# I.O.S.

STATUS REPORT
ON GEOCHEMICAL FIELD RESULTS
FROM ATLANTIC STUDY SITES

BY
T.R.S. WILSON, J. THOMSON,
D.J. HYDES AND S. COLLEY

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OCEAN DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTE
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Abstract (100-200 words as desired)

This report summarises the results of preliminary geochemical investigations at three North Atlantic study areas.  The two eastern sites, on the Cape Verde abyssal plain (VC2) and east of Great Meteor Seamount (GME) were visited during 1982. The results presented are preliminary.  Studies in the western Atlantic, close to the Nares Abyssal Plain study site are more detailed and are presented in a separate paper.  The report shows for the first time the relative redox status of the three sites.  The differences are unexpectedly large, the most reduced cores being recovered at GME and the most oxidised at CV2.  The sporadic nature of Recent sediment accumulation at these sites is also emphasised.

In order to place these preliminary results in context their relevance to the production of mathematical system models is discussed in a closing section.  The necessity for such models to rest on sound foundations of geochemical understanding is noted.  Suggestions on future research priorities are offered for discussion.

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ABSTRACT

This report summarises the results of preliminary geochemical investigations at three North Atlantic study areas. The two eastern sites, on the Cape Verde abyssal plain (CV2) and east of Great Meteor Seamount (GME) were visited during 1982. The results presented are preliminary. Studies in the western Atlantic, close to the Nares Abyssal Plain study site are more detailed and are presented in a separate paper. The report shows for the first time the relative redox status of the three sites. The differences are unexpectedly large, the most reduced cores being recovered at GME and the most oxidised at CV2. The sporadic nature of Recent sediment accumulation at these sites is also emphasised.

In order to place these preliminary results in context their relevance to the production of mathematical system models is discussed in a closing section. The necessity for such models to rest on sound foundations of geochemical understanding is noted. Suggestions on future research priorities are offered for discussion.

SUMMARY OF GEOCHEMICAL RESEARCH AT I.O.S.

The major lines of study in progress at I.O.S. are here summarised. A brief rationale for each is also included for convenience, although it must be emphasised that these are here simplified for space reasons, and are not exhaustive.

i) The detailed mineralogical and chemical study of the sediment solid phase, using core samples collected from the study sites. This gives information on the origin of the sedimentary material, which must be reconciled with theories derived from sedimentological evidence, and on the fluxes of various elements to the sea bed (scavenging). The ion-exchange capacity and its distribution between the various mineral phases is also determined on these samples for reasons noted below.

ii) The analysis of carefully collected pore water profiles. From this study it is possible to assess the rates of dissolution and precipitation of components of the solid phase, and to study the processes which determine the redox potential and pH of the environment. These physico-chemical parameters determine the equilibrium chemical state of the released waste nuclides, which can strongly influence the rate of migration through the sediment column.

iii) All cores used in this study are dated using the Thorium-230 excess method. This allows us to measure accumulation rates and, in conjunction with i) above, elemental fluxes, and provides an important test of the consistency of sediment accumulation rate at the site. At the same time information on the behaviour of natural radionuclides in the water column and sediment is obtained. These natural analogue studies are potentially most informative, particularly in relation to long-term migratory behaviour.

iv) The processes of bioturbation are studied by inspection of fresh cores. The thorium-230 excess profiles can also provide some direct evidence of the depth to which the sediment solids are stirred, since surface sediments which have been bioturbated downward can be identified by their thorium-230 content. Bioturbation is significant for the removal of newly adsorbed material from contact with the water column, and possibly the provision of fresh adsorbing sediment at the sediment water interface. Conversely, this process could in certain circumstances also act to accelerate the transfer of material from the sediment to the sea.

v) Particulate material from the water column is sampled by means of filtration for studies on its mineralogy and

composition, in order to estimate vertical fluxes through each depth horizon. This is intended to provide information on the particulate transport flux and on rates at which particulate material is dissolved above and at the sediment-water interface. Because it is not site specific, discussion of the in-situ filtration system and its results is beyond the scope of this report and is mentioned here only for completeness.

RECENT FIELD PROGRAMME

Since the inception of this project the IOS have undertaken three cruises to disposal research areas. (Discovery Cruises 108, February 1980; 125, February 1982; 129 June 1982). Sites in the Nares Abyssal Plain, the Cape Verde 2 area (CV2) and east of Great Meteor Seamount (GME) have been sampled for the studies outlined above, except that filtration studies in the water column were not made in the Nares area. Because the two latter cruises are relatively recent, sample work up is not yet complete, but a range of samples suitable for first stage studies has been obtained for all three sites.

CURRENT STATUS OF IOS GEOCHEMICAL STUDIES ON N.ATLANTIC RESEARCH AREAS

FIELD STUDIES

1. Nares Abyssal Plain.

The cruise to thee Nares abyssal plain area (Discovery 108) was in fact planned before the start of HLRW contract work. The opportunity was taken to obtain samples and test methods at an earlier stage in the HLRW contract than would otherwise have been possible. The Site Selection Task Group of the NEA Seabed Working Group had not at that time designated defined sub-areas for intensive work, so that most of the data from Cruise 108 serves to provide a geochemical background to the area, defining the various processes and sediment source contributions for the area as a whole rather than for any specific study site. In particular, it seems likely that the study site is more oxidising and has a slower accumulation rate than the average of our cores although this remains to be demonstrated. The detailed discussion of the results is too extensive for incorporation into this report directly, and is available as a separate document. (Carpenter et al., 1983).

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## 2. Eastern Atlantic Area

Cruises 125 and 129, during the first half of 1982, were designed to give intensive sampling coverage to areas within study sites Cape Verde 2 (CV2) and east of the Great Meteor seamount (GME). Because of bad weather during cruise 125 no work on the GME site was possible, and this objective was transferred to Cruise 129. By contrast the weather conditions on this latter cruise were excellent and the sampling programme at both sites was fully completed. At the time of writing much work remains to be done on these samples, but preliminary results are most promising.

The discussion that follows is based on an incomplete data set, since at the time of writing not all samples had been worked up. For this reason a complete tabulation and detailed discussion of the data is not the object of the present report. Rather, we have sought to draw out the most important general conclusions and pass them on as rapidly as possible.

The most significant fact to emerge so far is that the two sites have very different redox profiles. The CV2 station (10552) is considerably more oxidising, presumably because of a lower supply of organic detritus at this site. The oxygen data (which result from an experimental method developed under IOS science-vote funding) show that oxygen is present at all depths sampled, and extrapolation

indicates that this probably persists to at least 10m depth
(Figure 1). By contrast, the oxygen profile at GME (10554)
shows oxygen falling to zero at 30cm depth. Reduction is
much stronger at this station, nitrate being reduced almost
simultaneously with oxygen, and manganese becoming mobilised
at 45cm. This latter fact is particularly significant. The
solid manganese hydroxide phase, which has a considerable
adsorptive capacity, cannot exist below about 40cm at this
site. It will be most instructive to investigate the effect
which this has on the total exchange capacity of the
sediments from the lower part of these cores. At the same
time, preliminary results from other laboratories have
indicated that Technetium moves rapidly through oxidising
sediments as an anionic Tc VI species. In more reduced
conditions, and in the presence of Fe II, it has been
reported to be immobilised. However there is some
controversy over this point and a partial retraction of
earlier announced results has recently been issued. (L.
Bush pers. comm. 1983). More precise laboratory migration
data will be needed in order to decide if this
immobilisation can occur at the redox levels observed at in
the GME area (station 10554) and this laboratory work will
assume critical importance if reduced sites such as GME are
selected for more intensive study in the future.
An interesting further aspect of the oxygen results is the
presence of non-zero oxygen concentrations observed below

the oxygen minimum near 30cm (Figure 1). This minimum coincides with a green band relatively high in organic material. It is already clear that this band could be responsible for a significant part of the oxygen consumption at this site. The observation of oxygen in the pore waters below this depth is not consonant with a simple one dimensional diffusion-reaction model at steady state. Suggested explanations include the possibility that the pore water system is not at steady state (difficult to reconcile with the rates of accumulation measured radiometrically)or that horizontal movement of oxygen, perhaps by pore fluid advection, is possible. On a kilometer scale, and especially in the southern part of this site, the green band becomes discontinuous (R. Schuttenhelm, pers. comm.) and dissolved oxygen presumably penetrates more deeply into the cores. This could provide a source for the observed oxygen in the 50-400cm interval. Confirmation of these preliminary conjectures by further detailed observation will obviously be an important objective of future sampling at the GME Site. This will require intensive sampling at an array of sites within the study area as well as extension of geochemical studies deeper into the sediment column.

The solid phase samples collected during Cruise 129 are in the process of being analysed, chemically and mineralogically. Some aspects of this work are described in greater detail in subsequent sections of this report. Data

are shown here for the GME site (10554) (Table 1, Fig.2): the CV2 site data are not yet available, but some information has been obtained by analysis of samples from a French core (KS06).

The GME site data are represented here by core 10554-11K, the appearance and gross mineralogy of which is summarised in Figure 2. Only two short sections, comprising about 5% of the material sampled, exhibit characteristics indicative of slow pelagic sedimentation from the water column. With these exceptions, the sediment at this site consists of a series of rapidly deposited turbiditic sediments one of which, a green band at about 40cm, appears to be relatively high in organic material. As discussed above, the oxygen concentration falls to zero at the depth of this band. The core then becomes reducing, and as a result manganese is mobilised as the soluble Mn II ion. This is free to migrate and becomes precipitated at a higher point on the redox gradient, where more oxidising conditions occur (Fig.2). The preliminary mineralogical profiles also show that CaCO is much lower in this layer than above and below it, but we do not have sufficient information as yet to decide if this is a depositional or a diagenetic feature. The ion-exchange data, which is discussed below, also reflects the mineralogical profile. Trace element enrichment in the marls is probably a result of lack of dilution by carbonate minerals, but the possibility of redox remobilisation for

elements such as Fe, Mn, Ni, Cu and Co cannot be excluded at this stage. Further studies in progress are intended to show the extent to which redox processes control the migration and deposition of these elements. In view of the multi-valent nature of many of the actinide elements present in HLR waste, it seems very probable that the migration of some of these elements also will be influenced by redox sensitive mechanisms.

The Kullenberg core (KS06) obtained at the CV2 site during a French research cruise has been studied in collaboration with Dr. Boust of the Institute de Protection et de Surete Nucleaire, Cherbourg. Bulk sediment samples were analysed for major and trace element composition and the results, together with the mineralogical data, and data on the redox state of iron, have been used to interpret the sedimentation regime of the Pliocene-Pleistocene section and to place constraints on the possible sources for the non-carbonate component. Below 11.3m, there is a dark brown pelagic clay of Pliocene age, containing illite, smectite, kaolinite chlorite and palygorskite, with some quartz, dolomite and feldspar. Transition metal abundances in these brown clays suggest the presence of a hydrogenous component: this is a source of similar composition to that identified in our Nares material (Appendix I). and thus probably reflects the slow sedimentation rate typical of such material. It is not yet possible to derive a sedimentation rate for the more

calcarous intervals at this site. Studies on the rare-earth elements are proceeding, with the intention of using the distribution of these elements to provide predictions of the likely behaviour of the analogous actinides in this environment.

## Field studies of eastern Atlantic areas - interim summary

Although only one station has been occupied at CV2 (10552) and GME (10554) several cores have been collected in each area and preliminary results have considerably advanced our knowledge.

The most important observation is that the redox profile at GME is considerably more reducing (negative Eh) than that at CV2, and that the former site exhibits in consequence a more complicated chemistry. Because of insufficient laboratory information on the influence of redox potential on the migration rate of nuclides, it is not yet possible to decide the significance of this observation in terms of radionuclide migration. It is clear that the difference in redox potential between the sites is strongly influenced by the sporadic input of organic-rich turbidites at GME: such episodes do not appear in the CV2 cores. This behaviour imposes a time-variable element into events at GME.

For these reasons it is not generally possible to derive a constant sediment accumulation rate from the thorium-230 excess data at GME. Turbidite layers complicate the

sequence by causing abrupt changes in thorium-230 excess contents following the introduction of older material into the succession. It is also not possible to generalise too closely for a particular site: the box and Kasten cores from GME appear similar visually, but the results of radionuclide measurements indicate that lateral inhomogeneities occur over quite small distances.

The results from this suite of cores indicate that a simple model of pelagic sedimentation is not generally applicable, and that an acceptable model must encompass the episodic supply of material in large and small quantities by turbidity currents (up to 3m thick layers in 10554 11K). The introduction of material with high organic carbon contents with accompanying high uranium values complicates thorium-230 excess decay patterns as does the potentially interesting evidence of remobilisation of natural radionuclides. For instance there is evidence of preferential migration of one natural radionuclide (uranium-234) relative to other uranium isotopes in one core studied. Our preliminary results suffice to place overall limits on the range of sedimentation rates at the study sites, but also indicate that relevant depositional mechanisms are far from simple.

Effort will therefore be directed toward a quantitative explanation for the observed abnormal concentrations of uranium and the processes which are evidently remobilising

this element in the cores studied, in order to determine the significance of such processes for model studies. More generally, our results indicate that Eh may be expected to vary, with consequent mobilisation of redox-labile elements. Further studies will concentrate, at GME, on defining the variability of the observed geochemical pattern horizontally, in depth and with time. Sampling transects in a N-S and an E-W direction are proposed, and a system will be developed to obtain good quality pore water samples from piston cores as well as the existing box and Kastenlot cores. This will permit geochemical sampling to ~10m: deeper work will require specialised sampling, such as the Hydraulic Piston Corer deployed from Glomar Challenger.

## LABORATORY STUDIES ON MATERIAL COLLECTED FROM N.E. ATLANTIC STUDY SITES

### Introduction

The degree to which a radionuclide reacts with the surface of sediment particles as it migrates through the sediment has a critical influence on the effectiveness of a sediment as a barrier to migration. We are not, as yet, in a position to measure these processes directly, but by measuring the cation exchange capacity of the sediment can assess the reactivity of deep sea sediment, and discover how this varies with the bulk composition of the sediment and

with geographical location. The value of measuring the cation exchange capacity of a sediment sample derives from the fact that this gives us a reproducible means to evaluate the surface activity of the sediment: because specific adsorption sites may or may not interact with a given exchange cation it is not at present possible to predict quantitatively the behaviour of the sediment with respect to cations other than that used in the measurement. However, it is to be expected that predictable relationships should exist between the mineralogy of a sediment and its activity with respect to a given cation, and our studies are planned so as to allow insight into such relationships

## Measurements of Cation Exchange Capacity

To date we have carried out work on three aspects of this study. Firstly we have investigated a number of different methods of measuring the total cation exchange capacity in order to identify methods which would give acceptable reproducibility, and to make a preliminary assessment of any systematic differences between different methods.

Secondly, we have applied these methods to samples from two deep-sea sediment cores to see if differences could be measured in relation to the composition of the sediment at these sites.

Thirdly, we have carried out experiments in which the total cation exchange capacity (TCEC) was measured on sediment

modified by removal of the organic and amorphous oxide components, both of which are considered to have potentially large contributions to the TCEC.

RESULTS

Four different methods of measuring TCEC have been investigated. Two of these (Barium magnesium compulsive exchange, and sodium-22 saturation) were found to give consistently reproducible results. Figure 3 shows a comparison of the application of both the Ba/Mg and the Na-22 methods to actual sediment samples. For this type of sediment the two methods give very similar results which suggests the same property of the sediment is being measured by both methods.

The material in core 10164, taken from a station close to the Nares Abyssal Plain study site, is predominantly composed of clay minerals with only a small proportion of quartz and calcium carbonate present as calcite. This rises to a maximum (4.4% as CaO) at 130cm depth, (see Fig.4). This in turn corresponds to one of two points in Fig.3 where a discrepancy exists between the two methods of measurement. The upper point of discrepancy corresponds to a diagenetically produced manganese solid phase enrichment. When the methods are applied to material from the calcite-rich Core 10554 11K a considerable discrepancy is observed between the two methods over the length of the core for which measurements have been made (see Fig.5). Where the

calcium content is about 30% (CaO on a dry weight) the Ba/Mg gives cation exchange capacities which are more than double those measured by the Na-22 method. A true cation exchange reaction, which is simply the electrostatic bonding of an ion to a charged surface, is very rapid. In these systems equilibrium should be established as soon as the sediment and surrounding solution have been thoroughly mixed. Exchange capacity should therefore be independent of whether or not the material is then shaken for a few minutes or several hours. This is not the case with the Ba/Mg method. Figure 6 shows that with increasing calcium carbonate content the apparent cation exchange capacity increases with increased reaction times. It would appear therefore that the divalent Ba and Mg ions are able to undergo a specific-ion-electrostatic exchange reaction with sites on the calcite surface which are not available to mono-valent sodium ions.

The exchange capacities we have measured at these sites are relatively low at around 20 meq/100g compared to observations in coastal sediments where capacities of the order of 100 meq/100g have been reported (eg Boatman and Murray 1982. Limnology and Oceanography 27(1) 99-110). The dominant clay mineral at both sites is illite and, in the degraded form found in these sediments, this component is capable of accounting for all the non-calcitic exchange capacity measured in these samples. In coastal sediments

the exchange capacity is much higher than would be predicted from the exchange properties of the component clay minerals; the difference is considered to be due to organic and amorphous oxide coatings on the mineral grains. The exchange capacity of coastal sediments is very sensitive to how they are handled - freezing a sample can reduce the exchange capacity by 50% (Boatman and Murray) other workers have shown that similar reductions in exchange capacity can be brought about by removing the organic matter from the sediment. In contrast, the material in cores 10164 and 10554 has a low organic carbon content, only a fraction of a percent, and the amorphous oxide coatings are presumably well-aged. Correspondingly, the treatment of samples appears to have little effect on the exchange capacity. Fig. 10 shows that drying the sediment at 110 C has little effect on the exchange capacity. Similarly, removing organic coatings with sodium hypochlorite, and oxide coatings with oxalic acid, does not have major effects on the exchange capacity. The indication is that the organic matter is relatively refractory. (In core 10554 its removal actually increases the exchange capacity.) In both cores removal of oxide coatings decreases the exchange capacity suggesting that they do contribute to the exchange capacity of these sediments (Figs. 8 and 9). The effect is larger for the GME samples than for the Nares pelagic clays, even though the latter are richer in manganese oxide.

## Cation exchange capacity study: interim summary

We have found that the cation exchange capacity of sediments from the study site GME and a Nares Abyssal Plain core measured by Na-22 exchange, is low compared to coastal sediments (of the order of 10 to 30 meq/100g). The exchange capacity is less where the sediment contains higher proportion of coarser grained calcite material. The surface of the sediment particles also appears to be relatively refractory in comparison to coastal sediments. Removing the organic and amorphous oxide coatings produces only small changes in the total exchange capacity. The presence of a slower exchange mechanism for Barium ions on the surface of calcite has been shown; this demonstrates the possible significance of specific interactions between particular cations and particular mineral phases.

THE INTERACTION BETWEEN FIELD MEASUREMENTS AND MODEL STUDIES
For many reasons, it will never be possible to conduct a full scale field trial of the chosen disposal system. In spite of this, the system must have a very high degree of reliability and long-term integrity. Consequently, very careful attention must be given to the design of system models. The production of such models must be an iterative process, in which the models are continually refined from an initial crude approximation. This refinement has two aspects. The model may be conceptually refined, that is the

processes chosen for inclusion in the model may be added or discarded in the light of improved understanding of the natural system. Second, it may be quantitatively refined by improvement of the model representation of the important processes as experimental data are produced.

The process is iterative because early versions of the model can be subjected to sensitivity analysis. This indicates the sources of uncertainty in the operation of the model and thus stimulates investigations into the processes which make the greatest contribution to this uncertainty. In turn, the results of the investigations can be incorporated in the next generation of the model. The purpose of the present discussion is to examine the relevance of this procedural paradigm to the actual situation existing in radionuclide migration studies.

Seabed Working Group System Model

The result of a first iteration of a complete system model was presented at the NEA Seabed Working Group in Paris in early 1981 by the Systems Analysis Task Group. In this model the sediment barrier (disposal medium) was considered to behave as a simple one-dimensional diffusive system with linear equilibrium sorption on the sediments, and radioactive decay. This was adequate to show semi qualitatively that the sediment barrier exerted the most significant control of the final dose to man, and hence to focus attention on the need for an improved sediment model.

The next stage of the iteration process is now underway.  A number of possible sediment models have been considered, in which more realistic, and possibly less conservative, assumptions are made about the processes which are active. A major obstacle to the evaluation of these proposals is the lack of information on the natural system, considered in detail below. This has arisen because of an inevitable mismatch between the effort necessary to design an improved model and the much greater effort necessary to obtain the data to do full justice to it. In the present instance the ratio of these efforts is far from the optimum. As a result, there is some danger that the increasing sophistication of the models may mislead the unwary into believing that our understanding of the system is greater than is in fact the case. The rate determining step in this study is not the improvement of models but the process of obtaining experimental information, especially natural systems and processes.

## Evaluation of model components

In order to focus the discussion more clearly at this point, it is necessary to consider separate components of the total system. It is important that the experimental and theoretical (modelling) aspects of each of these components should be drawn together when selecting research priorities. This preliminary note is intended to review the current

state of our knowledge from the experimental standpoint, so as to stimulate discussion and interaction with those working on system models.

## Accumulation rates

The rate of burial is, in principle, probably more closely defined than any other property of the system, since both paleontological and natural radio-isotope methods are available. At least one core from each study area in the N. Atlantic has been studied at I.O.S. by some dating technique. Within the overall averages quoted, the major uncertainty derives from the intermittent nature of the deposition. Pelagic accumulation rates as low as 0.2cm/1000yr occur. It is clear, however that material redistributed by turbidity currents forms a major part of the upper sediment column at many of these sites, and local rates as high as 20cm/1000yr have been noted.

At greater depths within the sediment, the reduction of volume due to overburden pressure and loss of porosity causes the burial rate to fall significantly below the accumulation rate. This loss of porosity appears to be unpredictable, particularly at sites rich in turbidites, so that only direct measurement will suffice for this parameter.

## Advection

Considerable evidence, both chemical and physical, has now
been accumulated in support of the hypothesis that movements
of pore fluid occur in response to natural thermal fields.
However, the phenomenon, as might be expected, is mainly
encountered near to the ridge crest, where sediment
thickness is relatively thin and thermal gradients high. It
appears much less likely that significant natural advection
would be encountered in the much thicker sediment blanket of
study areas. It is possible to test for the existence of
vertical advection by inspection of pore water gradients
over very long sediment sections. The only suitable
sampling method is Hydraulic Piston Coring, which requires a
specialised drillship such as Glomar Challenger: there is
no doubt that such deep sampling for sediment and pore water
must be an essential step in the evaluation of a study site.
Since it should, in principle, be possible to detect natural
vertical advection and so to avoid this phenomenon, it could
be argued that it is in order to set this parameter at zero.
The possibilities of horizontal natural advection, and of
artificial vertical advection driven by the heat produced by
the canister, have not been addressed experimentally,
although theoretical treatments are available.

## Diffusion

The diffusive movement of ionic species in free solution is a well studied process, and sufficient information exists for many species to permit calculation of the value appropriate to solutions of sea water composition. Rather more uncertainty exists with respect to the prediction of the obstructive effect of the sediment particles from porosity data. However, the uncertainty so introduced is not large, perhaps a factor of two or so (Table 2), and electrical conductivity methods for the measurement of the obstructive effect are providing improved information.

## Adsorption

If an ion adsorbs to the surface of an immobile solid phase for some fraction of the time, and is itself immobile while so adsorbed, its migration rate through the bulk sediment will be reduced by a factor proportional to the fraction of the time which the ion spends in the solution phase. If the ion is adsorbed for a large fraction of the time its migration rate will become very slow. Hence the passage of a concentration front through an adsorbing porous saturated medium is greatly slowed by such retention (note that only transient diffusion is thus affected: if a steady-state is achieved, the mass flux through such a medium is identical to the mass flux in the non-adsorbing case, since all sites are occupied at all times. Because of radioactive decay and

the long time periods needed to establish steady-state in strongly adsorbing systems this point is only of potential interest for less strongly adsorbed nuclides with long half-lives. This subset of nuclides is of course important for other reasons also). Considerable data now exists on the adsorption of waste radionuclides onto various minerals, although the Atlantic study site material is not yet documented for all important nuclides. The assumptions (not all of which are conservative) necessary to convert this information into migration rates have not yet been verified. There is a need for greater understanding of the physical and chemical processes involved since the standard assumption of reversible linear adsorption is certainly not true for many important nuclides. Because of the lack of information, the next model iteration will almost certainly be forced to use this simplistic assumption, but this is undesirable for future iterations.

A further limitation on the use of laboratory batch adsorption data is the uncertainty in relating the experimental conditions to those of the natural environment. This is a particular problem in the case of redox-sensitive nuclides with several possible chemical forms: it is not possible to predict the likely chemical form of these nuclides within the sediment environment. Firstly, the natural redox field is not yet well documented. Secondly the conditions in the relevant laboratory batch experiments

are often uncertain enough to make it difficult to know which valence state was predominant during the experiment, so that much of the literature data may be of limited usefulness.

More recent laboratory studies have made considerable efforts to control and measure the speciation of the active nuclide. Similarly, some advanced experiments are being performed which use direct migration measurements to verify the assumptions previously necessary and to elucidate adsorption mechanisms. This area of work is probably advancing as rapidly as necessary, and it is to be expected that laboratory data will become adequate in accuracy and coverage within the next few years. Care should be taken to eliminate from the data-set any laboratory measurements not well-controlled for speciation variation.

Because of the long lead time for environmental measurements it is possible to say that improved information on the natural redox field will not become available until at least 1984-5 and for some sites may take longer. Also, redox profiles at sediment depths greater than 4m will probably not become available until after 1985, as provision has not yet been made for the necessary rapid shipboard work-up of piston cores. This will be an urgent objective of the medium-term study programme. In the long term, deeper measurements (>10m) will not become available until an Hydraulic Piston Corer, or alternative long coring device,

is deployed on this study. A reasonable interim treatment would be to assume that deeper sediments are not grossly dissimilar to the shallower sediments already sampled, but it must not be forgotten that there is no direct evidence that this is true in the study areas.

## Bioturbation

Within the upper metres of the sediment, disturbance by organisms becomes increasingly important as the sediment-water interface is approached. Because organisms vary in their size and feeding habit this disturbance exhibits quite different characteristics at different points on the ocean floor. Broadly, one may distinguish between activities which characteristically disturb significant quantities of solid sediment and those which irrigate the upper layers by systematic and sustained movement of bottom seawater through burrow systems. In general, most intense activity of both forms is confined to the upper 10cm or so of the sediment, but increasing evidence of deeper penetration is becoming available with improving sampling techniques. Various approaches to the study of bioturbation have been suggested. Direct study of the chemical microstructure of the sediment on a millimetre to centimetre scale is yielding some interesting preliminary results. Perhaps more relevant to the present discussion are attempts to parameterise the system in terms of solid phase diffusion

coefficients. Fall-out plutonium adsorbed onto sediment particles is distributed with these particles, and the growth of this tracer into the sediment by this process has been studied by GUINASSO and SCHINK, (J Geophys Res. 80 3032-3043). A more sophisticated attempt (COCHRAN and KRISHNASWAMI, Am.J.Sci. 280, 849-889 1980) has given a reasonable explanation for the observed distributions of radium, thorium, uranium and lead-210 in terms of the movement of sediment by bioturbation, diffusion in pore water, radioactive decay, and adsorption onto sediment particles. This is the most sophisticated deep sea diffusion-bioturbation model to have been tested against observed distributions in this way. At the present time, only Pacific sediment has been studied. It is a medium term objective of our programme to prepare a similar treatment of the N. Atlantic study sites. Because of manpower and equipment constraints, the necessary data collection cannot be undertaken until the thorium-230 excess profiles in the study areas have been well documented. Data collection is projected to commence in 1985 for this project, but it may be necessary to make more than one cruise before sufficient information for a satisfactory model treatment is available.

## Water column:  Chemical behaviour of suspended particulate material

The systems model does not deal only with the passage of dissolved nuclides to the water column but includes the processes of sediment resuspension and resedimentation and the adsorption and desorption of dissolved material on this suspended material. This is not directly within the scope of this report. Relatively little information is available on these processes and it is not at the moment easy to evaluate their likely importance for any given site, nuclide or ocean basin, with the possible exception of thorium-230, which has received considerable attention. It will be important to define the accuracy which is demanded by the models in order to deploy our field resources to best effect. In general it is possible to state that sporadic indications of nepheloid layers (relatively dense layers of suspended material) have been observed in many parts of the world ocean. In the low energy regime which probably applies to all the study sites such resuspension is probably not an intense process, although density-driven currents might resuspend material as a by-product of local sediment redistribution. Sediment Thorium-230 data suggests that such processes have been significant in some parts of the GME area.  is not easy to measure directly because of its sporadic nature. The other important process, the steady downward flux of particulate material, is continuous but diffuse and so also presents problems for direct

measurement. For these reasons, the accumulation of direct data on these processes, although very necessary, will inevitably be a long-term process. The IOS program has embarked on this process (see page 2) but in order to provide statistically significant information on a more rapid timescale an attempt to derive useful information from the sediments themselves has also been undertaken.

This work is illustrated by our Nares Abyssal Plain results (Appendix 1). A component of the sediment has been identified which appears to have been scavenged directly from sea water. This component covaries strongly with thorium-230, which is known to be strongly adsorbed, and this almost certainly represents the net integrated flux of the transition elements included into the sediments after stripping from the water column. Since the content of these elements in the overlying water column is known, together with the accumulation rate of sediment on a weight area time basis, it is in principle possible to derive a net adsorption value per unit mass of sediment for this group of elements. A further necessary refinement, not yet attempted, is to apply a diagenetic model to the observed alkalinity profile in order to derive a measure of the rates of conversion of organic to inorganic carbon. It is not at present known which component is responsible for the observed scavenging of transition elements to the sea floor. One possible major problem with this approach which has

recently become clear is caused by the predominantly non-pelagic sedimentation regime observed at the study sites. The input of large quantities of sedimentary material to the disposal sites by bulk transport processes (turbidity currents) violates several important assumptions used in this approach and thus robs it of much of its power. It may be necessary to locate areas of predominantly pelagic sedimentation and to make use of the (not unreasonable) assumption that the scavenging process is position-invariant in its characteristics.

Although this approach may permit the derivation of some information relevant to the quantification of the processes included system models of the water column, it is clear that at present models tend to be overspecified for the quality of the available field data. In this situation it is particularly important that sensitivity studies are used to verify the model, and to direct field investigations to the refinement of the most critical parameters. It will obviously be helpful while the field data are being improved to turn to laboratory sources for data to describe the scavenging process: it is worthwhile pausing to consider the relevance of laboratory data to models of this type.

It is a relatively simple experiment to suspend surficial sediments in sea water and to measure the partition of a radionuclide between the solid and solution phases. There are a few special precautions which should be observed: for

instance the concentrations of solid phase and of nuclide should be as low as possible so as to approximate to the in situ conditions. The known dependence of K values on concentration renders the use of high concentration data most inadvisable. In principle, however, our understanding of the partition of a nuclide between suspended particulate material and sea water can be made adequate for the purpose at hand.

A much greater problem arises for the two other processes included in the model, exchange of particulate material between the sediment and water column, and exchange of dissolved material across the benthic boundary layer. The latter is the more amenable problem, since it is possible to derive some idea of the controlling processes from the behaviour of natural radionuclides and other diffusing species. As mentioned above in the section on bioturbation, which is a closely related topic, we hope to be in a position to address this problem after 1985. Until appropriate field data can be collected and worked up it will be necessary to rely on literature data derived from other programmes, mainly in the Pacific (e.g. COCHRAN and KRISHNASWAMI, Am. J. Sci 280 849-889 (1980)).

The exchange of particulate material between the sediment and water column is difficult to quantify because it is a sporadic process. Consequently, it is necessary to make a long series of observations at the site of interest in order

to define the long term mean for the site. Alternatively, it is possible to make observations on a basin-wide basis, using geographical rather than temporal spread to average the variability. This latter approach seems the most practical, and has the advantage that observations by workers not directly concerned with the designated study areas can be utilised. Again, however, work is at an early stage and at the time of writing there seems to be insufficient data to estimate either quantity of resuspended material in the water column of the N. Atlantic basin or the rate at which this material is removed to the sedimentary column. Further, it is difficult to estimate when this data will become available. For the moment, it might be adequate to utilise known sediment accumulation rates to approximate the "single pass" fluxes of detrital phases and of biogenic material through the water column, but very great care would be necessary to avoid accumulation rate data influenced by non-pelagic sedimentation processes.

## Field data input to migration models. A summary

Although numerical models of the disposal system (systems models) are essential to the development of a balanced programme it is not easy to be sure that their predictions are valid. There are three main difficulties. Firstly, the quality of the input data may be inadequate. Secondly, the model may not represent the most important physical and

chemical processes. Thirdly, because the model represents a situation which does not as yet exist, it is impossible to test it as a complete entity.

Unfortunately, the results of a correct systems model are not distinguishable from those of a seriously flawed version by simple inspection of the output. Rather, it is necessary to examine the assumptions and data used to generate the model. In the present case, this cannot be done without access to direct field measurements on the natural system.

The present version of the systems model, presented at the NEA Paris meeting in 1981, makes use of simple approximations to the true behaviour of nuclides within the sediment; these are known to be inaccurate. The model is adequate to show that the concept of sea disposal has merit, but has little predictive value from a quantitative standpoint. This note is concerned with the strategy by which field data can be used to improve future systems models.

Although the systems model cannot be tested directly, it is possible to construct numerical descriptions of parts of the natural system (subsystem models). If these are constructed in such a way that their predictions can be tested against field measurements, then the assumptions on which they are based can be tested. By careful choice of subsystem model, assumptions necessary to the systems model can thus be tested against field observation.

This is a developing part of the studies at IOS. We would of course welcome discussions with colleagues engaged on systems modelling. This is important because the results of their sensitivity analyses indicate critical areas. In addition it is necessary that the subsystem model results should be relevant to the system model and this can only be achieved by close liaison.

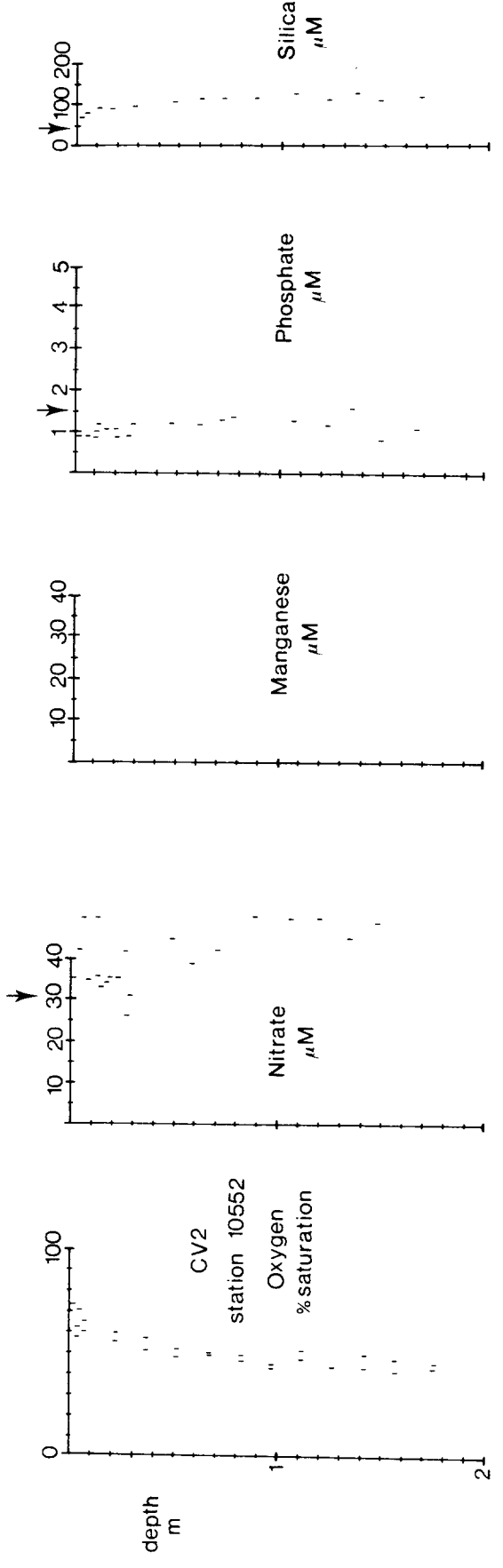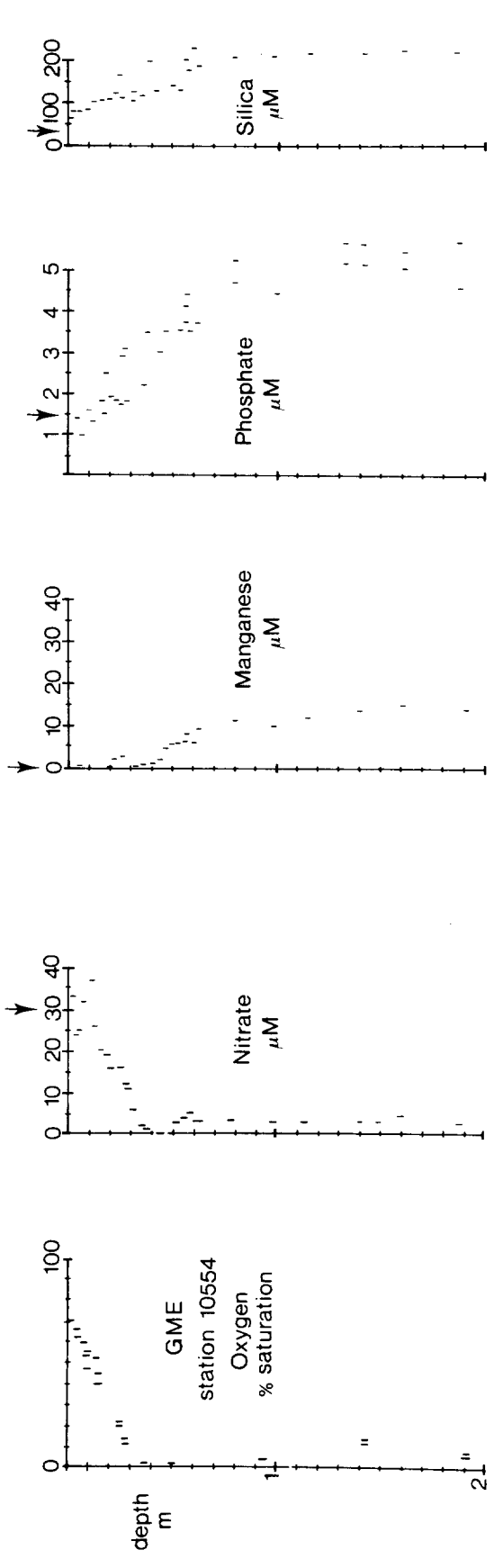Figure 1   Pore water composition observed at stations CV2 and GME.

GME station 10554

Oxygen % saturation

Nitrate μM

Manganese μM

Phosphate μM

Silica μM

CV2 station 10552

Oxygen % saturation

Nitrate μM

Manganese μM

Phosphate μM

Silica μM

depth m

Figure 2   Station 10554 (GME) solid phase manganese content.

Mn O (% weight)

0    1·10    0·02

Depth
m

1·0

3·0

4·0

Core 10554 # IIK

Light brown coloured carbonate ooze (turbidite)

Green homogenous layer (turbidite)

Pelagic ooze

Light brown coloured carbonate ooze (turbidite)

Gradational boundary

Light grey/brown coloured carbonate ooze (turbidite)
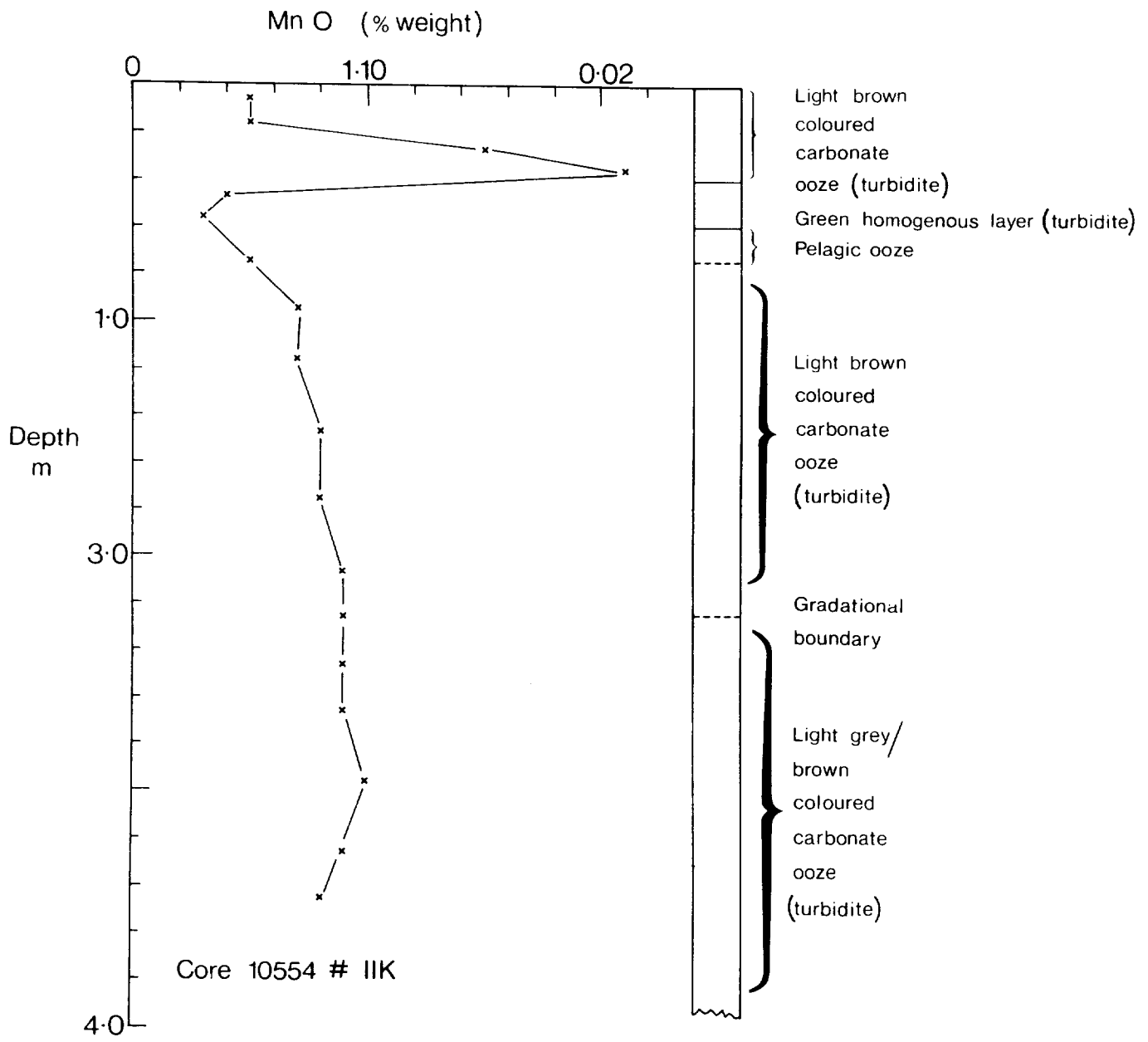
Figure 3   Comparison of Na-22 (closed circles) and barium/magnesium (open circles) cation exchange capacity.
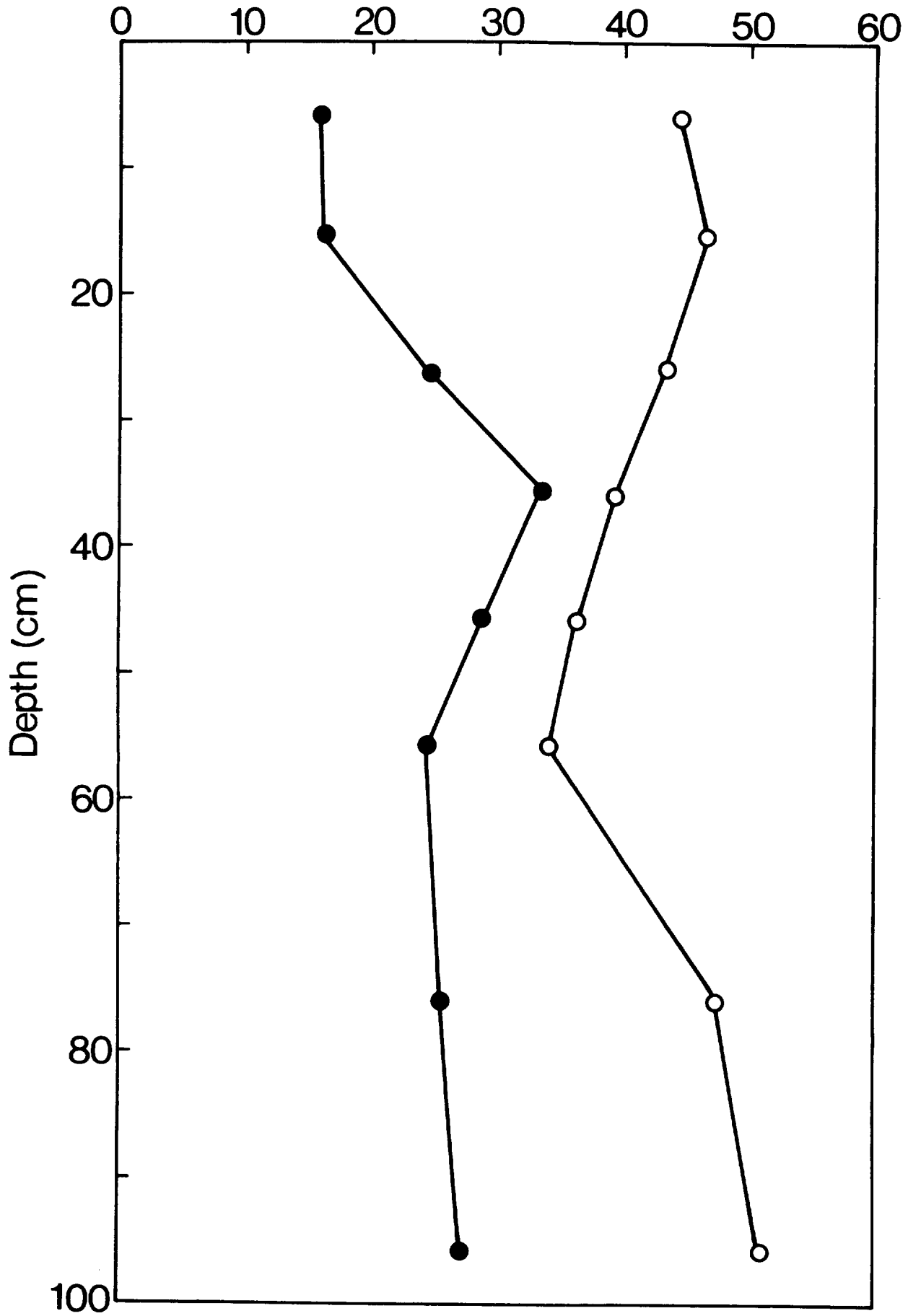
Figure 4  Core 10164 1K.  Solid phase calcium content  (Open circles).
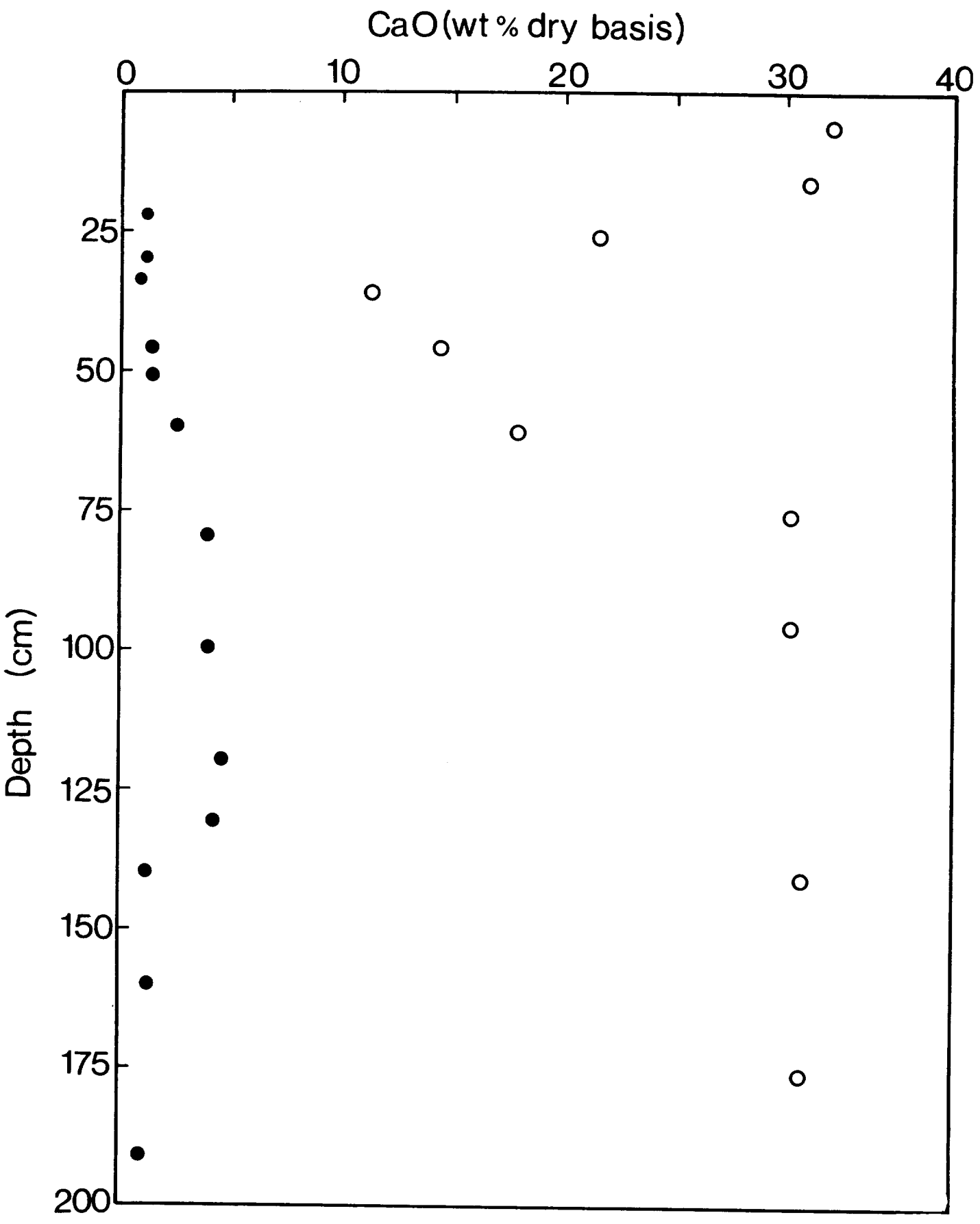
Figure 5   Comparison of Na-22 and barium/magnesium method in
           the presence of calcite-rich sediment. (Circles : Core 10554
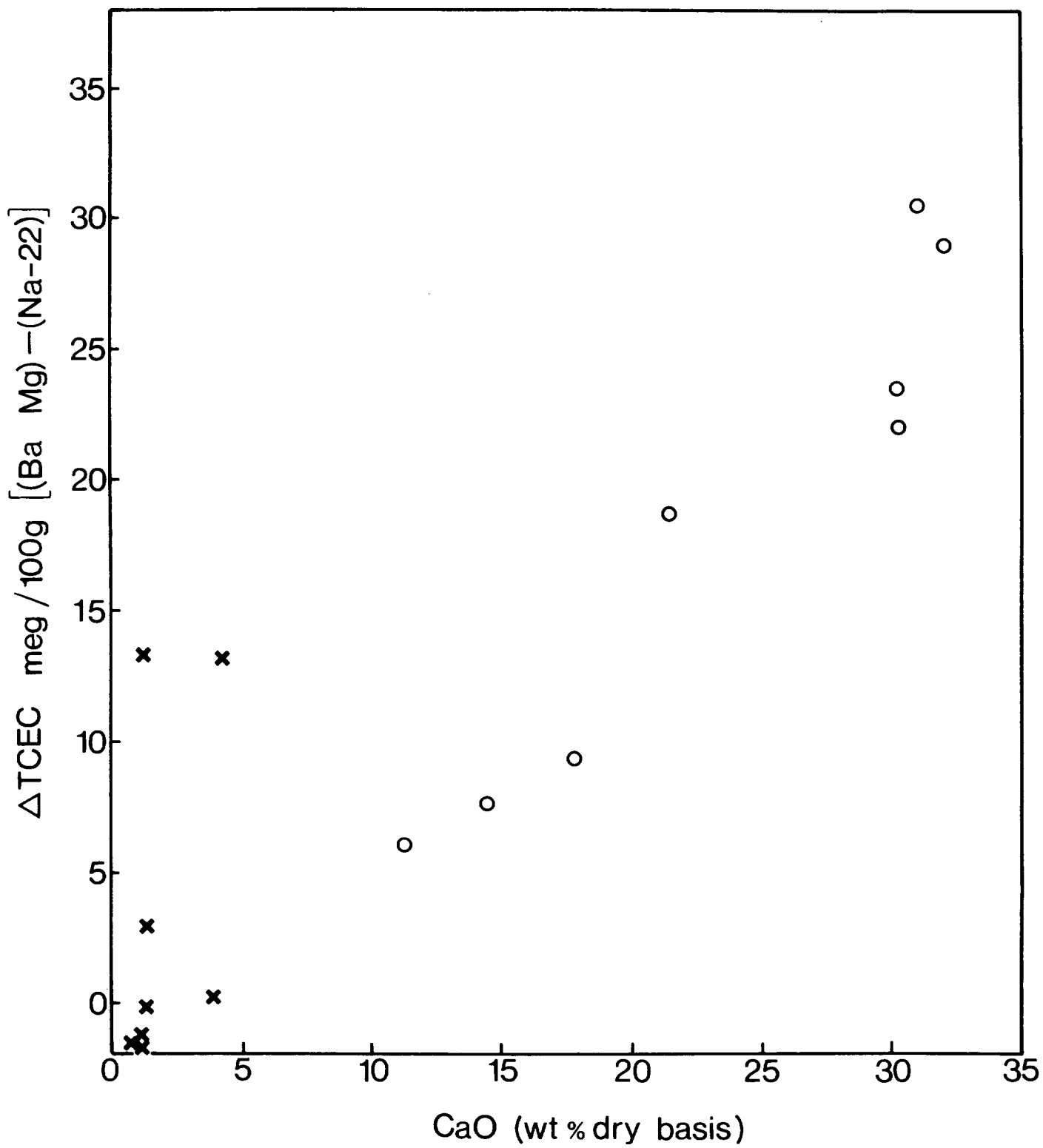           crosses : Core 10164).
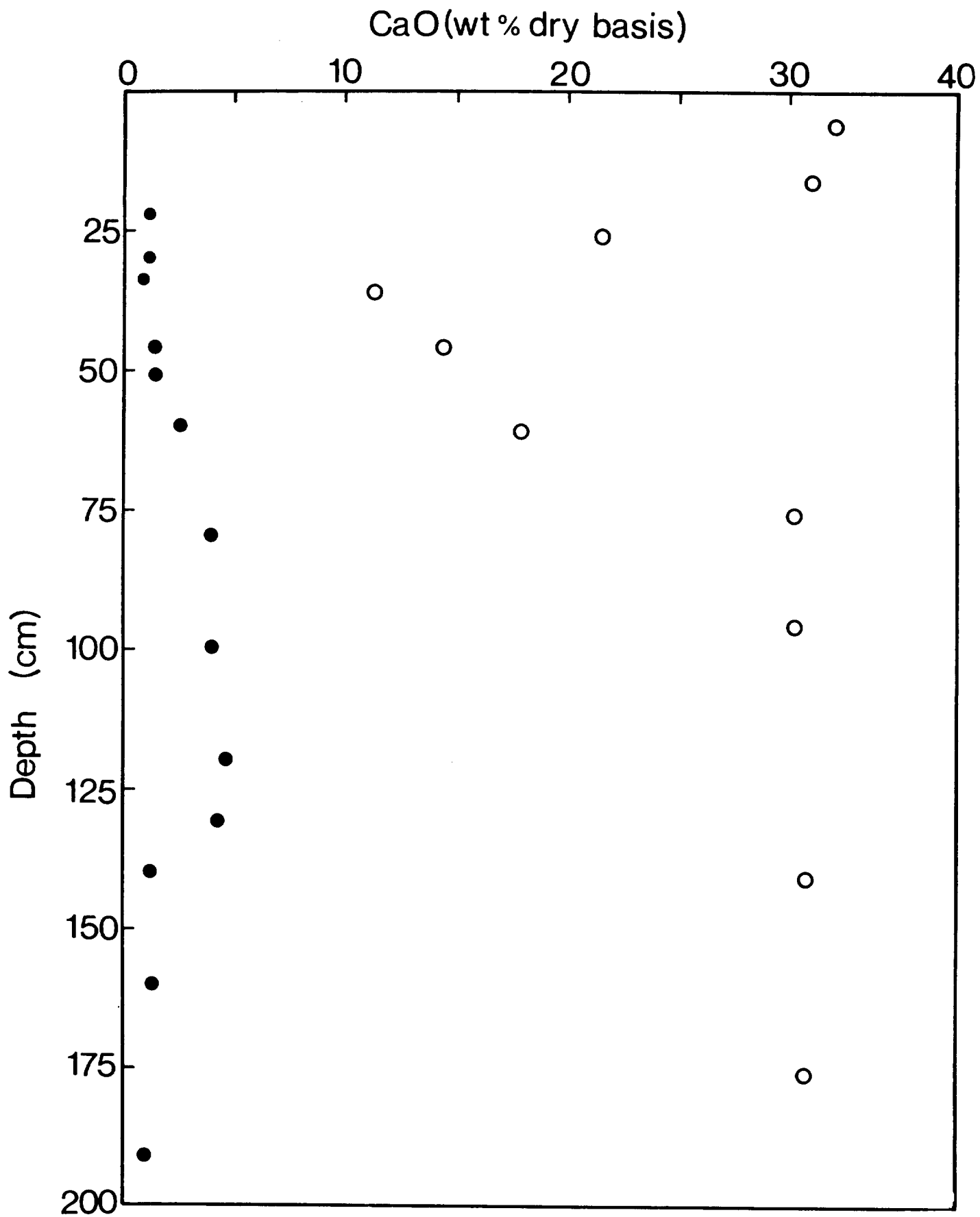
Figure 5  Comparison of Na-22 and barium/magnesium method in
the presence of calcite-rich sediment. (Circles : Core 10554
crosses : Core 10164).

Figure 6  Effect of procedural variation.
          Open circle Ba/Mg large tubes both rinses overnight
          Open triangle Ba/Mg small tubes, both rinses overnight
          Open square Ba/Mg small tubes, only Mg rinse overnight
          Closed circle Na-22 15min equilibration
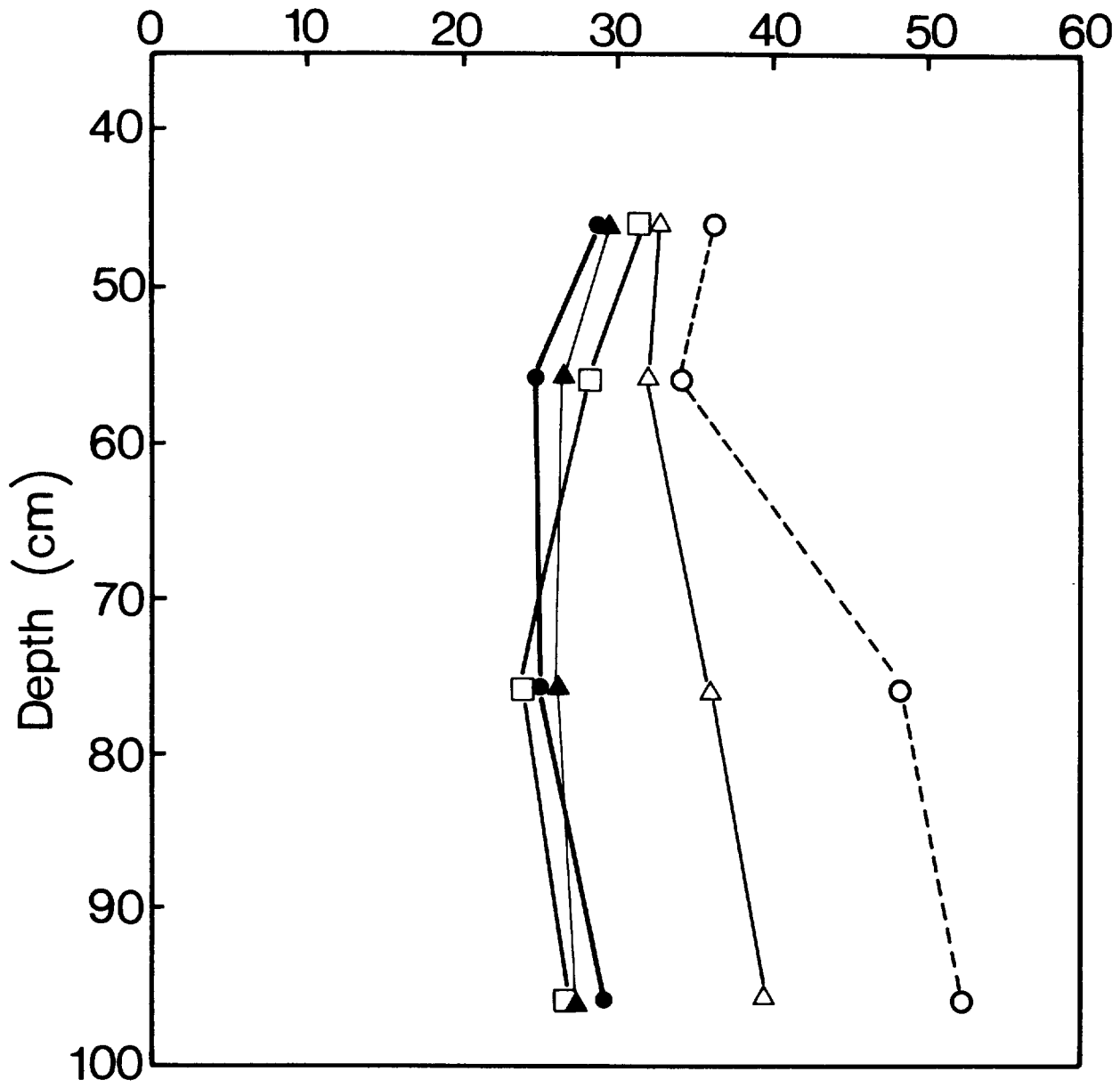          Closed triangle Na-22 final rinse overnight.

Figure 7  Sodium-22 method:  effect of various leaches on TCEC
core 10164 1K.  Closed circles - before leach, open
circles - after hypochlorite leach.  Crosses - after
hypochlorite and oxalate leach.
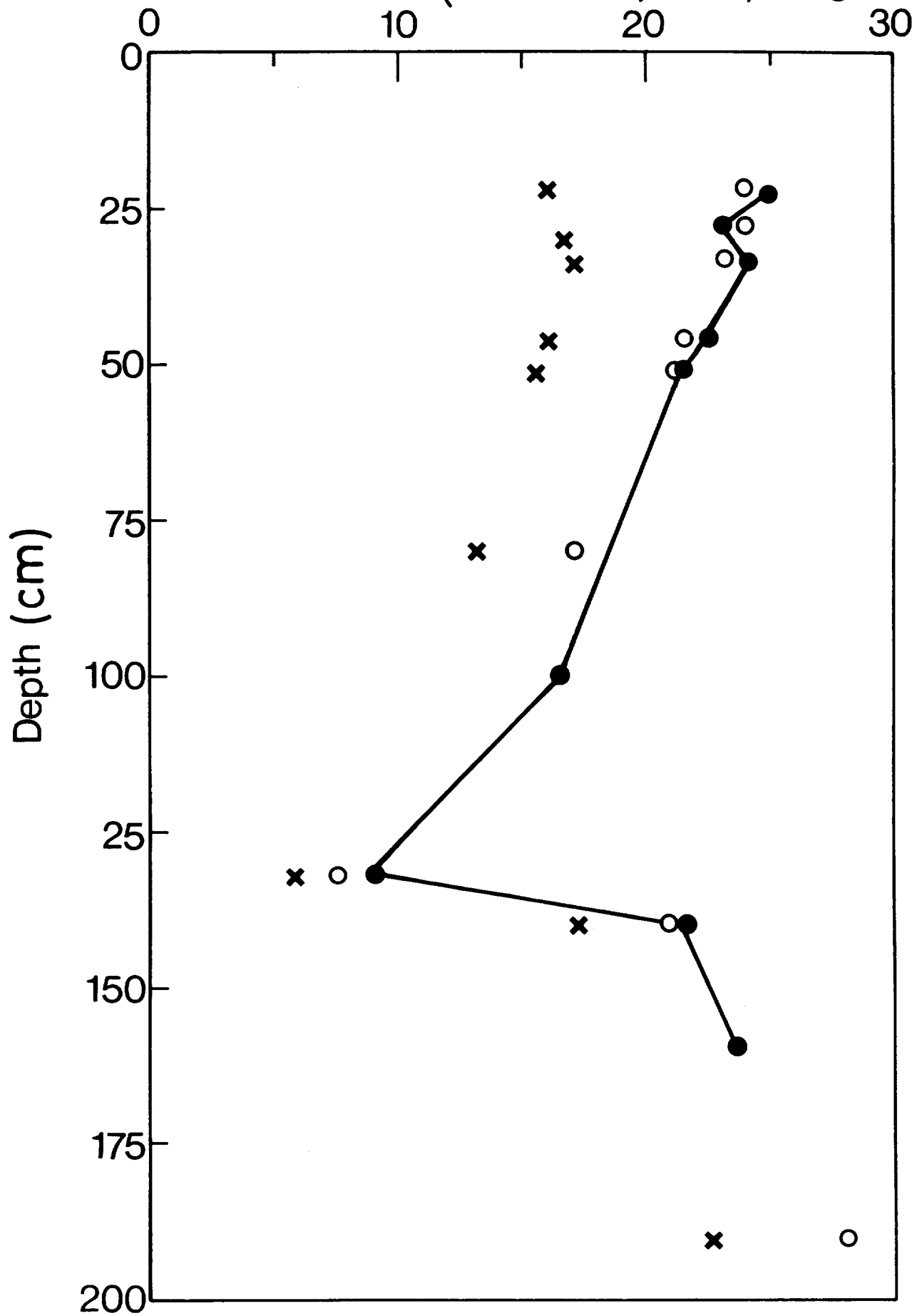
Figure 8  Sodium-22 method:  effect of various leaches on TCEC
         core 10554 11K.  Closed circles - before leach.  Open
         circles - after hypochlorite leach.  Crosses - after
         hypochlorite and oxalate leach.