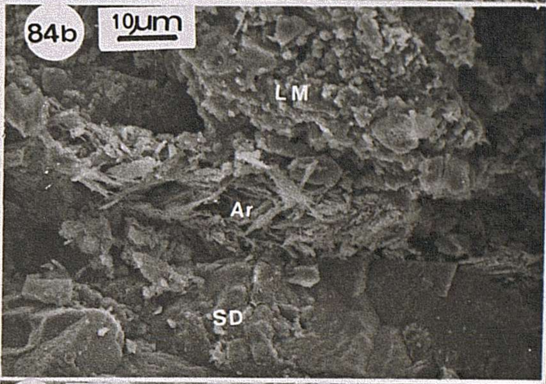
b. 'void-like fill' rhombs of siderite; direction of growth is left to right, although no significant changes of crystal sizes are apparent.

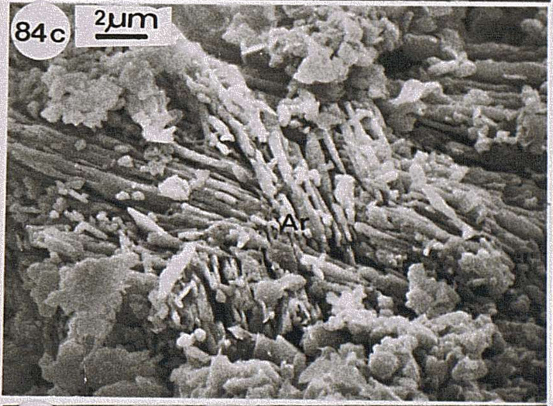
c. aggregation of siderite rhombs.

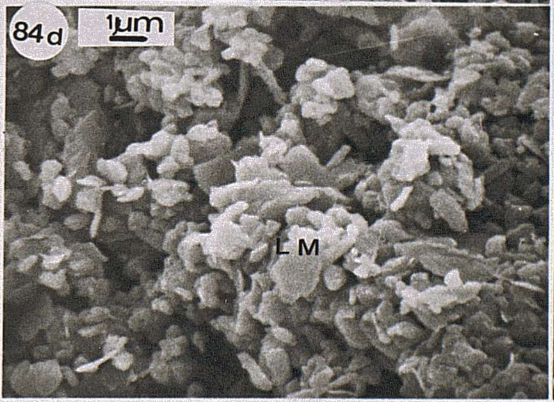
d. siderites crystallized from solution with c-axis perpendicular to surface of a 'quartz mould'.

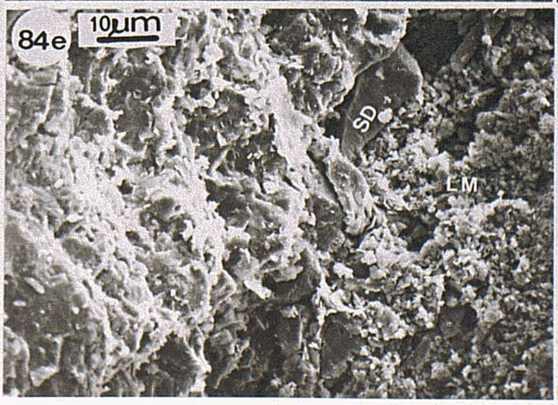
e. as d, but with the silt-sized quartz grains still in place.

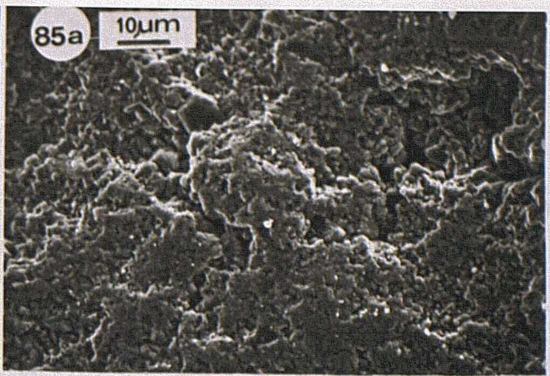

84a
20µm
LM
SD

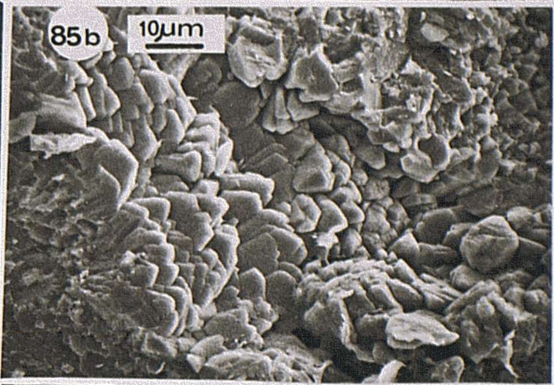

84b
10µm
LM
Ar
SD

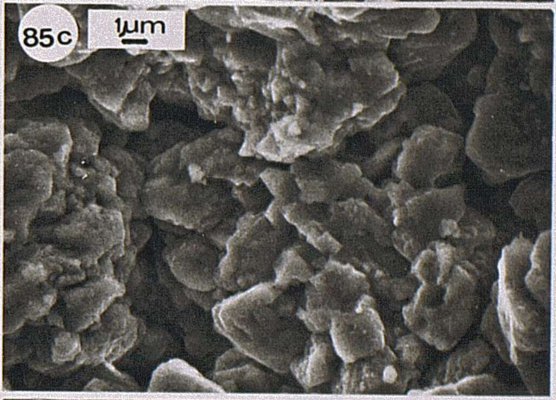

84c
2µm
Ar

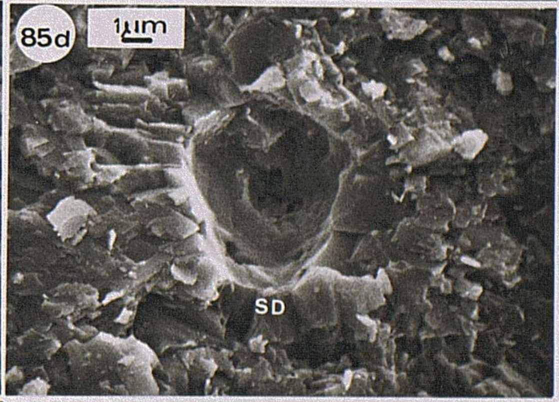

84d
1µm
LM


84e
10µm
SD
LM


85a
10µm


85b
10µm


85c
1µm


85d
1µm
SD

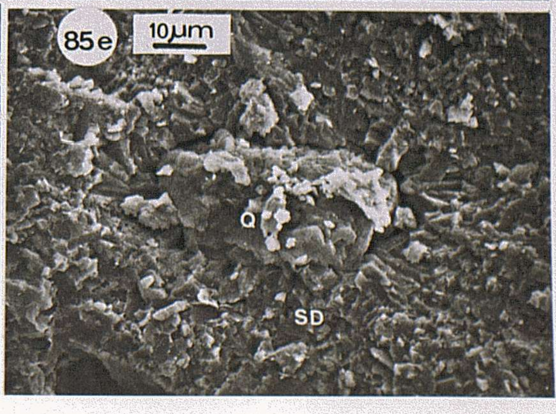
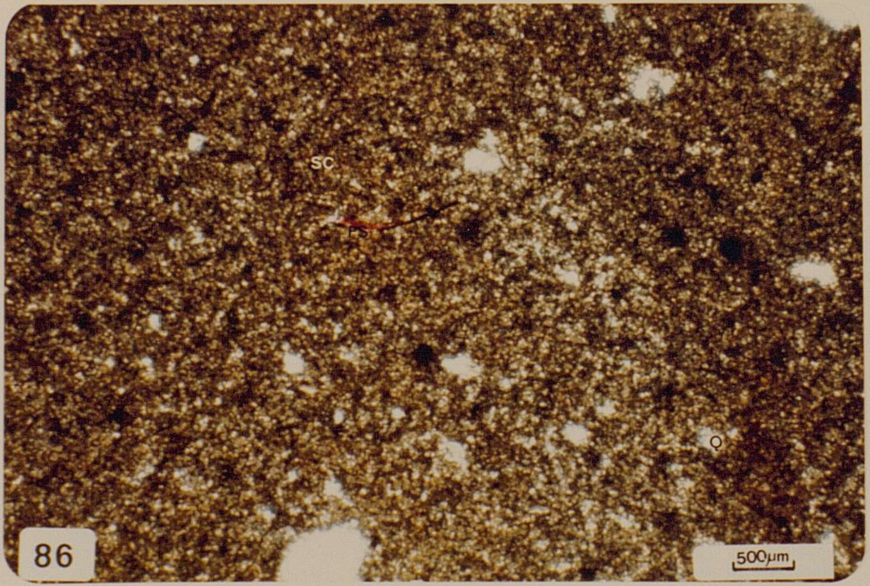

85e
10µm
Q
SD

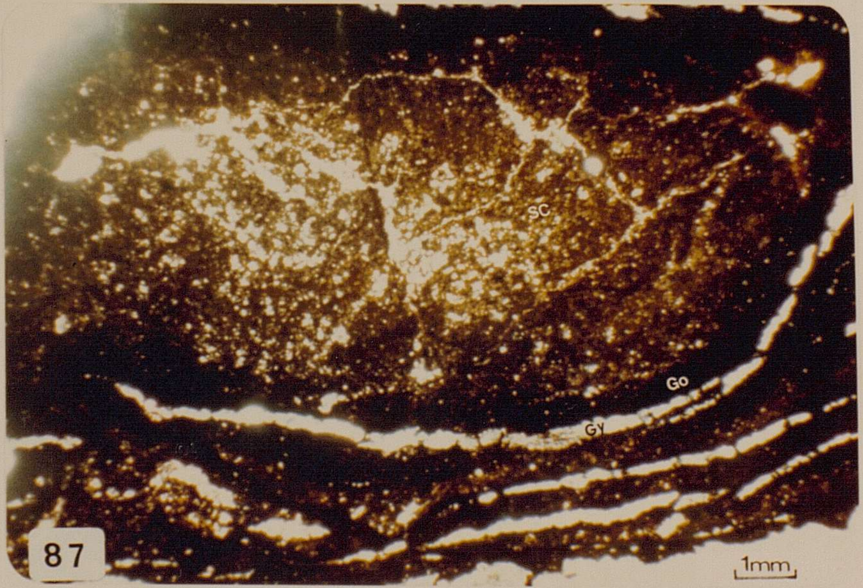
Plate 86. Photomicrograph of a stained sideritic ironstone showing remains of a partially sideritised aragonitic shell (stained red) within a fine textured siderite-clay matrix.

Sample BLH-36, Mammal Bed, 'Lower Headon Beds', Beacon Cliff, Long Mead End.

Plate 87. Photomicrograph of (recently-) oxidised marine ironstone nodule showing outer, alternating layers of goethite (Go) and gypsum (Gy); and inner, unaltered fine textured sideritised clay (SC).



86



87

Plate 88. Electron micrographs of steely scales on altered sideritic ironstone nodule; Sample WBLH-10, 'Lower Headon Beds', Whitecliff Bay, Isle of Wight, showing -

a. low magnification view of mounds (m) and flowery, spherulitic masses of goethite pseudomorphed on siderites (s).

b. as a, at higher magnification.

c. as b, at higher magnification.

d. as c, showing stacks of thin, serrated-edged goethite plates pseudomorphed on siderite rhombs in spherulitic aggregation.

e. as d, at higher magnification.

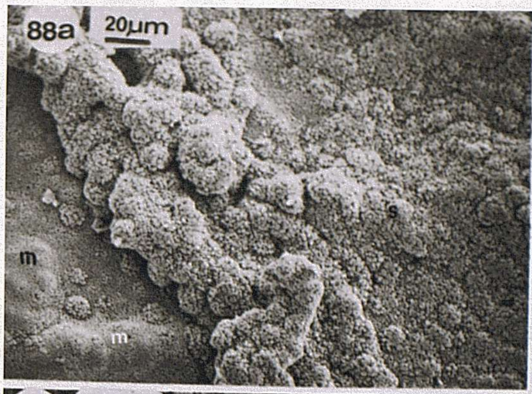
f. books of rhomb-like goethite crystals (RG) stacked face to face, but twinned edge to edge, and very likely to have differentiated from the spherulitic goethite plates.

g. as f at higher magnification.

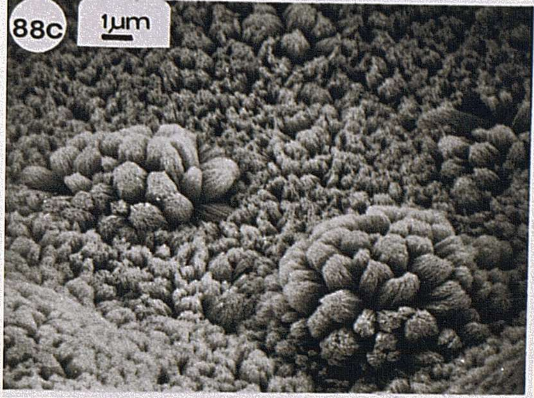
h. 'shrub-like' mass of differentiated platy/prismatic crystals of goethite (& lepidocrocite?) (P), and rounded glaebular goethites (g).

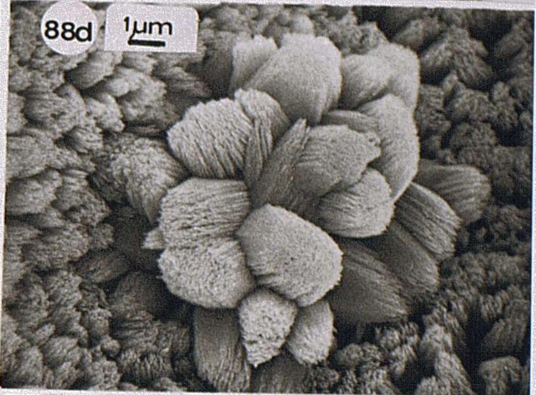
i. as h at higher magnification.

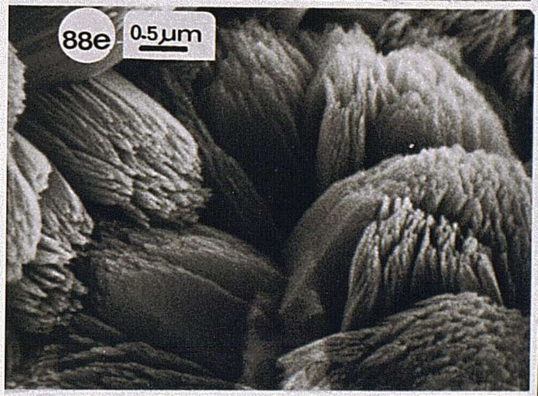
j. crust of poorly-differentiated goethites.

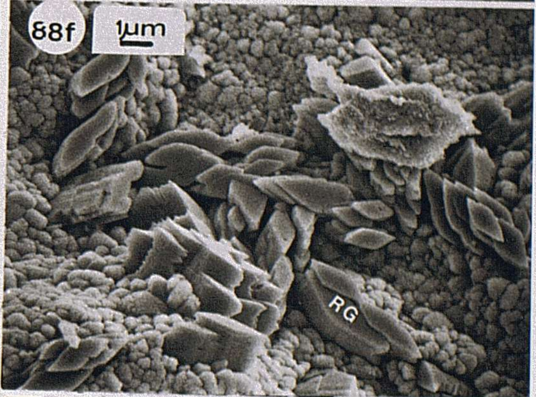

88a
20µm
s
m
m

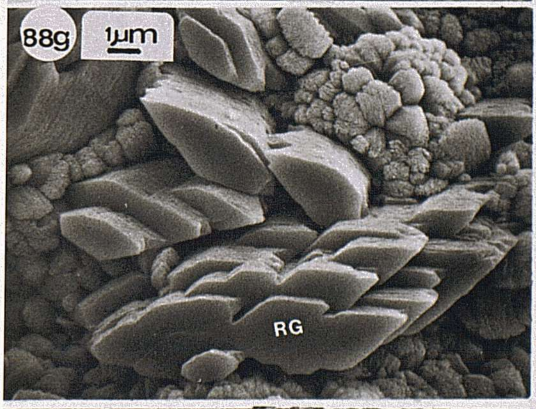

s
m
88b
2µm

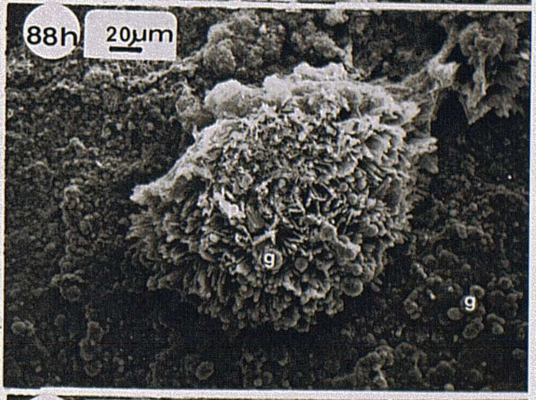

88c
1µm

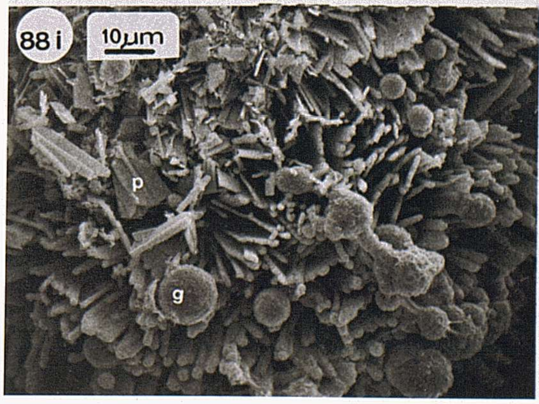

88d
1µm


88e
0.5µm


88f
1µm
RG


88g
1µm
RG


88h
20µm
g
g


88i
10µm
p
g

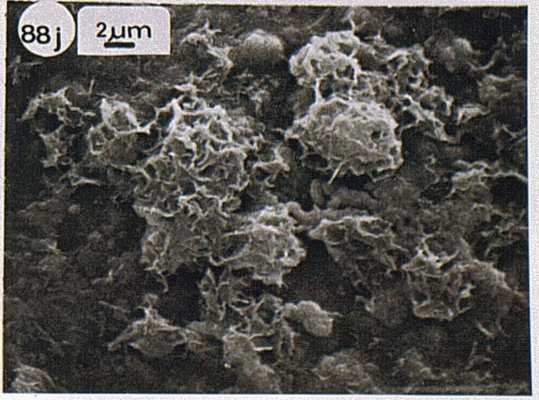

88j
2µm

Plate 89. Electron micrographs of orange-brown earthy crusts on altered sideritic ironstone nodule; Sample WBLH-10, 'Lower Headon Beds', Whitecliff Bay, Isle of Wight, showing -

a. clods of clay-sized lepidocrocite crystals.

b. as a at higher magnifications.

c. aggregated lath and plates of lepidocrocite.

d. some platy clay particles within finer-sized lepidocrocite matrix.

e. quartz grains within matrix of fine lepidocrocites.

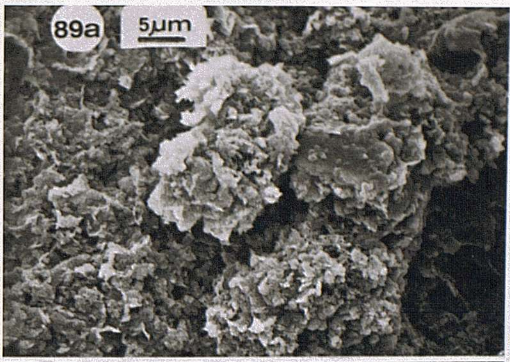
f. differentiated intertwined platy goethites (Go) and poorly-differentiated or crypto-crystalline masses (Crp).

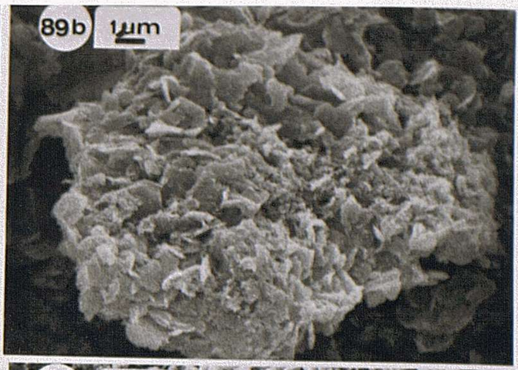
g. fine lepidocrocites (Lp) and differentiated goethites (Go).

h. as f and g at higher magnification.

i. as h emphasizing the 'star' or 'leaf-like' intertwining of the differentiated platy goethite crystals.

j. as h showing the poorly differentiated mass.


89a
5µm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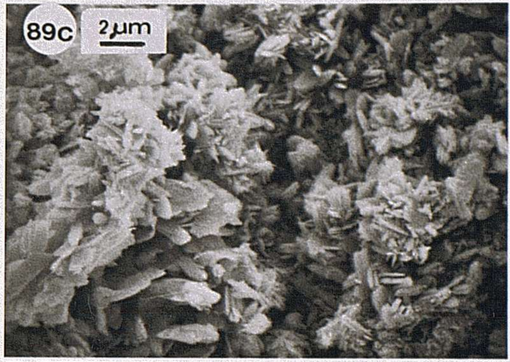
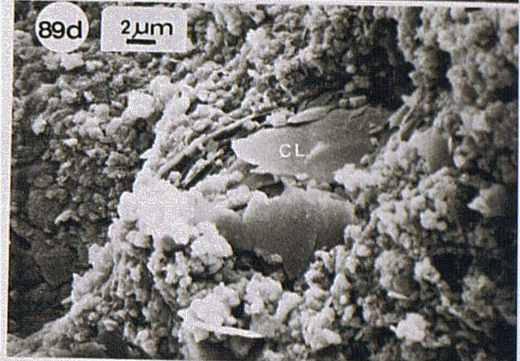
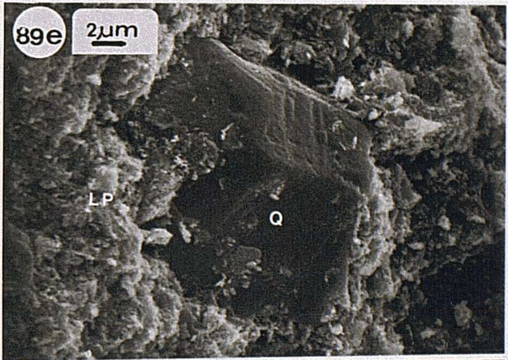
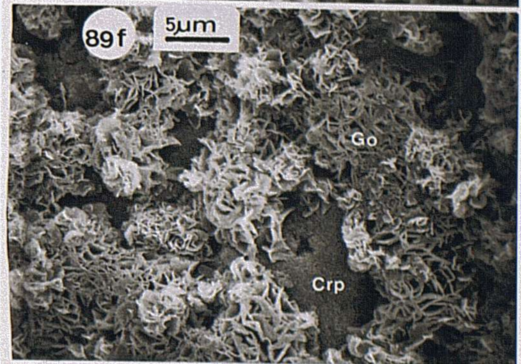
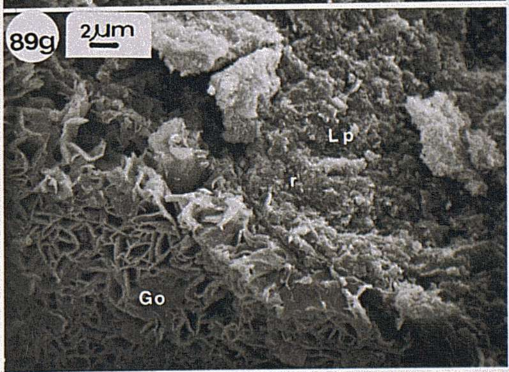
1µm

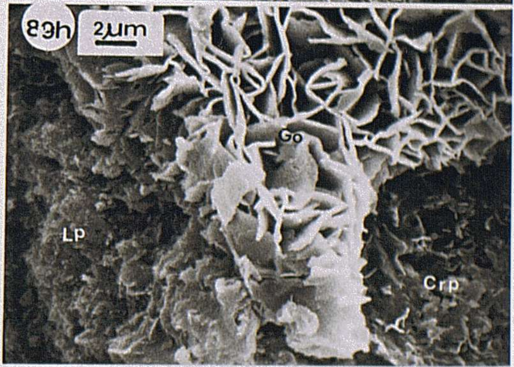

89c
2µm

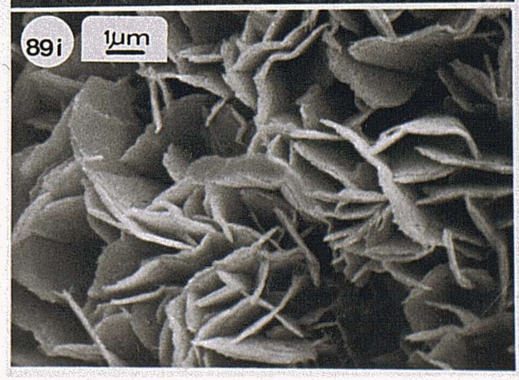

89d
2µm
CL


89e
2µm
LP
Q


89f
5µm
Go
Crp


89g
2µm
Lp
r
Go


89h
2µm
Go
Lp
Crp


89i
1µm

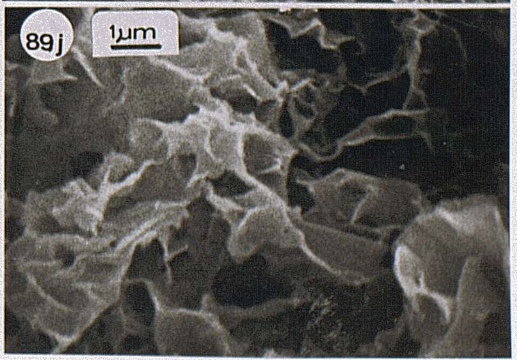

89j
1µm

Plate 90. Electron micrographs of steely scales on indurated sand. Sample BLH-12, 'Lower Headon Beds', Hordle Cliff, Long Mead End, showing -

a. low magnification view of the comprising flowery mass of laths and platy crystals.

b. as a. at higher magnification; also showing lepidocrocite plates (Lp) differentiated from a crytocrystalline mass (crp).

c. as b at higher magnification.

d. intertwined plates of lepidocrocite with prismatic terminations.

e. thin, 'star-like' intertwined plates of lepidocrocite.

f. prismatic laths and plates of goethite/lepidocrocite.

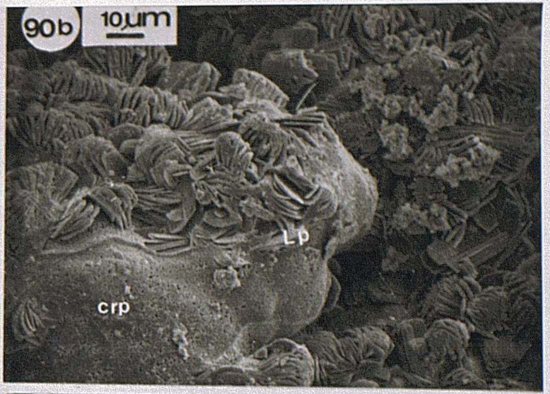
g. euhedral prismatic goethite (pg) and thin lepidocrocite plates (Lp).

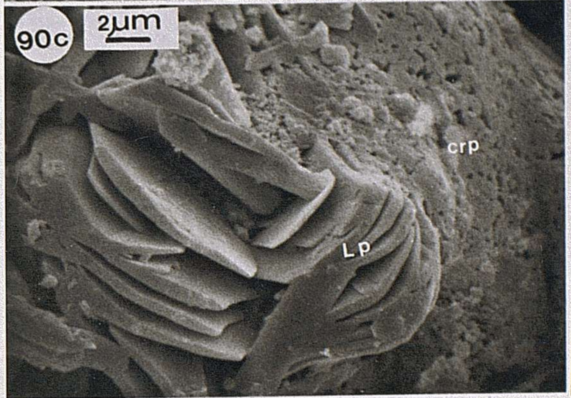
h. vuggy lepidocrocite plates (Lp) differentiated from a cryptocrystalline mass (crp).

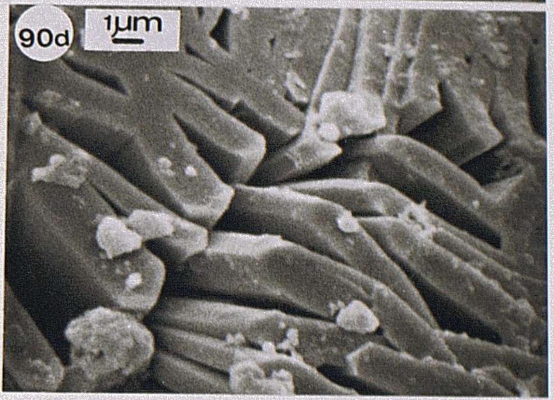
i. twinned prismatic (?) crystals of goethite(?).

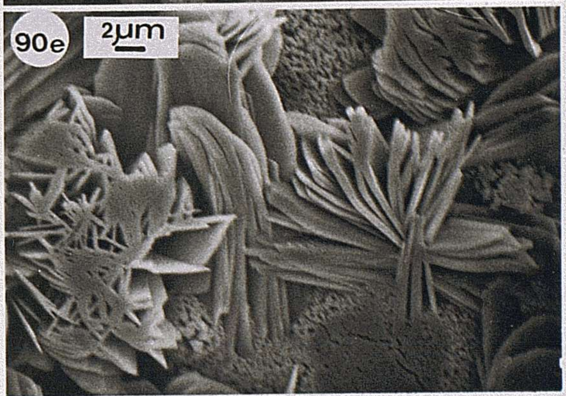
j. same as i.

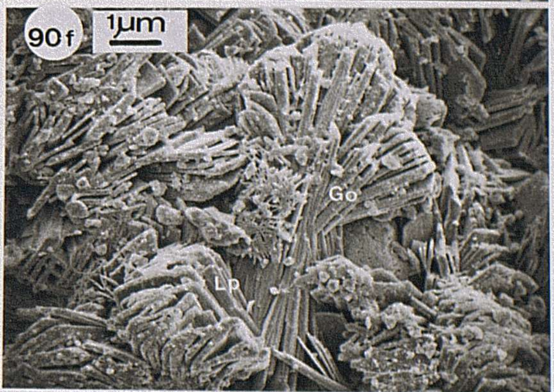

90a

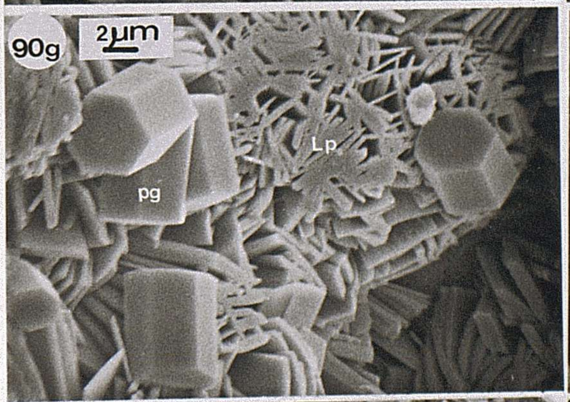

90b

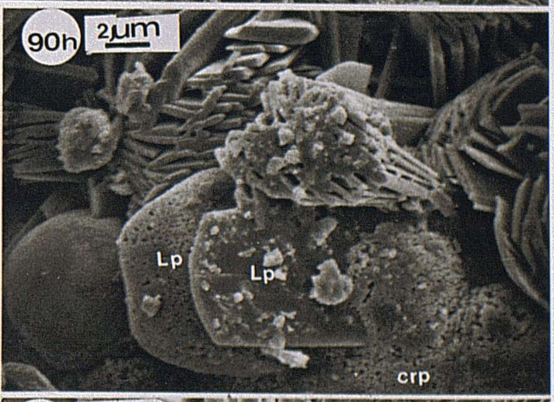

90c

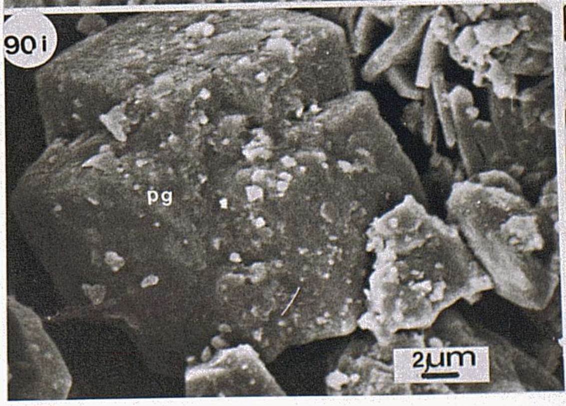

90d

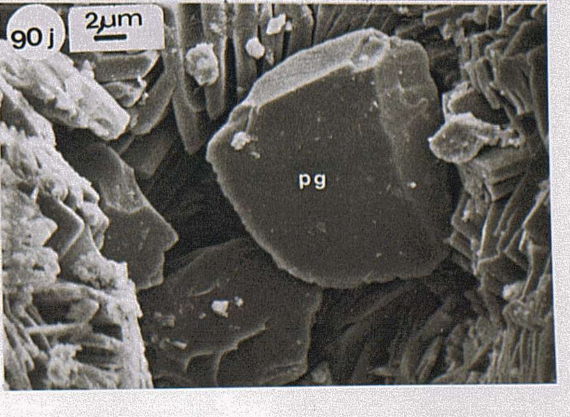

90e


90f


90g


90h


90i


90j

APPENDICES

APPENDIX 1

DESCRIPTION AND LOCATION OF SAMPLES

SAMPLE NO.		DESCRIPTION	LOCATION
Lower Headon Beds			
BLH	1	Mottled clayey-sand	500m West of Paddy's Gap
	2	Dark-green clay	"
	3	Dark, carbonaceous marly-clay	"
	4	Fossiliferous green clay	"
	5	Indurated ferruginous sand	Hordle Cliff,Nr.Hordle Ho.
	6	Greyish-white sand	"
	7	Greenish clay,laminated and fossiliferous	"
	8	Dark, lignitic clay	"
	9	Ferruginous, purplish-white sand	"
	10	Dark, lignitic clay	"
	11	Ferruginous sand with pyritised rootlets and gypsiferous bodies	"
	12	Brownish-red goethitic and rootlet-bearing sand (see Plates 11,12)	Hordle Cliff,30m east of Long Mead End
	13	Purplish-white sand	"
	14	Greenish clay	"
	15	Dark-brown lignitic-clay	"
	16	Purplish-white clayey-sand with rootlets	"
	17	Fossiliferous greenish clay	"
	18	" "	"
	19	Creamy-white fossiliferous limestone	"
	20	Thin lignitic band at base of BLH 19	"
	21	Fossiliferous green clay	"
	22	Clay-ironstone concretion (Plate 10)	"

BLH	23	Purplish-white sand with clay laminations	Hordle Cliff, 30m east of Long Mead End
	24	Purplish-white sand with clay and pockets of shells	"
	25	Fossiliferous lignitic-clay	"
	26	Brownish, ferruginous sand	"
	27	Fossiliferous lignitic-clay	"
	28	Lignitic clay with leaf remains	Beacon Cliff, 10-100m west of Long Mead End
	29	Purplish-brown sand	"
	30	Purplish-white sand with rootlets	"
	31	" "	"
	32	Bright-green clay	"
	33	Sideritic ironstone band	"
	34	Greyish clayey sand	"
	35	Greyish clayey sand with shell drifts	"
	36	Sideritic ironstone concretions	"
	37	Green Clay	"
	38	"	"
	39	Greenish-Clay with drift carbonaceous materials	"

Barton Sand Formation

BBB	1	Lignitic clay with mottled sand and clay lenses	Beacon Cliff, eastern side of Becton Bunny
	2	Mottled brown and green clay	"
	3	Lignitic clay	"
	4	Ferruginous brownish sand	"
	5	Mottled green clay with rootlets	"

BBB 6	White sand	Beacon Cliff,eastern side of Becton Bunny
7	White sand with rootlets (and pockets of shells at Long Mead End)	"
8	White Sand	"
9	White Sand	Beacon Cliff,western side of Becton Bunny
10	Sparsely fossiliferous greyish sandy-clay	"
11	Scattered greyish nodular clay ironstone	"
12	Sparsely fossiliferous greyish sandy-clay	"
13	" "	"
14	Drab, carbonaceous clayey-sand	Below Gulf Course, east of Barton-on-Sea seafront
15	Bioturbated white sand	"
16	" "	"
17	" "	"
18	" "	"
19	Fossiliferous bluish sand	"
20	" "	"
21	Fossiliferous bluish-white sand	Barton-on-Sea, 100m of sea front
22	" "	"
23	Greyish clay with masses of shells; siderite-cemented to hard band with preserved burrows (see Plates 8 and 9)	"

Barton Clay Formation

BBB 24	Fossiliferous brown clay	Barton-on-Sea sea-front
25	Bedded/nodular greyish calcareous concretion	"

BBB 26	Friable sideritised clay encompassing BBB 25	Barton-on-Sea sea front
27	Fossiliferous brownish-grey clay	"
28	" "	"
29	" "	"
30	" "	300m West of Barton-on-Sea seafront
31	Greyish-Green septarian calcareous concretion	"
32	Fossiliferous earthy (drab) sandy-clay	"
33	" "	"
34	Mottled sandy-clay with and carbonaceous matter	"
35	Glauconitic sandy-clay	200m east of Chewton Bunny
36	Greenish, septarian calcareous concretion	"
37	Fossiliferous, glauconitic-green sandy-clay	"
38	" "	(See Plates 2,3, & 4)
39	Greenish septarian calcareous concretion	
40	Fossiliferous green sandy-clay	50m east of Chewton Bunny
41	" "	"
42	Greyish calcareous nodules	"
43	Sideritised clay encompassing BBB 42	"
44	Greyish-green sandy-clays with shell drifts and plant matter	"
45	Glauconitic, greyish-green sandy-clay	300m west of Highcliffe Castle
46	" "	"

BBB	47	Sparsely-fossiliferous dark-green	300m west of Highcliffe Castle
	48	" "	"
	49	" "	"
	50	Brownish-red nodular sideritic ironstone	"
BHC	1	Dark-green glauconitic sandy-clay	"
	2	" "	"
BPB	1	Brownish, loamy and carbonaceous sand-supported pebble bed (Plate 1)	"

ALUM BAY - HEATHERWOOD POINT (ISLE OF WIGHT Figs. 3,6a & 6b).

Lower Headon Beds

ALBH	1	Fossiliferous friable creamy-yellow limestone	Heatherwood Point
	2	Lignitic limestone band	"
	3	Fossiliferous friable creamy-yellow limestone	"
	4	Grey, marly clayey-sand	"
	5	Greenish sideritised shelly-limestone (Plate 22)	"
	6	Brownish-yellow fossiliferous limestone	"
	7	" "	"
	8	Greenish sideritic ironstone concretion	"
	9	Greyish-green clay	"
	10	Greyish-white sand	"

ABLH	11	Dark lignitic clay	Heatherwood Point
	12	Ferruginous brown sand	"
	13	Dark lignitic clay	"
	14	Mottled-grey sand	"
	15	Mottled, purplish-white sand	"
	16	Mottled green clay	"
ABBB/FS	1a	Buff-red(10YR 8/6) clayey sand	(Plate 18a,b)
	2a	Pallid greyish clayey-sand (10YR 7/4)	"
	3a	Indurated dark-red (10YR 5/4) sand with kaolinite lenses (Plates 18c,d)	
	4a	Friable, yellowish-red (10YR 6/6) sand with reddish goethite mottles	"
ABBB/FS	1b	Purplish-red (5YR 8/4) clayey sand	50m south of Heatherwood Point (Plate 19a,b)
	2b	Redish (10R 6/6) clayey-sand with red mottles	"
	3b	Pallid greyish-sand (5YR 7/2 to 10YR 8/2)	"
	4b	Brownish (10YR 6/6) sand yellow	"
	5b	Friable brownish-yellow (10YR 6/6) sand	"
	6b	Indurated, dark-red (10YR 4/6) sand	"
	7b	Friable brownish-yellow (10YR 6/6) sand	"
	8b	Pallid,greyish sand with red mottles (10YR 7/4)	"

ABBB	19	White sand	Heatherwood Point
	18	"	"
	17	Greyish-green pipe clay (Plate 17)	Alum Bay, north side of Alum Bay Chine (Plate 14)
	16	White sand	"
	15	Yellowish clayey-sand	"

Barton Clay Formation

ABBB	14	Mottled sandy clay, sparsely fossiliferous	"
	13	Brownish-grey sideritic ironstone nodule	"
	12	Greyish-blue sandy-clay	"
	11	Mottled sandy-clay	"
	10	Fossiliferous massive greyish-brown clay	"
	9	Mottled sandy-clay	Alum Bay, south of Alum Bay Chine (Plate 15)
	8	Glauconitic, green calcareous concretion	"
	7	Dark-green, glauconitic sandy-clay	"
	6	Mottled sandy-clay	"
	5	Glauconitic, green calcareous concretion	"
	4	Scattered greyish-white calcareous nodules	"
	3	Mottled sandy-clay	"
	2	Fossiliferous glauconitic-green sandy-clay	"
	1	" "	"
ABHC	1	Glauconitic mottled-green sandy-clay	"
	2	Mottled sandy-clay with plant debris	"
ABPB	1	Goethite-cemented sandy-pebble	"

WHITECLIFF BAY (ISLE OF WIGHT - Figs 4 & 7)

'Lower Headon Bed'

WBLH	1	Fossiliferous green clay	Whitecliff Bay, road-path behind Whitecliff Bay Hotel (Plate 24)
	2	" "	"
	3	Dark, lignitic-clay	"
	4	Greyish-white sand	"
	5	" "	"
	6	Brownish-red sideritic sandy-ironstone band	"
	7	Dark, lignitic clay	"
	8	Mottled-green clay	"
	9	Lignitic clay	"
	10	Nodular sideritic ironstone (Plate 25)	"
	11	Mottled-brown clay	"
	12	Dark, lignitic clay	"
	13	Mottled and carbonaceous clay	"

Barton Sand Formation

WBBB	9	Loamy, brownish-yellow ferruginous clayey-sand	"
	8	Yellowish sand	"
	7	Yellowish sand	Cliff face, Whitecliff Bay (Plate 23)
	6	White sand	"
	5	Yellow sand with goethitic moulds of plant matter	"

Barton Clay Formation

WBBB	4	Greyish-blue sandy-clay	"
	3	Bluish-green sandy-clay	"
	2	Scattered sideritic ironstone nodule	"
	1	Fossiliferous glauconitic sandy-clay	Foreshore 5m south of zig-zag path to the beach.

APPENDIX 2

ESTIMATION OF BULK SAMPLE MINERALOGY BY X-RAY DIFFRACTION

Procedure :

a. From the diffraction traces of powdered samples, identify and list all mineral phases present;

b. for each mineral, measure the intensity, I_m, of the least overlapped or most intense reflection (see Ch.3);

c. Multiply I_m by the mineral's intensity factor, I_f, to obtain the relative intensities, I_{RM};

d. sum up I_{RM} of the mineral phases and normalised to 100%.

These for Sample ABBB 1 (Figure 12) is as follows :

Mineral	Reflection A	Intensity I_M	Intensity Factor I_f	Relative Intensity I_{RM}	% Mineral
Quartz	3.34	2216	1	2216	40.4
Total Clay	4.56	28	90	2520	45.9
	(2.56)*	(22)	(139)	(3058)	(50.7)
Anatase	3.51	[42]*	[2.5]+	[105]	[1.9]+
					[0.6]++
Potassic Feldspar	3.24	55	3.75	206	3.8
Sodic Feldspar	3.18	49	2.72	133	2.4
Calcite	3.03	151	1.52	230	4.2
Pyrite	2.71	75	2.08	156	2.8
				Σ5491	Σ100%

( )* Estimate within 20% of that obtained from the 4.56 Å clay reflection. Not recorded because the 2.56Å reflection in many samples is not intense enough to be measured.

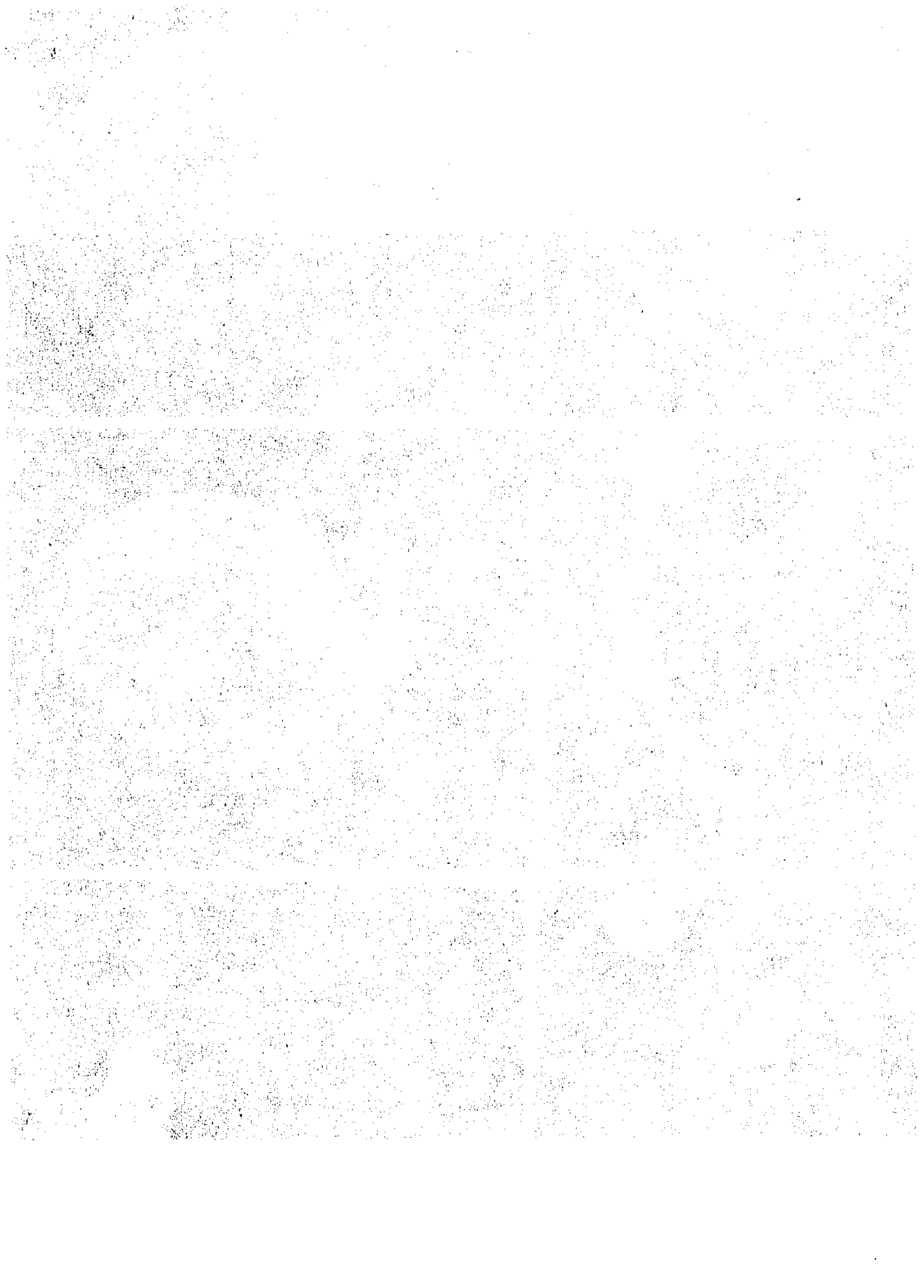
[ ]* Anatase reflections overlapped by many other minerals (i.e.clays, feldspars)

[ ]+ Anatase intensity factor from specpure material give too high estimations, [ ]+, compared to chemically-determined TiO_2 [ ]++ which is recorded as a more accurate estimation.

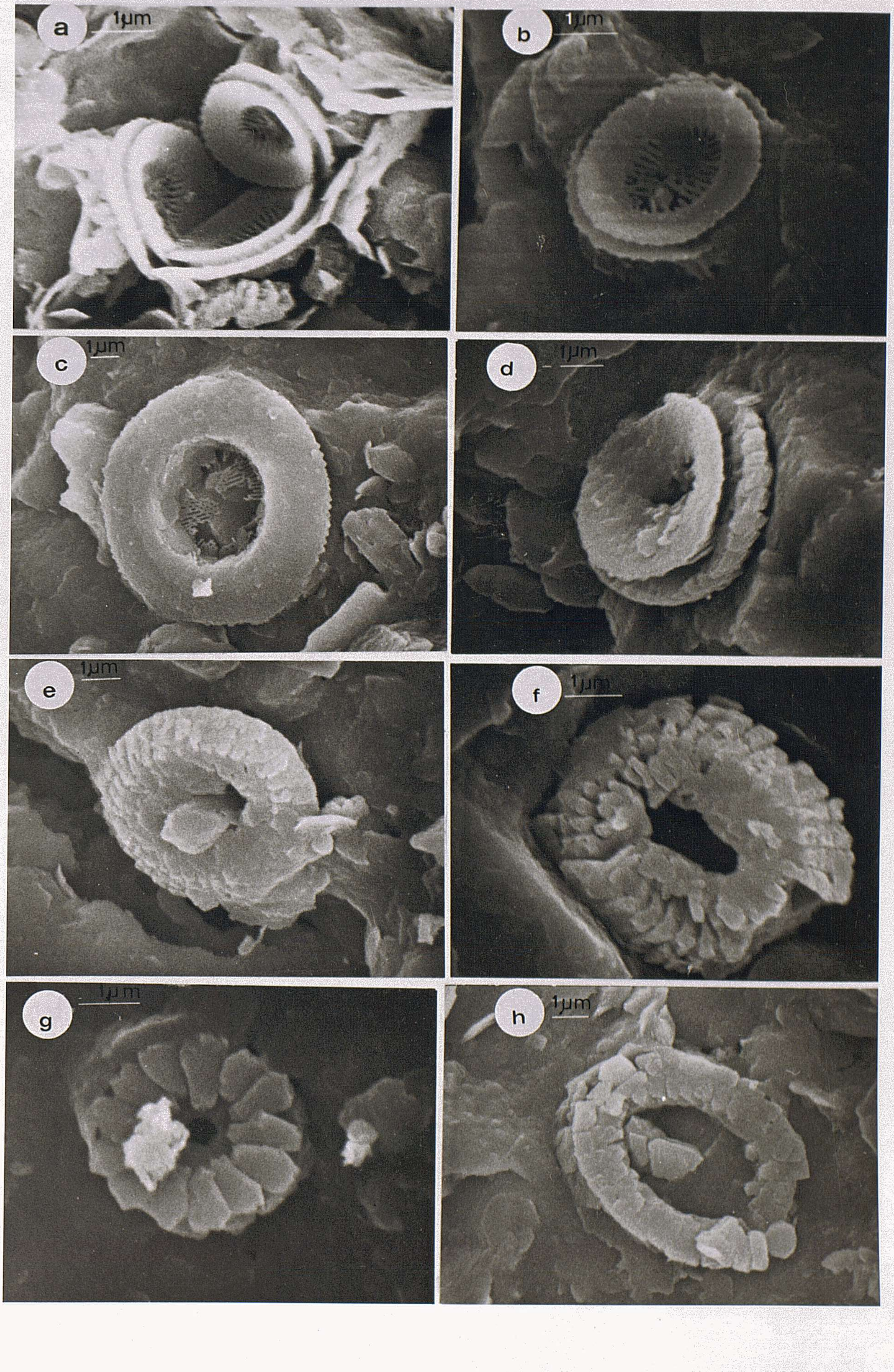
APPENDIX 3

Electron micrographs of coccoliths within burrows preserved in sideritised clay.

Sample BBB-23, Shell Band base of the
Barton Sand Formation, Barton-on-Sea.



Coccolith

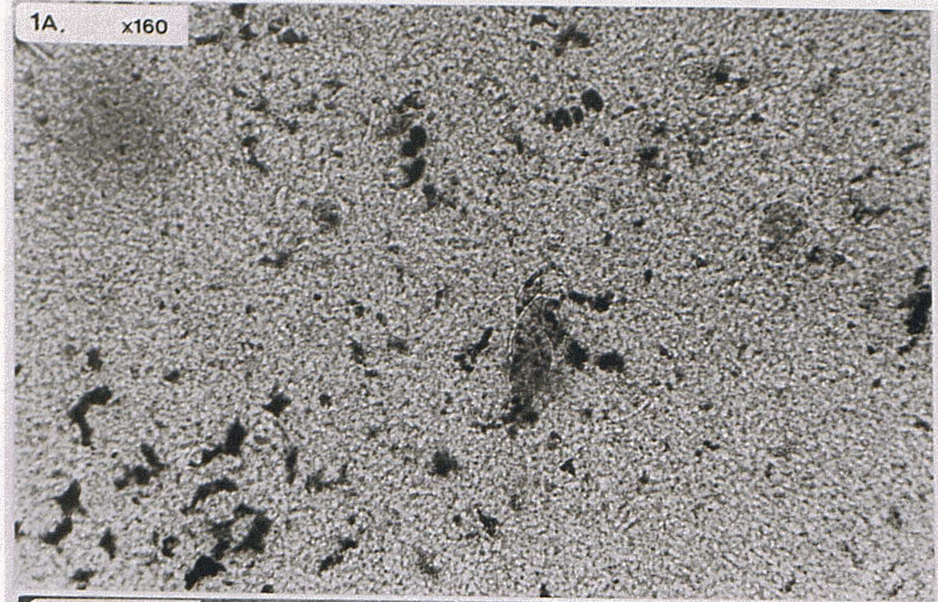


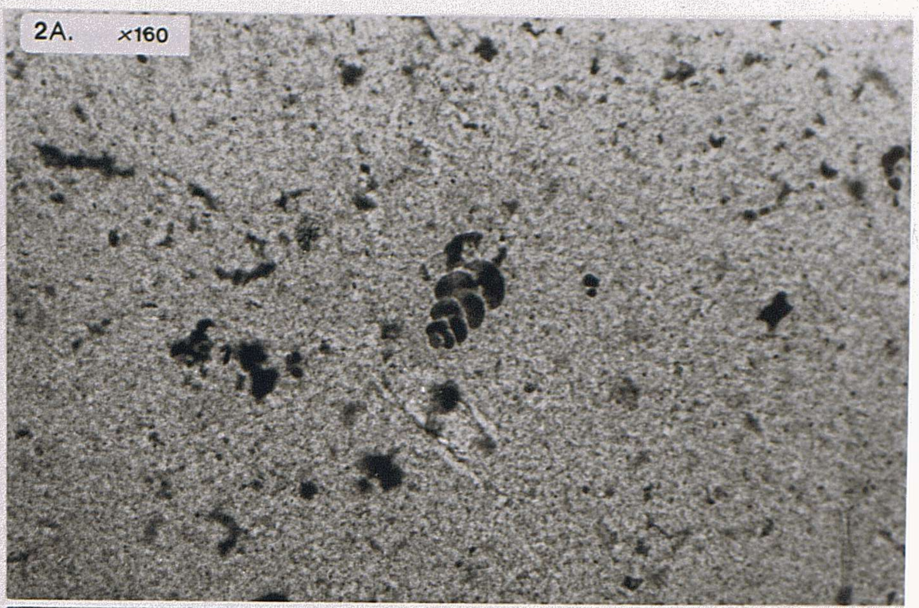
APPENDIX 4

Microfossils from the Flint Pebbles

(Identification assistance given by Prof.C.D. Curry -Pers.Comm.1982)

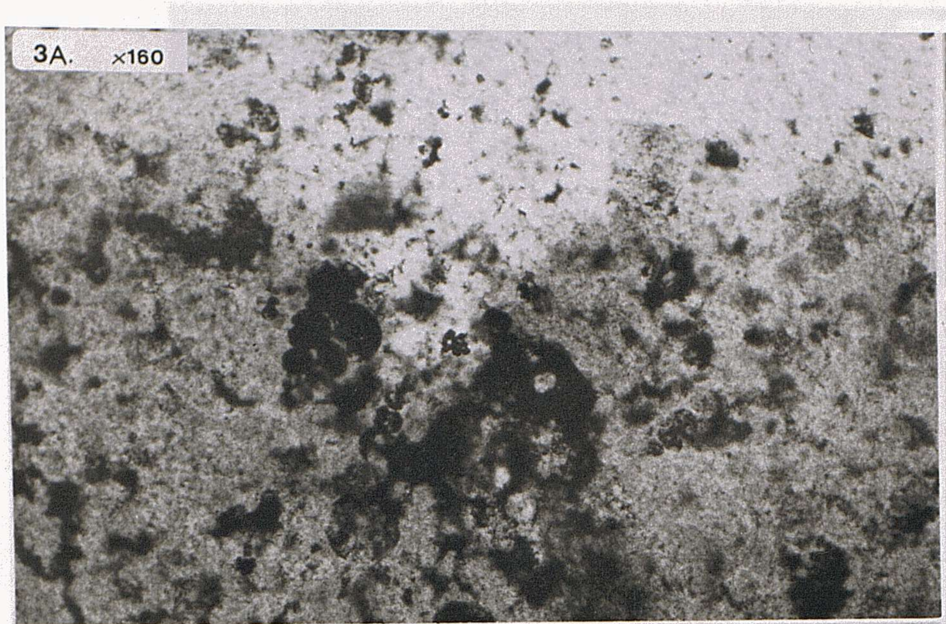
Plate 1a & b	Bolivina sp; possibly Bolivunta eleyi; Upper Cret.Chalk.
Plate 2a & b	Probably Eouvigerina sp; Upper Cret.Chalk.
Plate 3a & b	Heterohelix sp. Upper Cret.
Plate 4	Indeterminable.
Plate 5	? Juvenile Lenticulina ?
Plate 6	Hedbergella. Upper Cret.
Plate 7	? Praebulimina. Upper Cret.Chalk.
Plate 8	? Praebulimina or Eggerella. Upper Cret.
Plate 9a & b	? Valvulineria. Upper Cret.
Plate 10a & b	? Hedbergella. Upper Cret.
Plate 11A & b	Eggerella, or possibly Arenobulimina. Cret.
Plate 12a,b & c	Spheres of Oligostegina of unknown affinities.
Plate 13a & b	Dinoflagellate.


1A. ×160


2A. ×160

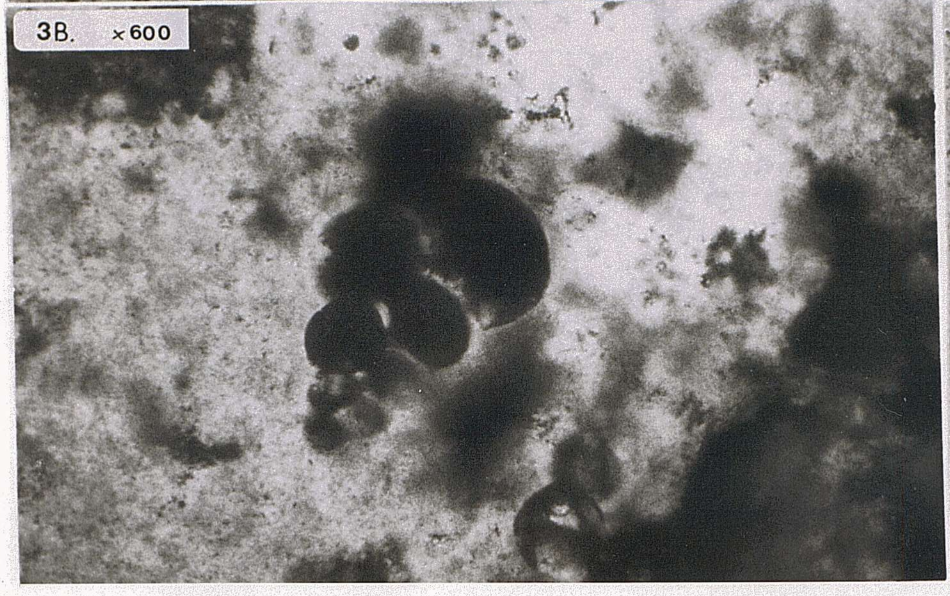

1B. ×400


2B. ×600

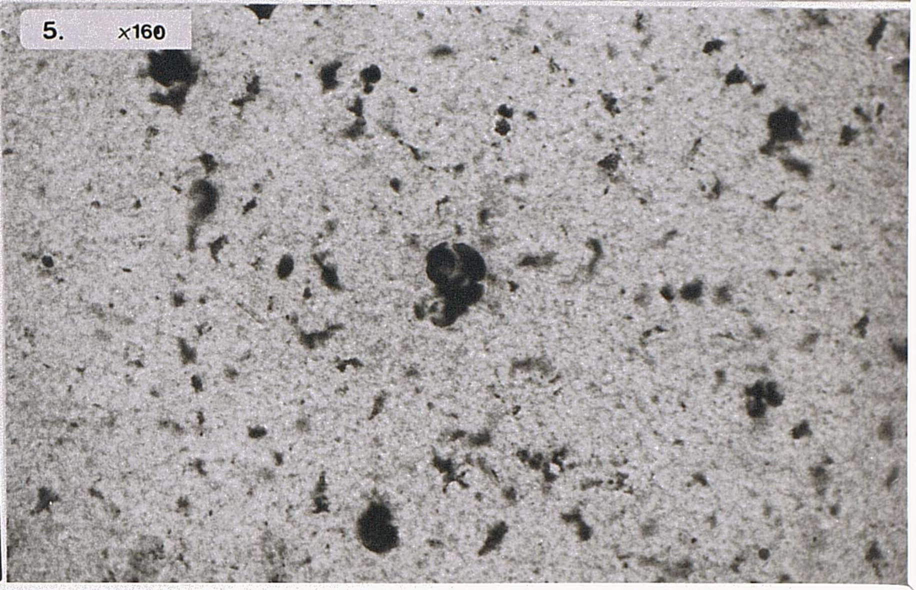


3A. ×160

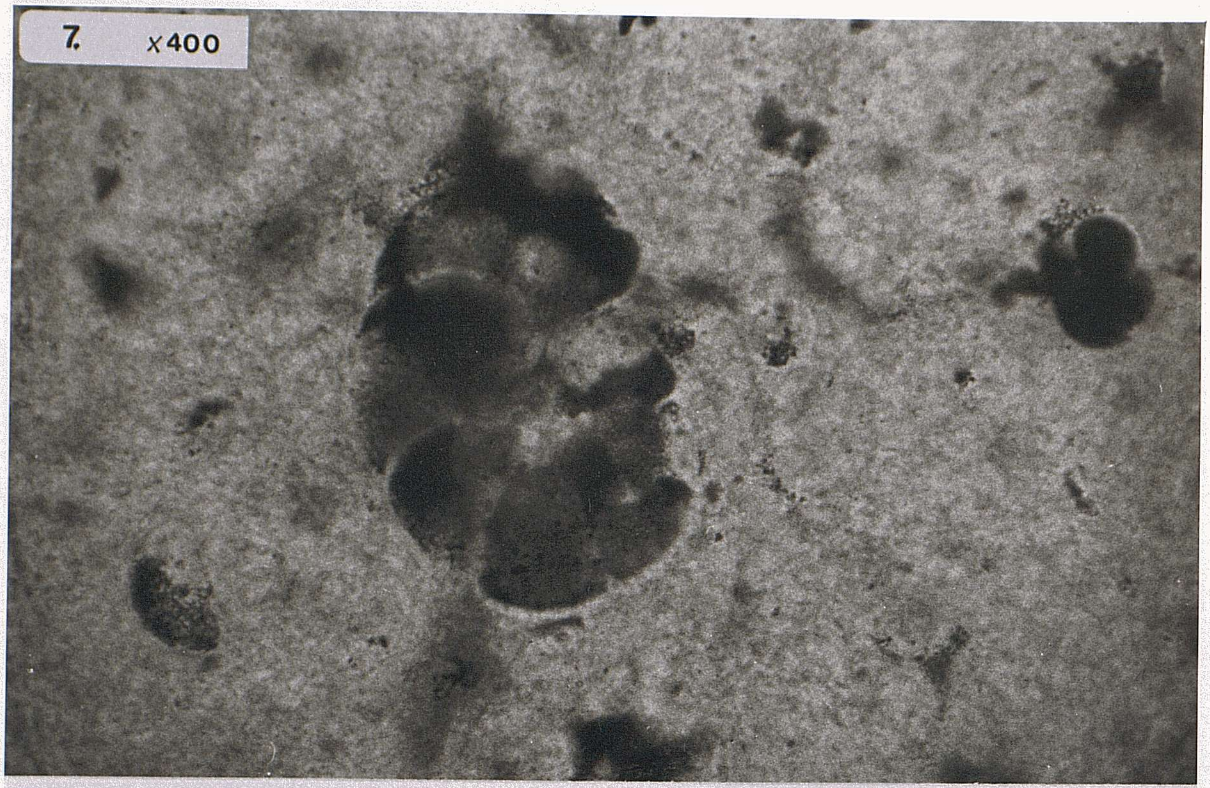
4. ×160



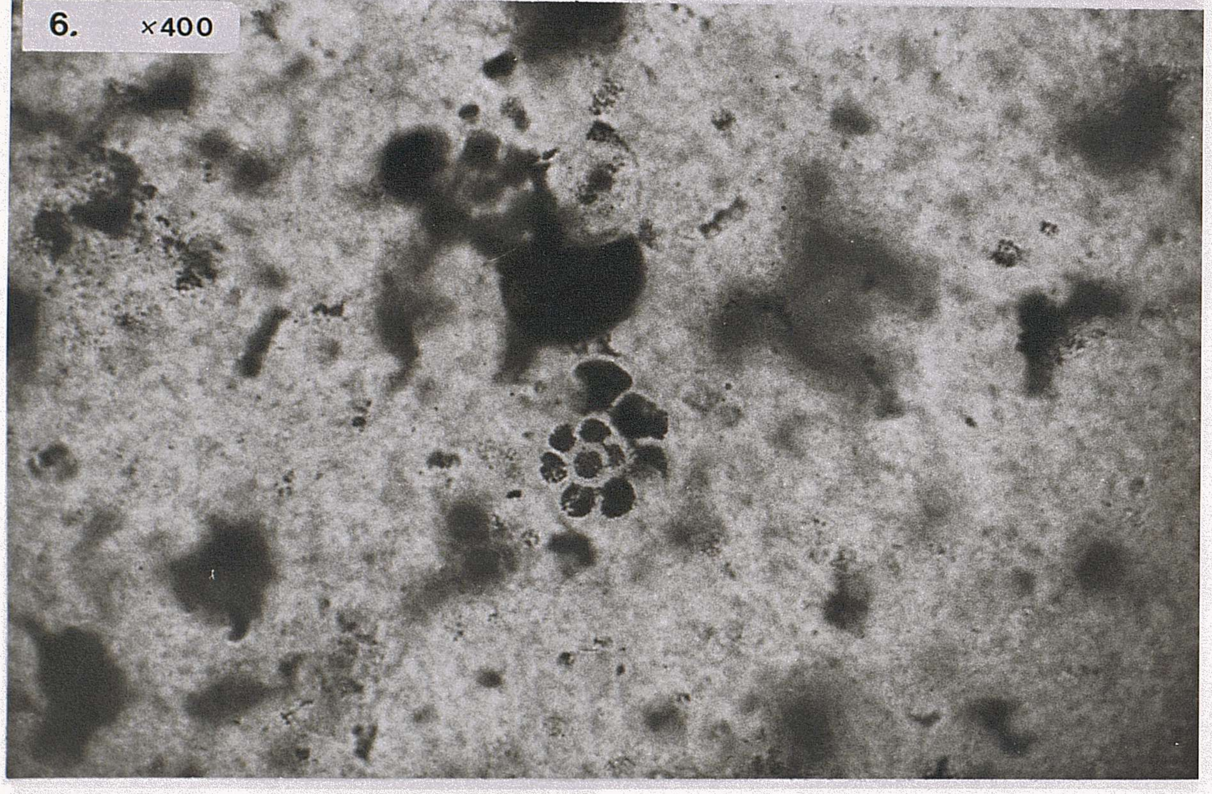
3B. ×600



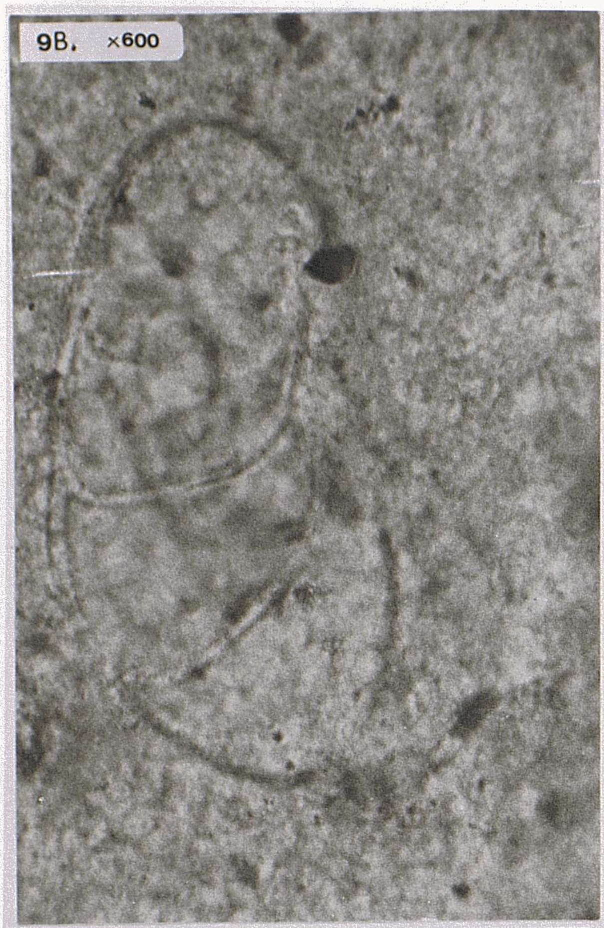
5. ×160

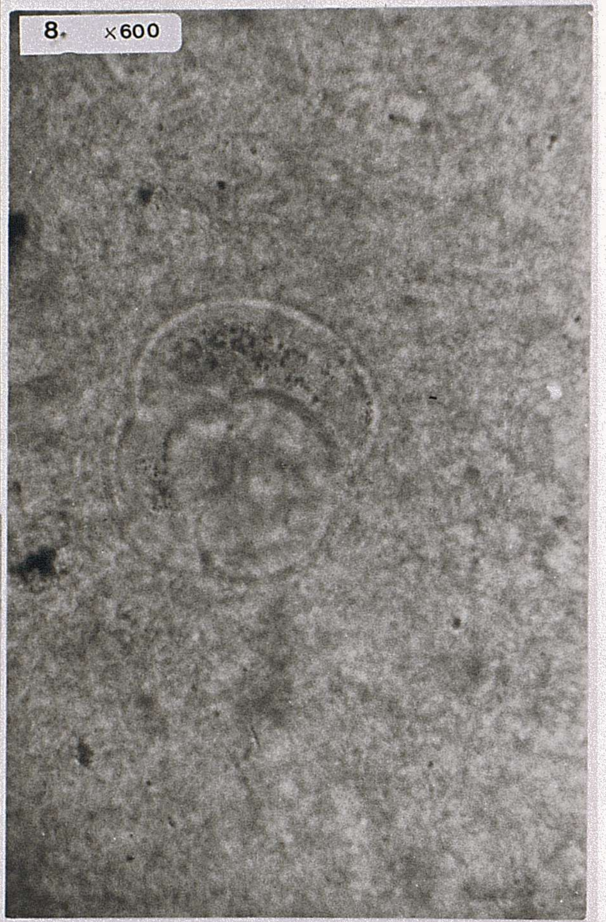


7. ×400

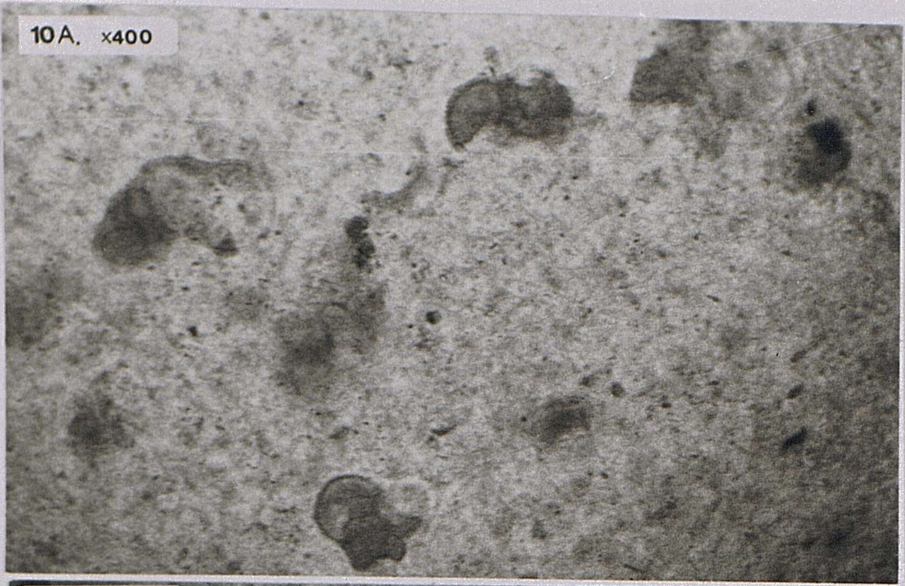


6. ×400

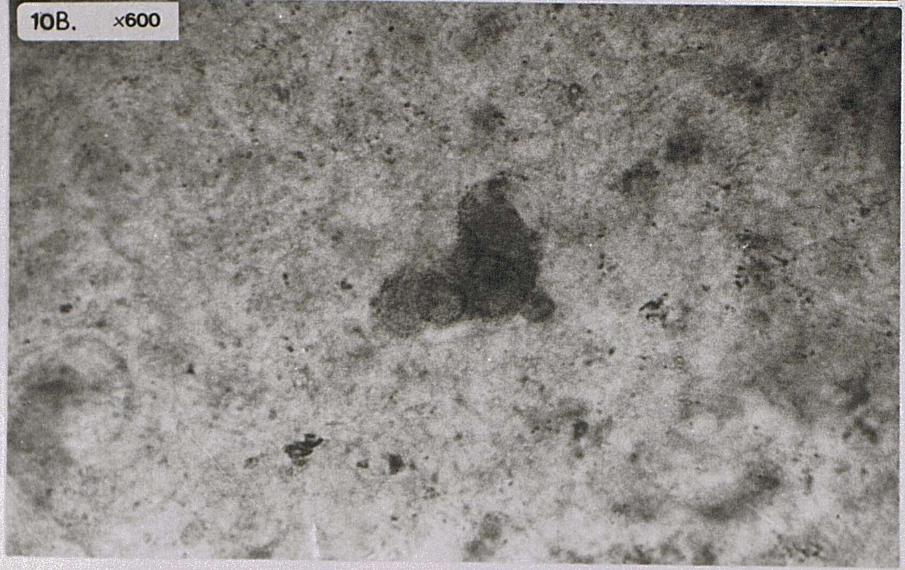

9B. ×600


8. ×600

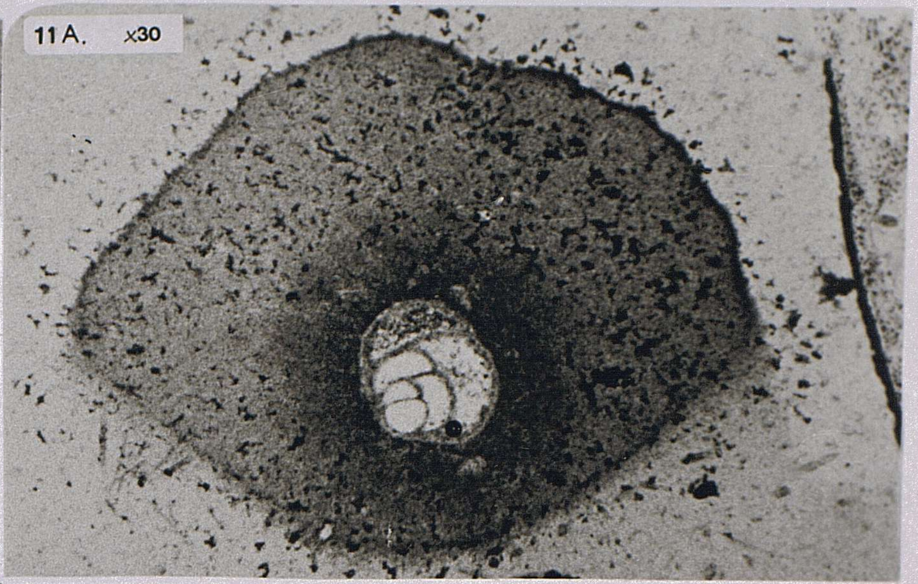

9A. ×600



10A. ×400

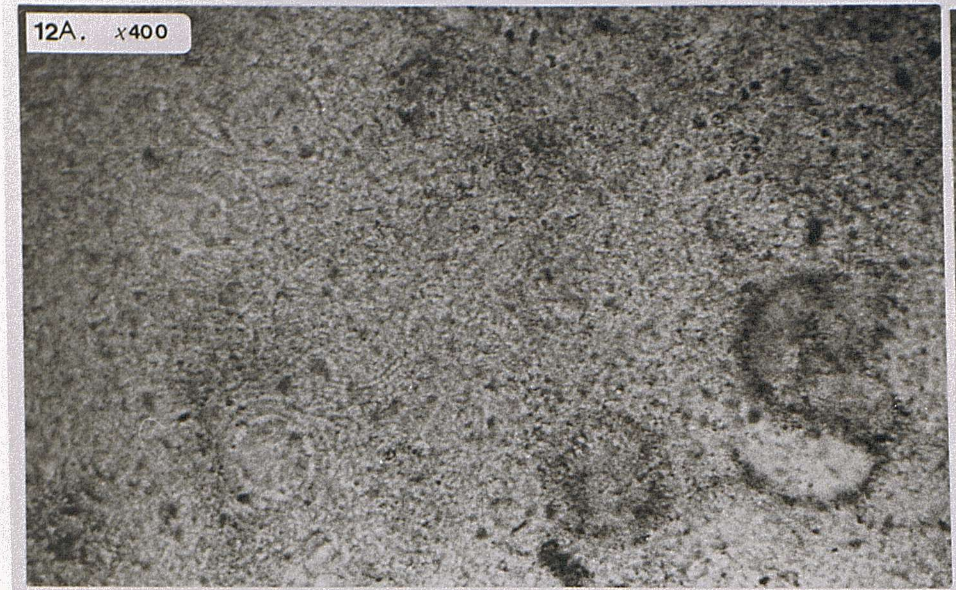


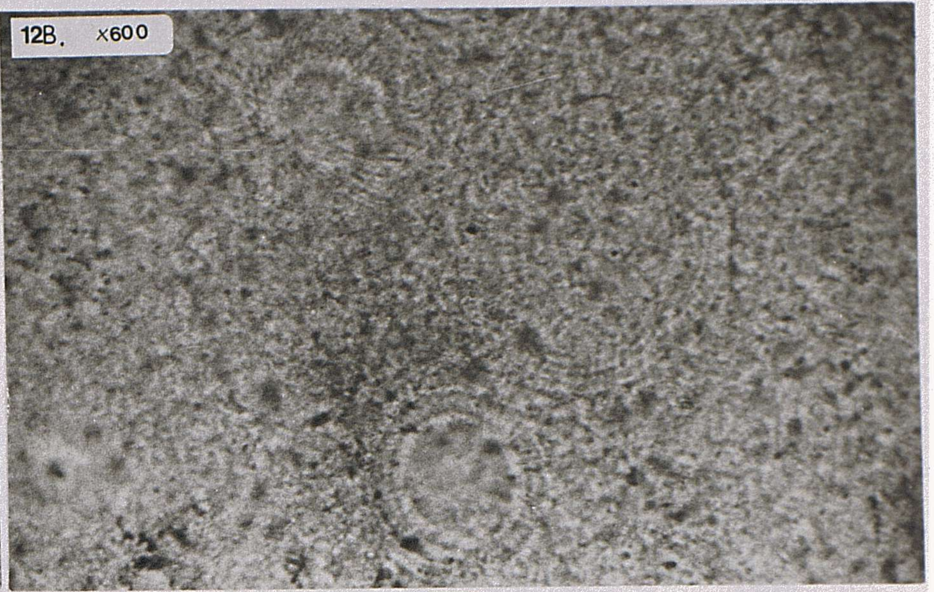
10B. ×600



11A. ×30

11B. ×55


12A. x400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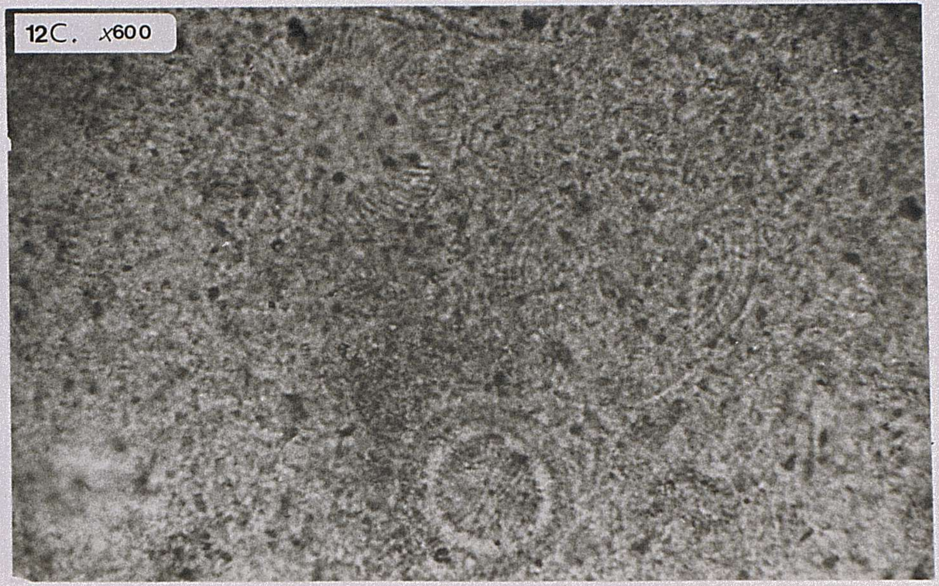
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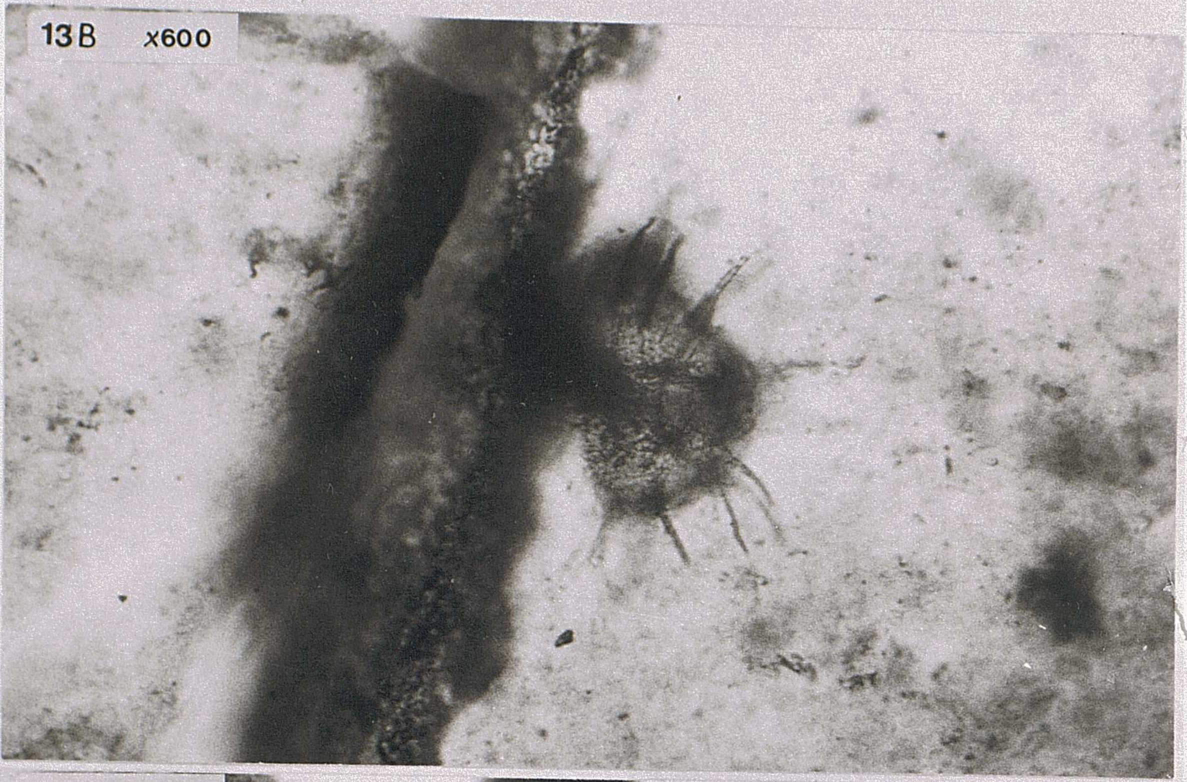

13B x600

13A x400