PRELIMINARY STUDIES OF THE TOTAL CATION EXCHANGE CAPACITY OF SEDIMENTS FROM TWO NORTH ATLANTIC STUDY SITES

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Abstract

Initially four different methods of measuring total cation exchange capacity were compared. There were two chemical methods (ammonium saturation with displacement into seawater, and barium saturation followed by replacement with magnesium) and two radiochemical methods (sodium-22 and caesium-134 saturation). The barium-magnesium and sodium-22 methods were then applied to sediment samples from Core D10164#1K from the Nares Fracture Valley, and Core D10554#11K from the eastern flank of the Great Meteor Rise. The material at site 10164 is a pelagic clay whereas at site 10554 it is carbonate ooze. The total cation exchange capacities (T.C.E.C.) of samples from the two sites are similar when measured by the sodium-22 method, the mean for Core 10164 was 21.7 meq/100g and 24.4 meq/100g for Core 10554. However for Core 10554 the barium-magnesium method gives a mean of 42.8 meq/100g. The difference in T.C.E.C. measured by the two methods appears to be due to the high calcite content of core 10554 sediment.

Measured exchange capacities are lower than in coastal sediments. In deep sea sediments organic matter either makes a very small contribution to the T.C.E.C. (core 10164) or actually blocks exchange sites (Core 10554). Amorphous oxides of iron and manganese contribute between 20 and 50% of the T.C.E.C.

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CONTENTS

1. INTRODUCTION

The degree to which radionuclides react with the surface of sediment particles as they migrate through the sediment will be of major importance in determining the effectiveness of sediment as a barrier to the release of radionuclides from an in-sediment repository into the overlying water masses. It is difficult to measure these processes directly. However if information can be gained from a more simple measurement of a particular sediment property, which can be directly related to the retention of migrating radionuclides by the sediment, then measurements of that property could be used as a "prospecting tool" for the identification of sites with high retentive capacity for radionuclides. It can be argued that the total cation exchange capacity is such a property. This argument is based on the assumption that the migrating radionuclide is in solution as a cation and that initially it will be retained at the sediment surface by electrostatic attraction.

For clay minerals and clay sized mineral grains there are three possible sources of cation exchange capacity on the surface of the minerals themselves (GRIM 1968). Broken bonds around the edges of silica alumina units give rise to unsatisfied charges which can be balanced by adsorbed ions. This is probably the major cause of exchange capacity for kaolinite minerals. Substitutions within the lattice structure result in unbalanced charges in the structural units of some clay minerals. In montmorillonites these give rise to about 80% of the exchange capacity. The third and a minor cause of cation exchange capacity is exchange with the hydrogen of structural hydroxyl groups. Exchange capacity due to broken bonds will increase with decreasing particle size, whereas exchange capacity due to lattice charges and structural hydroxyl groups is independent of changes in particle size. Exchange capacities of clay minerals range from about 1 meq/100g for well crystallized kaolinites to over 100 meq/100g for some montmorillonites.

In a detrital mineral assemblage such as a marine sediment the surface chemical properties of individual grains are modified by the presence of organic matter and coatings of precipitated amorphous oxides, as well as disruption of the surface by weathering reactions with the surrounding water. The extent to which the adsorptive properties of deep sea sediment are determined by these coatings is not known. Previously published measurements (McALLISTER 1964, RASHID, 1969, ROSENFELD 1979 and BOATMAN et al. 1982) were all made on coastal sediment, in which the organic matter and the oxides contributed considerably to the total cations exchange capacity, giving a material with an exchange capacity similar to that of montmorillonites. Organic matter present in sediments will tend to attach itself to exchange sites on the clay, and so mask the exchange properties of the core mineral (GREENLAND, 1971). Humic acids extracted from sediments have exchange capacities of several hundred meq/100g (SCHNITZER et al 1972, RASHID 1969). When they are present in a sediment the effective exchange capacity of that sediment will depend on how they are dispersed within it. The work of Hunter (1977) on the surface properties of particles in coastal waters suggests that carboxylate is the major functional group in the organic matter on these particles. The amorphous oxides are dominantly iron and manganese oxides. Defects in the structures of these oxides give rise to their exchange capacity. This is the most difficult phase to deal with because it will have a tendency to undergo both simple ion exchange (an electrostatic process as displayed by clay mineral and organic surfaces) which is rapidly reversible and specific sorption processes which may involve redox reactions between the adsorbed cation and the oxide (HEM 1977) which will not be simply reversible.

Deep sea sediments in general contain less organic matter, and oxide coatings might be expected to be less reactive by virtue of being older and so potentially more crystalline than in coastal sediments. It might therefore be expected that the exchange capacities of deep sea sediments will be lower than those of the coastal sediments studied so far. A further modification of the adsorption properties of deep sea sediments from those predictable from a knowledge of the continentally derived detrital mineral content will be caused by the admixture of biologically formed shell material. This will be silica and/or calcite (with some aragonite) and the amounts will vary geographically and with the depth of the overlying water column.

The work reported here compares the application of four different methods for measuring the total cation exchange capacity (T.C.E.C.), of pelagic sediments with differing calcite contents. The four methods chosen were, (a) ammonia exchange because this is traditionally the most frequently used cation in methods for measuring cation exchange capacity of soils and sediments; (b) the barium-magnesium compulsive exchange method (BASCOMB, 1964) because it is a chemically concise method, which apart from the radiochemical methods requires least handling and therefore causes least disruption of the sediment material: (c) and (d) radiochemical methods employing sodium-22 and caesium-134 respectively. Caesium-134 has been used previously for measurements of cation exchange capacity of sediments (BISCHOFF et al 1975, BOATMAN et al 1982) because it is readily adsorbed. However we considered sodium-22 to be worthy of investigation because use of a medium containing dominantly sodium ions would produce least change for marine sediments, for which the principal adsorbed cation _in situ_ is sodium (SAYLES et al., 1977). The purpose behind looking at a range of methods for measuring T.C.E.C. was two-fold. Firstly we wished to find a method which would give reliable results for a range of sediment types and, secondly we hoped by considering the consistency with which the different methods gave similar results to gain an insight into whether or not we were indeed measuring the cation exchange capacity of the sediment rather than a specific reaction between the various reagents and the sediment.

Initially the four different methods were compared through measurements on standard days and marine sediment. The barium-magnesium and sodium-22 methods were applied to a series of sediments from two study sites, which represent the two most common facies in the N. Atlantic - an abyssal pelagic clay from the Nares Plain, and a carbonate ooze from the Great Meteor East area. Chemical treatments of the sediment were then employed in conjunction with T.C.E.C. measurements to determine the extent to which the components of sediment - core minerals, organic matter and amorphous oxide coatings - contributed to the exchange capacity of the sediment.

2. THE SEDIMENTS

Core 10163#6K

This was a 1.85m Kastenlot core from a water depth of 5871m in the deep East Nares Abyssal Plain (23°43'N, 59°41'W). The core is composed of laminated brown and grey clays. The principal components are illite (45 to 55%) kaolinite (15 to 25%) quartz (10%) and chlorite (<10%). The calcite content was about 1% (wt % CaO), and organic carbon content was approximately 0.2% (wt % org C).

Core 10164#1K

This core is described in Figure 1. It was a 2.0m Kastenlot core from a water depth 6135m in the Nares Fracture Valley (26°14'N, 60°20'W). The principal components are illite (40 to 50%) kaolinite (20 to 30%), quartz (5 to 10%) and chlorite (<10%). The calcite content increases to 4.4% (wt % CaO) in a grey turbidite layer between 50 and 130cm depth (see Figure 2).

Core 10554#11K

This core is described in Figure 3. It was a 4.0m Kastenlot core from a water depth of 5370m on the Eastern Flank of the Great Meteor Rise (31°30'N 24°30'W). It is dominantly calcite, varying between 50 and 55% except between 30 and 60cm where it falls to a minimum of 20% in the 35 to 37cm section (see Figure 2). In this low calcite region the quartz content increases to between 4 and 9%., Elsewhere in the core quartz content is between 1.5 to 4%. The clay minerals present are dominantly illite and kaolinite.

3. METHODS

3.1 MEASUREMENT OF T.C.E.C.

The four methods of measuring T.C.E.C. employed in this work are described below.

Ammonia exchange (SAYLES et al., 1977)

Reagents 80% methanol in distilled water. 1M ammonium chloride, in 80% methanol 0.01M ammonium chloride, in distilled water adjusted to pH8, with a measured amount of dilute ammonia solution, calculate final ammonia concentration after pH adjustment. Filtered surface sea water.

Method Weigh (0.5 to 2g) sediment (wt B) into weighed 30ml centrifuge tube (wt A). Rinse three times with 25ml, 80% methanol. After each rinse centrifuge and decant off the supernatant liquid. Rinse twice with 25ml of 1M ammonium chloride, with the second rinse carried out over night. Rinse three times with 0.01M ammonium chloride. After each rinse centrifuge and decant off the supernatant liquid. Weigh the wet sediment (wt C). Rinse and centrifuge three times with seawater. Collect and combine the supernatants and measure the total volume (V ml). Weigh centrifuge tube and wet sediment (wt D). Dry sediment to constant weight (wt E). Measure the ammonia content and change in proton content (as the change in alkalinity) of the seawater. Ammonia concentrations were measured using an E.I.L. ammonia specific ion electrode. All alkalinities were measured by titration with dilute hydrochloric acid.

Calculation Final weight of sediment corrected for dried sea salt (F)
is $F = (E - A) - [(D - E) \times 0.025]$ ml.
corrected final volume of seawater v is
$v = V + [(D - E) \div 1.035]$ ml.
Corrected ammonia in v due to carry over from 0.01M ammonium chloride rinses.
correct $[NH_4]$meq = (measured $[NH_4]$ x v)-0.01 x [C-(F+A)]
$\mathrm{TCEC} = \frac{\text{corrected } (NH_4) + \Delta\text{alkalinity}}{F} \times 100$ (meq/100g)

Barium magnesium compulsive exchange (BASCOMB 1964)

Reagents

80% methanol
0.5N barium chloride, in 50% methanol
0.08N magnesium sulphate, aqueous solution

Method

Weigh (0.5 to 2g) of sediment (wt B) into weighed centrifuge tube (wt A). Rinse three times with 80% methanol, after each rinse decant and discard the methanol. Rinse three times with 0.5N barium chloride, with third rinse being carried out overnight. Rinse with distilled water. Weigh wet sediment. resuspend in 12.50g distilled water, add 12.50g 0.08N MgSO4, shake overnight. Centrifuge and collect supernatant for magnesium analysis. Weigh wet sediment (wt D) and dry to constant weight (E). Magnesium was determined by flame atomic absorption. Measure volume (V) and density (D) of supernatant magnesium sulphate solution.

Calculation

corrected volume of supernatant MgSO4 solution v = V+(C - E)ml.
For measured Mg concentration meq/l = M
Change in equivalent of Mg present Δ Mg meq.
Δ Mg meq = (0.08 x 12.5) - (M x V) meq.
Exchange capacity = $\dfrac{\Delta \text{ Mg}}{E\text{-}A} \times 100$ (meq/100g)

Sodium-22 radiochemical

Reagents

80% Methanol.
0.5N Sodium chloride aqueous solution
0.5N Sodium chloride aqueous solution containing 3μCi/l.

Method

Weigh sediment (wt B) into a weighed centrifuge tube (wt A). Rinse twice with sodium chloride solution, shaking for 15 minutes after each addition of solution. Rinse three times with sodium-22 chloride solution. Shaking for 15 minutes after each addition. Rinse four times with 80% methanol. After final centrifuging weigh wet sediment, and then count (C) the sodium-22 retained in the sediment in a gamma radiation counter. Then dry the sediment to constant weight (D). Count (K) a known volume (V) of the sodium-22 chloride solution.

Calculation Counts per equivalent of sodium $K' = \frac{K}{0.5 \times V}$

Counts per gram of sediment $C' = \frac{C}{D-A}$

Exchange capacity $= \frac{C'}{K'} \times 100$ meq/100g

Caesium-134 Radiochemical

The procedure was the same as for the sodium-22 method except that 0.5N caesium chloride solutions were used.

3.2 LEACHING STUDIES

A range of methods have been proposed for the removal of both organic matter and oxide coatings from sediments. For these experiments we chose, on the basis of the results of earlier measurements (HYDES, 1983), to use sodium hypochlorite solution to remove organic matter and an ammonium oxalate - oxalic acid solution to remove amorphous oxides.

Hypochlorite Leach

Reagents	Sodium hypochlorite solution, adjusted to pH 8.5 (5ml of 6 N. HCL to 100ml).
Method	Weigh 0.5g of sediment into a 13ml centrifuge tube. Add 10ml of mixed oxalate solution. Shake for 2 hours. Centrifuge

Oxalate Leach

Reagents	(A) 0.2M Ammonium oxalate aqueous solution (28.4g/1). (B) 0.2M oxalic acid aqueous solution (25.2 g/1). Mix 700ml of (A) with 535ml of (B) to give a pH 3.0 solution.
Method	Weigh 0.5g of sediment into a 13ml centrifuge tube. Add 10ml of mixed oxalate solution. Shake for 2 hours. Centrifuge.

4. RESULTS AND DISCUSSION

4.1 Comparison of methods

The ammonia and barium-magnesium methods were compared for two standard clays, montmorillonite (API, SWY-1) and kaolinite (API KGa-1) obtained from University of Missouri Source Clay Minerals Reository, and a series of samples of dried sediment from different depth intervals from Core 10163. The results shown in Tables I and II show broadly similar cation exchange capacities are obtained by both methods. The results from the ammonia method determinations are in each case higher, but more importantly both methods show the same trends in changes between different levels in the material from Core 10163. On the basis of these results and the greater ease of use of the barium-magnesium method no further use was made of the ammonia method.

When the sodium-22 method was applied to the standard clays the results compared well with those obtained with the barium-magnesium and ammonia methods (Table I). The barium-magnesium and sodium-22 methods give a markedly lower value for the kaolinite than does the ammonia method. For the ammonia method a large component of apparent exchange at this low level is accounted for by the measured change in alkalinity. This may correspond to reactions other than simple exchange, and so give a result which is different to that obtained by the barium-magnesium, and sodium-22 methods.

Our sodium-22 method was compared with the caesiun-134 method which has been used previously for the measurement of exchange capacity (BISCHOFF et al., 1975). The results from the two methods for standard clays were within the precision of the analysis indistinguishable. This was also the case when the two methods were applied to "wet" sediment from Core 10164. (See Table III). The good comparability of the sodium-22 and caesium-134 methods is an indication that they both measure a reproducible property of the sediment.

4.2 Preliminary treatment of samples

A point which has been emphasised by the results of BOATMAN et al., 1982 is that the exchange capacity of coastal sediments is very sensitive to the way in which the material is handled. Boatman and Murray noted a decrease of about 50% in the exchange capacity when the sediment was either frozen or dried. To investigate the significance of sample handling for deep sea sediments, material from two horizons from Core 10164, which had been stored at 4°C was subdivided into three portions. The first portion was maintained wet, a second portion was freeze dried and then lightly ground by hand in an agate mortar, and the third portion was oven dried at 110°C and then ground in a ball mill. The exchange capacity of duplicate subsamples of these materials was then measured by the barium-magnesium method. The results shown in Table IV show the reverse effect to that seen by Boatman and Murray. Material from the 21-23cm depth level show little change with treatment, but the dried samples from the 130-132cm level show a large increase in exchange capacity. Samples from a larger number of depths from this core were compared using the sodium-22 method, for sediment which had been stored at 4°C ("wet") sediment and sediment which had been oven dried at 110°C. These results (Table V) are in line with what is observed for coastal sediment, but the size of the effect is smaller. The dried sediment exchange capacity is between 5 and 20% lower than that of the "wet" sediment. The T.C.E.C. of this sediment is lower than that reported for coastal sediments, which probably reflects the ageing of the surface of this material to produce a less reactive surface. This in turn is reflected in the results shown in Table V, drying the sediment having a smaller effect on this more "refractory" material than it does for coastal sediments. The discrepancy between results obtained when "wet" and dried sediment are compared using the barium-magnesium and sodium-22 method is probably explained by the fact that, as discussed below, during application of the barium-magnesium method reactions other than simple cation exchange can take place between these divalent cations and the sediment surface. Further when the two methods were applied to all the samples from this core it turned out that we had chosen for the measurements in Table IV the two depths for which the methods disagreed most widely.

4.3 Contribution of calcite to exchange behaviour

A further investigation of the effects of changes in the methodology was carried out for both methods to look at the effect of reaction time on the measured T.C.E.C. of material from Core 10554. The sodium-22 method was found to be insensitive to the reaction time, whereas the barium-magnesium method was very sensitive to changes in both the reaction time and the size of reaction tube used (Figure 4). This second point is probably as a result of more vigorous agitation in the large sized reaction tubes. The dependence of the results of the barium/magnesium method on reaction time is most marked where there is greatest overall difference between the results obtained by the sodium-22 and barium-magnesium methods.

Both the sodium-22 and barium-magnesium methods were applied to samples from Cores 10554 and 10164. The T.C.E.C.

measured by these methods is plotted against depth for the samples measured in Figures 5 and 6. A clear offset between the two methods occurs for Core 10554 whereas the results from Core 10164 are similar down the length of the core except as already noted at 21-23cm and 130-132cm depth.

The most easily discernible difference between the materials in these two cores is in their calcite content (see Figure 2). If the difference in T.C.E.C. observed between the two methods is plotted against the calcium oxide content of the samples (which for these sediments is equivalent to plotting against the calcite content of the sediment) a clear linear relationship is seen (Figure 7). This suggests that the observed difference between the two methods is largely due to a specific interaction between barium and magnesium with calcite. That the measured barium magnesium T.C.E.C. is altered by changing both the times of reaction of barium and magnesium with the sediment (Figure 4) implies that it is predominantly an exchange reaction rather than simply the formation of a magnesium calcite phase. However a line plotted through the points shown in Figure 7 would not go through the origin, and two samples from Core 10164 repeatedly give values which are distinctly separate, from those observed at other levels in this core, these points suggest that a specific reaction of barium and magnesium with calcite can only be a partial explanation of the differences between the two methods. However at this stage we have no explanation for the high values seen at 21-23cm and 130-132cm in Core 10164. We can only note that the material from 130-132 is the base of the turbidite layer and was distinctly coarser grained than the surrounding material. This would normally be expected to produce a reduction in the T.C.E.C. because this material would have a relatively low surface area, which is what is observed in the sodium-22 measurements.

4.4 Contribution of organic matter to T.C.E.C.

As noted in the introduction it is not clear from previous observations whether or not we would expect organic matter in these sediments to make a positive or a negative contribution to the T.C.E.C.

The organic carbon content of these sediments are plotted against depth in Figure 8. In Core 10164 the organic carbon content increases with the calcite content in the turbidite layer, while the T.C.E.C. decreases. In this case any increase in T.C.E.C. due to increased organic carbon content may be being masked by an increase in the coarseness of the sediment. For Core 10554 the minimum in the calcite content corresponds to the maximum in organic carbon content. Both these factors, an increase in organic carbon and a decrease in sediment grain size would be expected to produce an increase in the T.C.E.C., and a maximum is seen where it would be expected in the sodium-22 measurements for this core. The maximum in the sodium-22 measurements and the minimum in the barium-magnesium measurements are uncoupled in Core 10554. This offset may be due to the organic carbon content producing a larger increase in the T.C.E.C. at 35-37cm than the fall in calcite content produces a decrease in the T.C.E.C. measured by the barium-magnesium method.

More direct evidence of the contribution of organic matter to the T.C.E.C. of sediment can be gained by selective removal of organic material from the sediment. The selection of leaches used was described in an earlier I.O.S. Report No. 157. Two leaches, one to remove organic coatings and one to remove amorphous oxide coatings were applied sequentially to sediment from Cores 10164 and 10554 and the T.C.E.C. was measured after each leach was completed. The results of these determinations are shown in Figures 9 and 10. Table VI, lists the organic carbon, maganese oxide and iron oxide content of the sediment and the changes in T.C.E.C. due to the leaches. These results suggest that organic matter makes very little contribution to the T.C.E.C. of sediment from Core 10164 and that in Core 10554 organic matter is actually blocking exchange sites. The largest changes in T.C.E.C. correspond to the samples containing the highest organic matter content. However outside the region between 40 and 60cm depth in Core 10554 where the organic carbon content exceeds 1%, the organic carbon content of this core is less than that in Core 10164. The T.C.E.C. of 10164 material shows little change on removal of organic matter whereas, even those sections of Core 10554 containing as little as 0.2% organic carbon show an increase in exchange capacity of about 6 meq/100g. This suggests two things either the organic material present in Core 10554 is dispersed differently to that in Core 10164 and/or its nature is different. The other possibility which must be borne in mind is that when any procedure such as a chemical leach is carried out on a natural mineral assemblage it will effect on the physical form of that assemblage. The amorphous coatings on mineral grains tend to cement individual grains together, so that removal of the coatings will increase the number of grains in the assemblage and concomitantly the surface area and the T.C.E.C. of the assemblage. Experiments on other sediments presented in I.O.S. Report No. 157 (Hydes 1983) demonstrated the importance to the interpretation of the results of leaching experiments of considering disaggregation of the sediment. These earlier results showed that when the order of application of the hypochlorite and oxalate leaches was compared, which ever leach was applied first increased the exchahge capacity and then the subsequent leach reduced exchange capacity. A suggested explanation for the above results is that the consistently high increase in T.C.E.C. seen down Core 10554 when organic matter is removed is that the material in this core which is coarser than in Core 10164 is disaggregated by the leach and that this process dominates over the effect of organic matter removal. For Core 10164 either removal of organic matter or disaggregation are unimportant, or the two processes are in balance.

4.5 Contribution or amorphous oxides to T.C.E.C.

The change in T.C.E.C. due to the removal of amorphous oxides is shown in Figures 8 and 10. For the material from both cores the decrease in exchange capacity is significant. Figures 11 and 12 show plots of the change in exchange capacity due to the oxalate leaches against the manganese and iron oxide contents of the sediment. Iron is present at greater concentrations than manganese throughout the sediment of both cores, and in Core 10154 the plots in Figure 12 suggests that the iron is making the more significant contribution to the T.C.E.C. However the suggestion from the plots Figure 11 for Core 10164 is that for this material manganese oxides are dominant over iron oxides in their contribution to the T.C.E.C. of the sediment. What this implies is that the formation of the coatings in the two cores must have been different:- either due to different diagenetic histories in the two cores or due to hydrogenous fluxes of the metals to these two sites being different.

5. CONCLUSIONS

All four of the methods used in this work produce similar results for the total cation exchange capacity of standard clays and clay rich marine sediments. This demonstrates that we are indeed measuring the number of ionic exchange sites on the surfaces of the grains of these materials. The comparability of the results breaks down in calcareous sediments, where the barium-magnesium method yields a substantially higher apparent T.C.E.C.

The exchange capacities measured by the sodium-22 method - means for Cores 10164 and 10554 were 21.7 and 24.4 meq/100g respectively - are similar to what would be expected for illite the predominant clay material in these sediments (GRIM 1968). This suggests that although there is a considerable amount of amorphous material present in these sediments it does not have an overwhelmingly high exchange capacity. The indication from chemical leaches is that organic matter only makes a small contribution to the exchange capacity of these sediments, or may even be blocking exchange sites. Interpretation of the data from the hypochlorite leaches to remove organic matter is complicated by the possibility that observed changes may have been dominated by the breaking up of particle aggregates rather than the removal of organic matter.

The results of the removal of amorphous oxides suggests that for the material in both cores this phase makes a substantial contribution, of between 20 and 50 percent of the T.C.E.C., in excess of the T.C.E.C. of the underlying mineral assemblage.

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TABLE I

Exchange capacity of standard clays, determined by (A) NH_4 exchange, (B) Ba/mg exchange and (C) Na-22 exchange. (3 subsamples measured at same time.)

Clay	NH_4 meq/100g	Ba/Mg meq/199g	Na-22 meq/100g
Kaolin	3.0	2.6	1.4
	3.0	1.2	1.4
	2.9	1.1	1.2
Montmorillonite	87.5	79.5	86.1
	85.9	78.2	86.1
	84.4	70.0	84.6

TABLE II

Comparison of the application of the NH_4 and the Ba/Mg methods to determination of T.C.E.C. samples from Core 10163.

Sample Depth cm.	NH_4 meq/100g	Ba/Mg meq/100g
5-7	18.5	18.5
	20.1	17.6
59-61	29.5	25.9
	30.4	24.6
129-131	20.6	17.2
	20.6	17.3
179-181	17.2	15.8
	16.3	16.4

TABLE III

Comparison of the application of the Cs-134 methods to that of the Na-22 and Ba/Mg to measurement of T.C.E.C. of "wet" sediment from Core 10164. Results for individual analyses.

Sample Depth cm	Cs-134 meq/100g	Na-22 meq/100g	Ba/Mg meq/100g
33-35	24.7	24.4	22.8
	25.3	24.1	22.5
45-47	22.4	22.0	20.6
	20.7	22.8	20.5
99-101	16.8	17.2	16.9
	16.4	16.6	17.0
130-132	9.5	8.6	23.2
	9.6	9.3	21.2

TABLE IV

Comparison of the different sample treatments prior to measurement of T.C.E.C. samples from Core 10164.

Sample Depth cm	Wet Stored 4°C	Freeze Dried	Oven Dried 110°C
21-23	40.9	39.9	42.7
	35.7	38.4	40.9
130-132	23.2	36.0	36.2
	21.2	33.6	35.8

TABLE V

Comparison of the results of measuring the T.C.E.C. of sediment from Core 10164 which was stored "wet" at 4°C until measurement and sediment which had been dried at 110°C measured using Na-22.

Sample Depth	Exchange Capacity meq/100g "wet"	Dried 110°C
33-35	24.4	23.4
	24.1	23.5
45-47	22.0	20.4
	22.8	20.7
50-52	21.2	20.2
	21.5	21.2
130-132	8.6	7.4
	9.3	7.4
139-141	21.1	20.5
	21.6	20.4

TABLE VI

Listing of the Corg, MnO, and Fe_2O_3 contents of the samples from Cores 10164 and 10554, and the change in T.C.E.C. after leaches to remove organic matter and amorphous oxides.

Core 10554

Sample Depth cm	Corg wt%	ΔT.C.E.C. Hypochlorite meq/100g increase	MnO Wt%	Fe_2O_3 Wt%	ΔTEC Oxalate meq/100g decrease
5-7	0.40	+5.9	0.05	2.64	4.9
15-17	0.15	5.6	0.05	2.69	5.0
25-27	0.25	10.2	0.15	4.95	9.7
35-37	1.75	13.6	0.21	6.46	12.4
45-47	1.30	10.8	0.04	5.03	11.4
55-57	0.20	8.2	0.03	4.66	7.4
75-77	0.20	6.9	0.05	3.89	8.9
95-97	0.10	10.4	0.07	3.69	13.4

Core 10164

		increase			decrease
27-29	0.10	0.3	0.32	8.11	7.0
33-35	0.16	-0.3	0.48	7.58	6.1
45-47	0.25	0.9	0.12	7.99	5.4
50-52	0.37	0.8	0.06	8.21	6.1
79-81	0.64	1.2	0.09	7.35	3.8
130-132	0.44	0.1	0.06	4.38	1.8
139-141	0.30	1.3	0.11	7.70	4.6
191-193	0.21	0.6	0.24	7.80	6.0

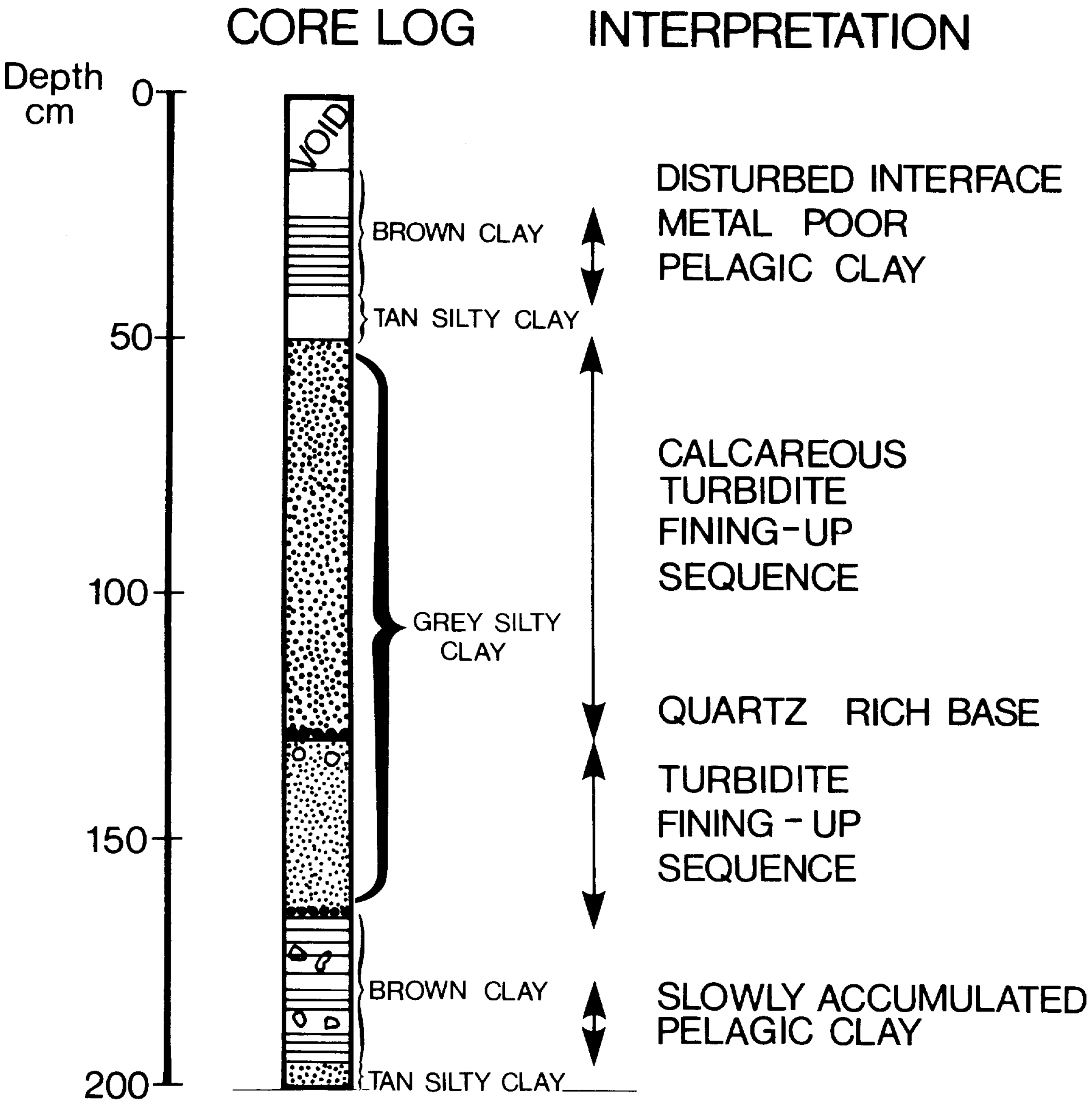
FIGURE CAPTIONS

1. Description of Core 10164#1K from Nares Fracture Zone.
2. Variation in CaO concentration with depth in O Core 10554 and O Core 10164.
3. Description of Core 10554#11K from the Great Meteor Rise.
4. Variation in measured T.C.E.C. with changes in method,
   - ○ - Ba/Mg Large tubes (30ml) both rinses overnight
   - △ - Ba/Mg Small tubes (13ml) both rinses overnight
   - □ - Ba/Mg Small tubes (13ml) only Mg rinse overnight
   - ● - Na-22 15 minute shakes
   - ▲ - Na-22 final rinse overnight
5. T.C.E.C. measured in Core 10554 by
   - ● - Na-22 method
   - ○ - Ba/Mg method.
6. T.C.E.C. Measured in Core 10164 by
   - ● - Na-22
   - O - Ba/Mg method.
7. Plot of the difference in measured T.C.E.C. between the Ba/Mg method and the Na-22 method against CaO content of the bulk sediment for material from O - Core 10554 and X - Core 10164.
8. Variation in organic carbon content with depth in
   ● - Core 10164 and O - Core 10554.
9. Results of removing organic and amorphous oxide coatings. For Core 10164 variation with depth of the T.C.E.C. of sediment
   - ● - before leaching
   - O - after hypochlorite leach
   - X - after sequential hypochlorite and oxalate leaches.
10. Results of removing organic and amorphous oxide coatings. For Core 10554 variation with depth of the T.C.E.C. of the sediment
    - ● - before leaching
    - O - after hypochlorite leach
    - X - after sequential hypochlorite and oxalate leaches
11. Plot for Core 10164 of change in T.C.E.C. on removal of amorphous oxides against
    - ● - bulk MnO content of sediment
    - O - bulk Fe_2O_3 content of sediment.

12. Plot for Core 10554 of change in T.C.E.C. on removal of amorphous oxides against

    ● - bulk MnO content of sediment

    ○ - bulk Fe_2O_3 content of sediment.



DISCOVERY CORE : 10164#1K

Fig. 1

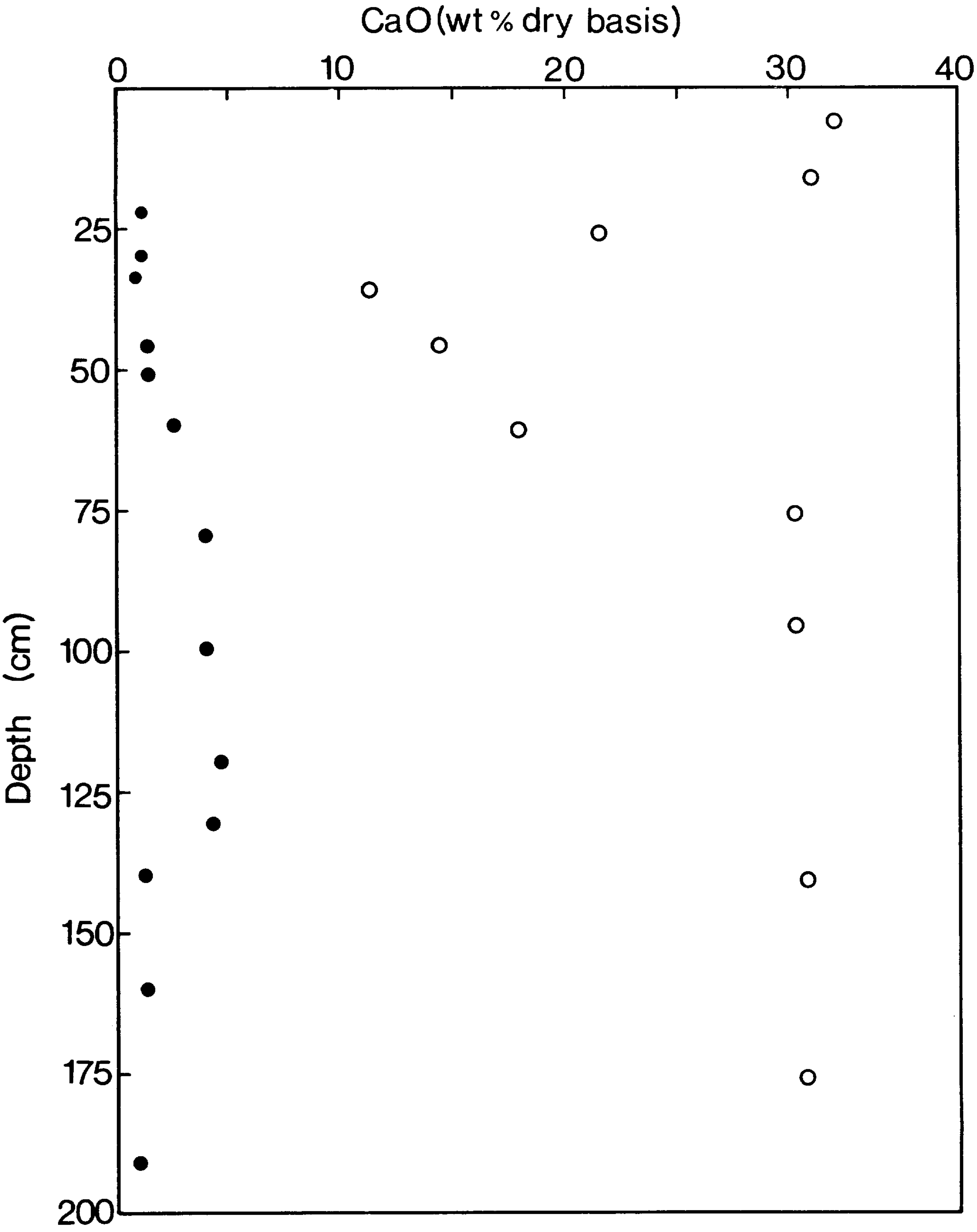

CaO (wt % dry basis)
0
10
20
30
40
Depth (cm)
25
50
75
100
125
150
175
200

Fig. 2

DISCOVERY CORE : 10554 # IIK.

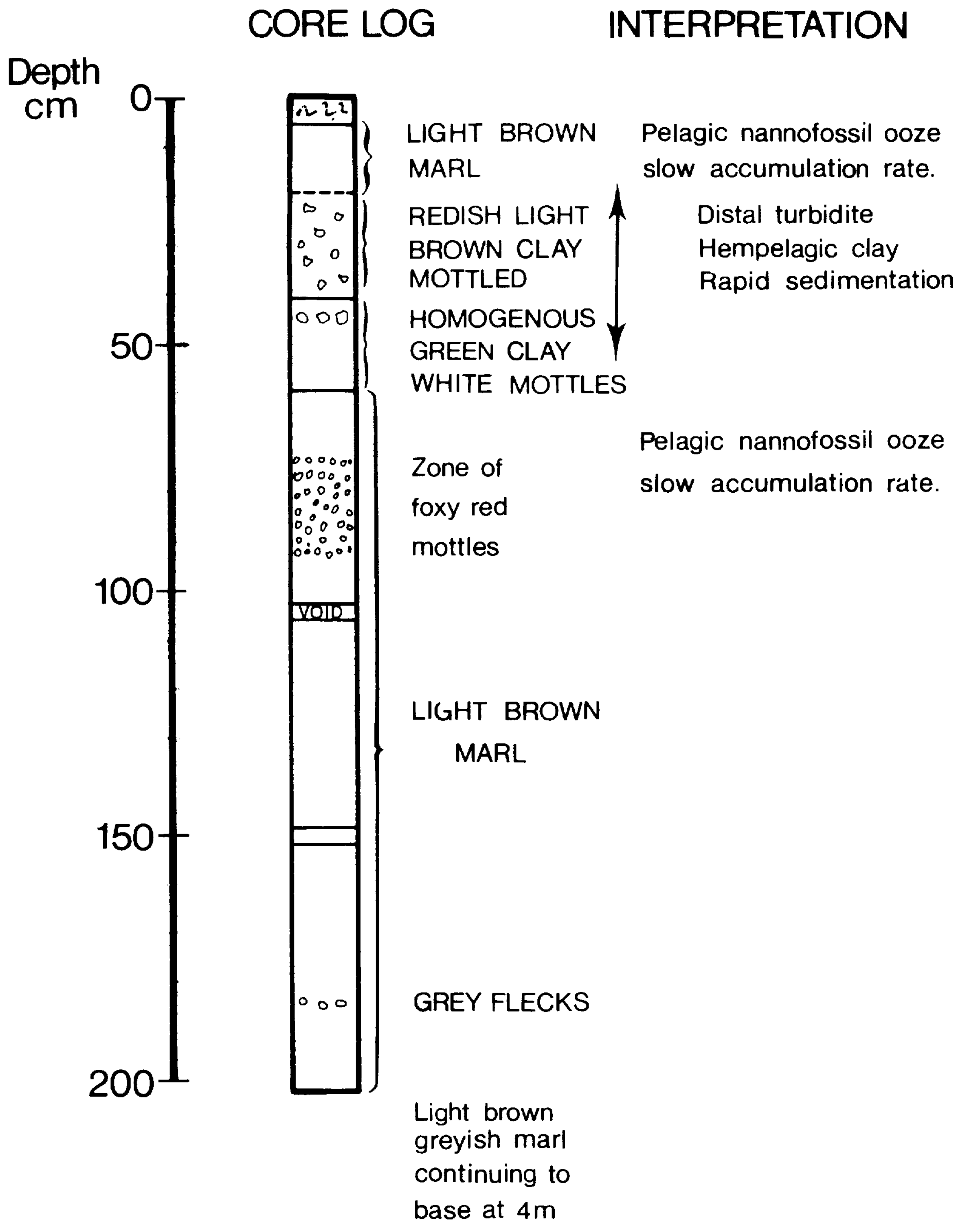


Fig. 3

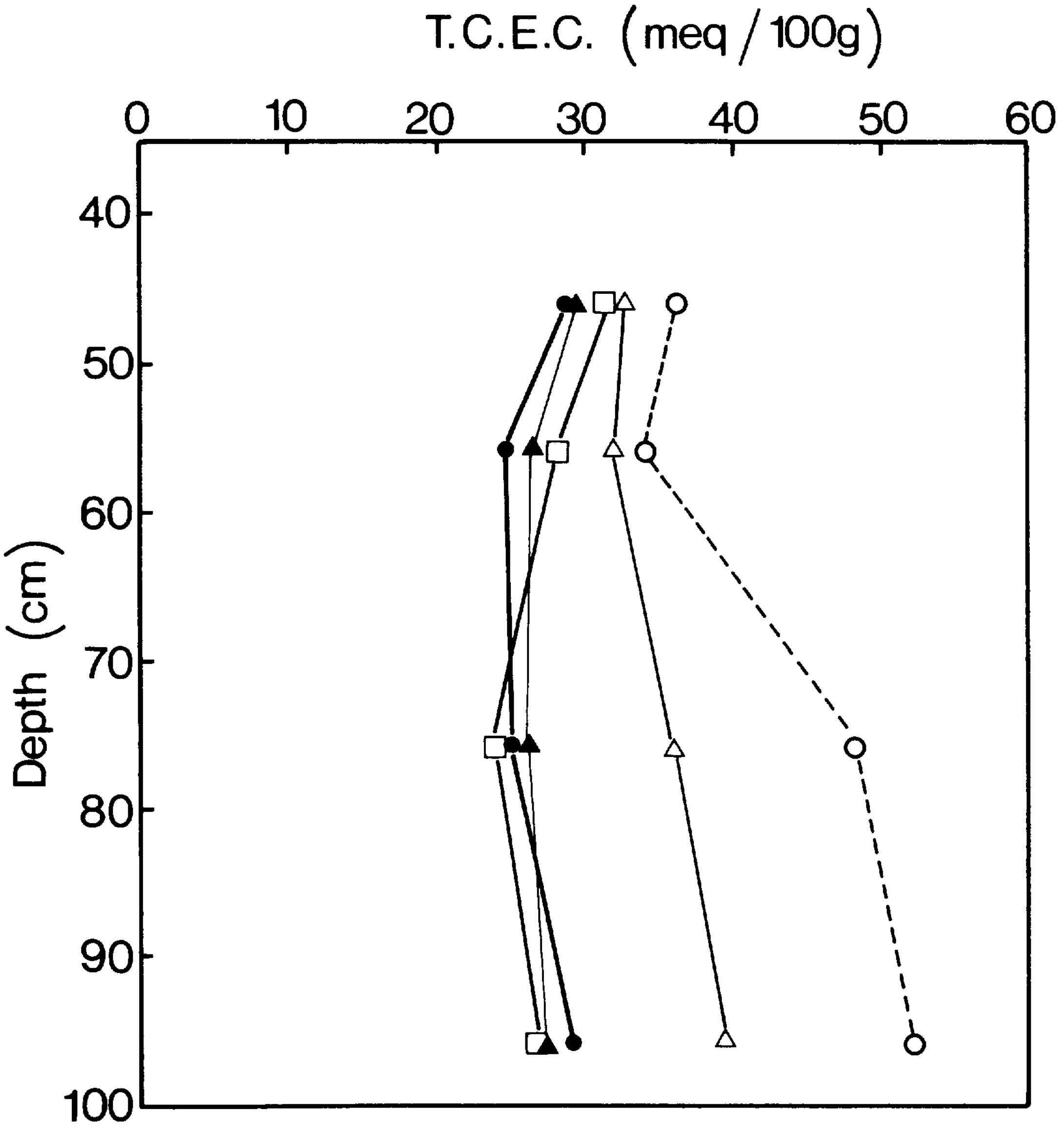


Fig. 4

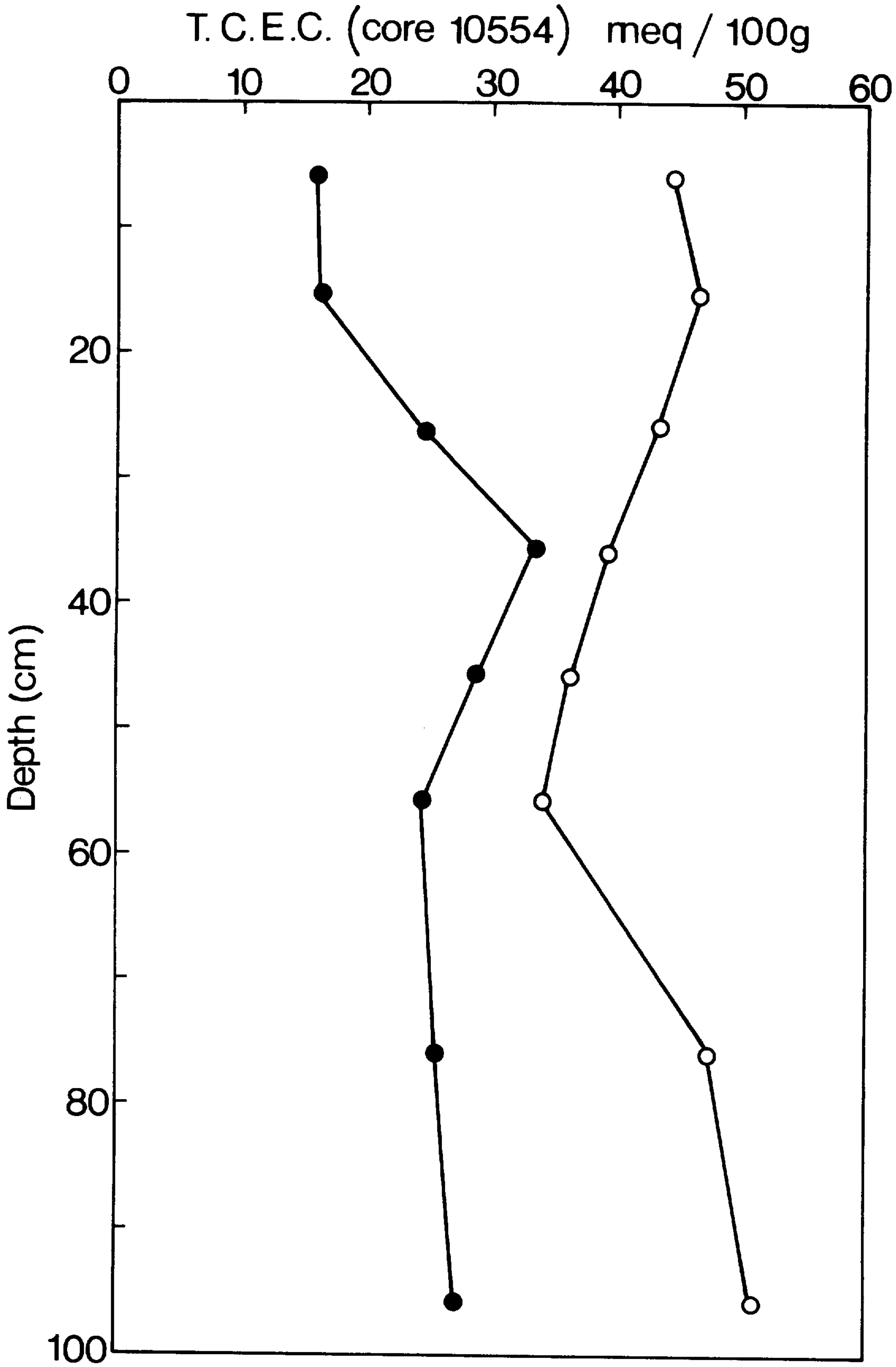

T. C.E.C. (core 10554) meq / 100g
0
10
20
30
40
50
60
Depth (cm)
20
40
60
80
100

Fig. 5

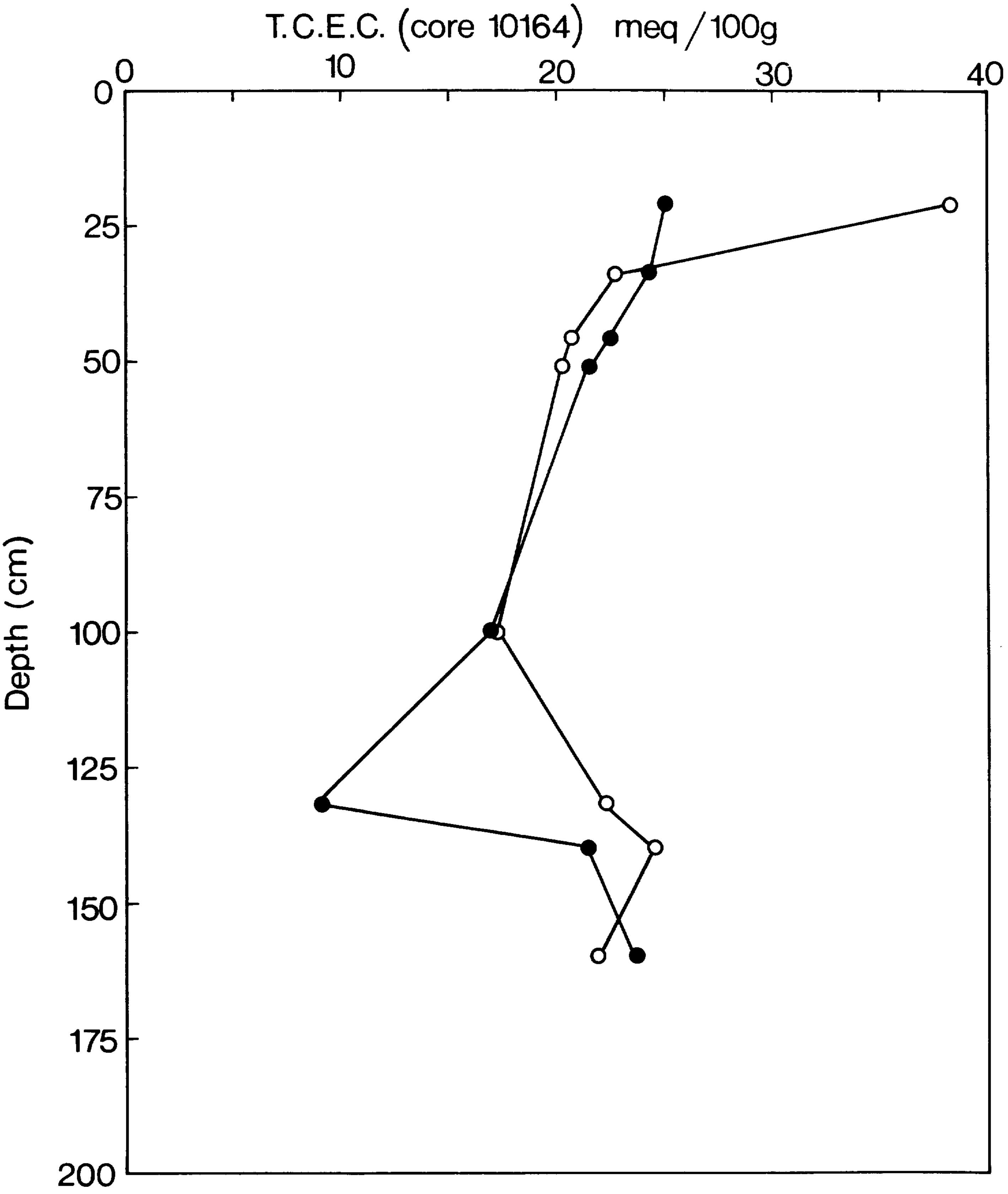

T.C.E.C. (core 10164) meq / 100g
0
10
20
30
40
0
25
50
75
100
125
150
175
200
Depth (cm)

Fig. 6

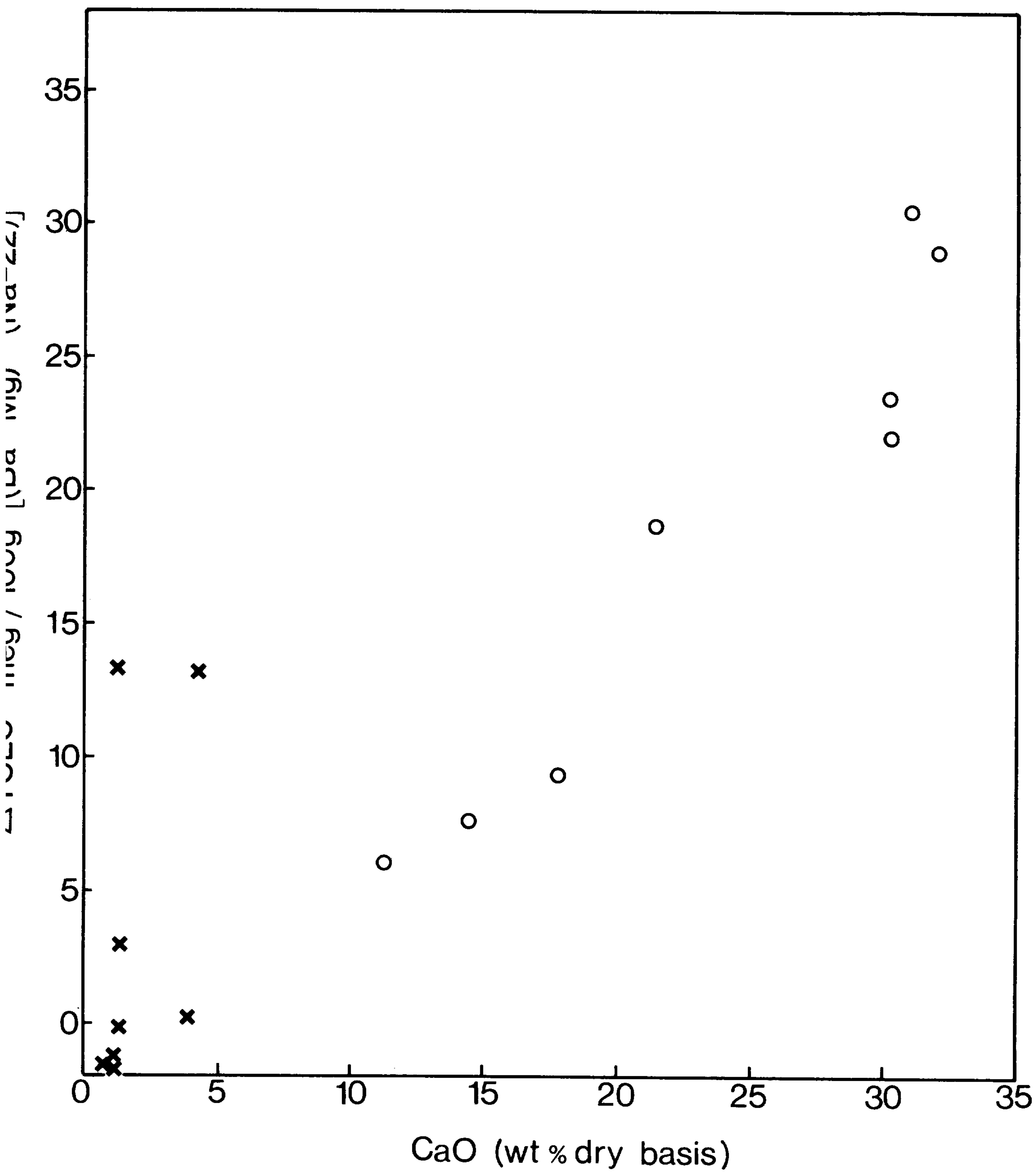


Fig. 7

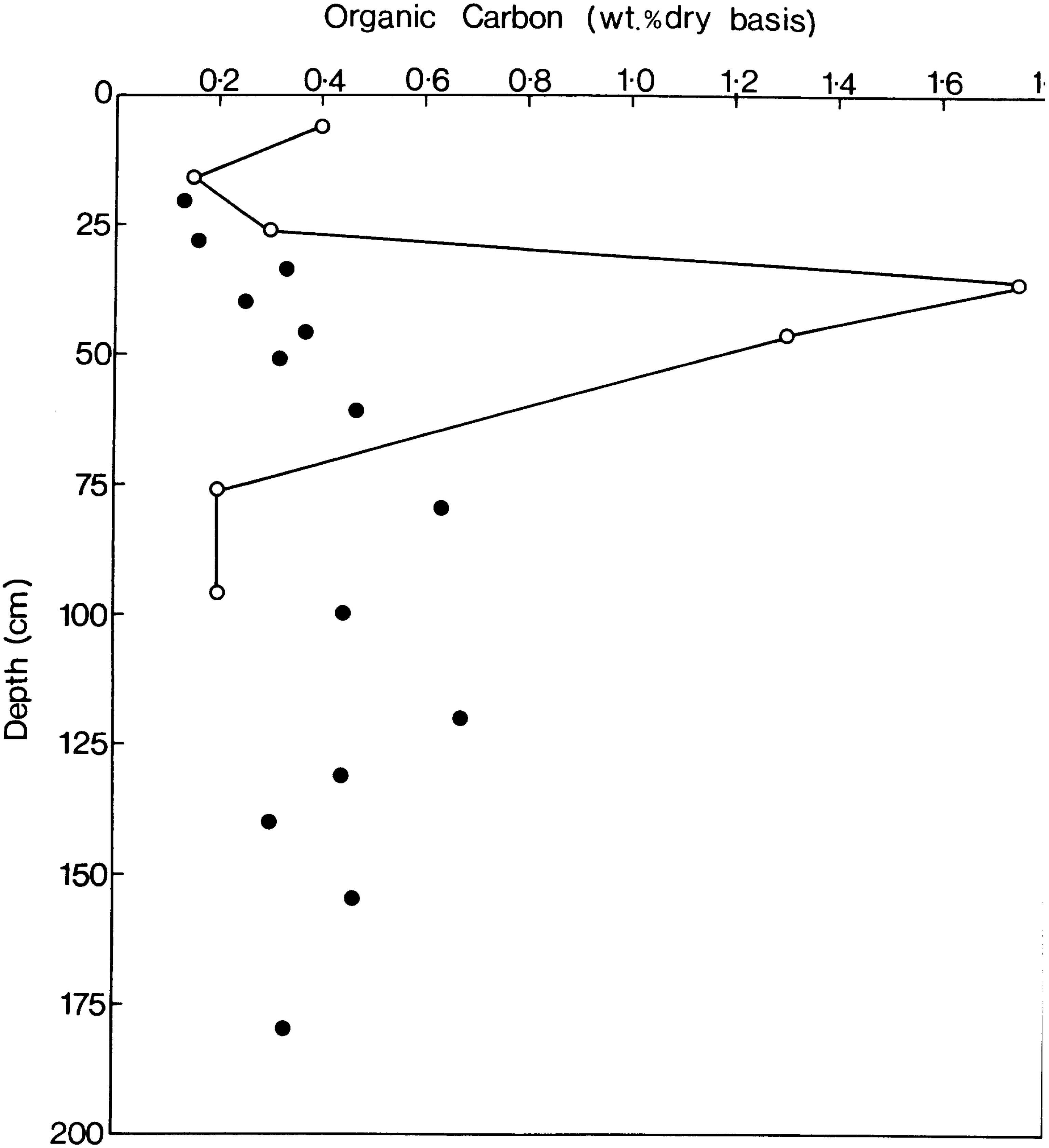

Organic Carbon (wt.%dry basis)
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·
0
25
50
75
100
125
150
175
200
Depth (cm)

Fig. 8

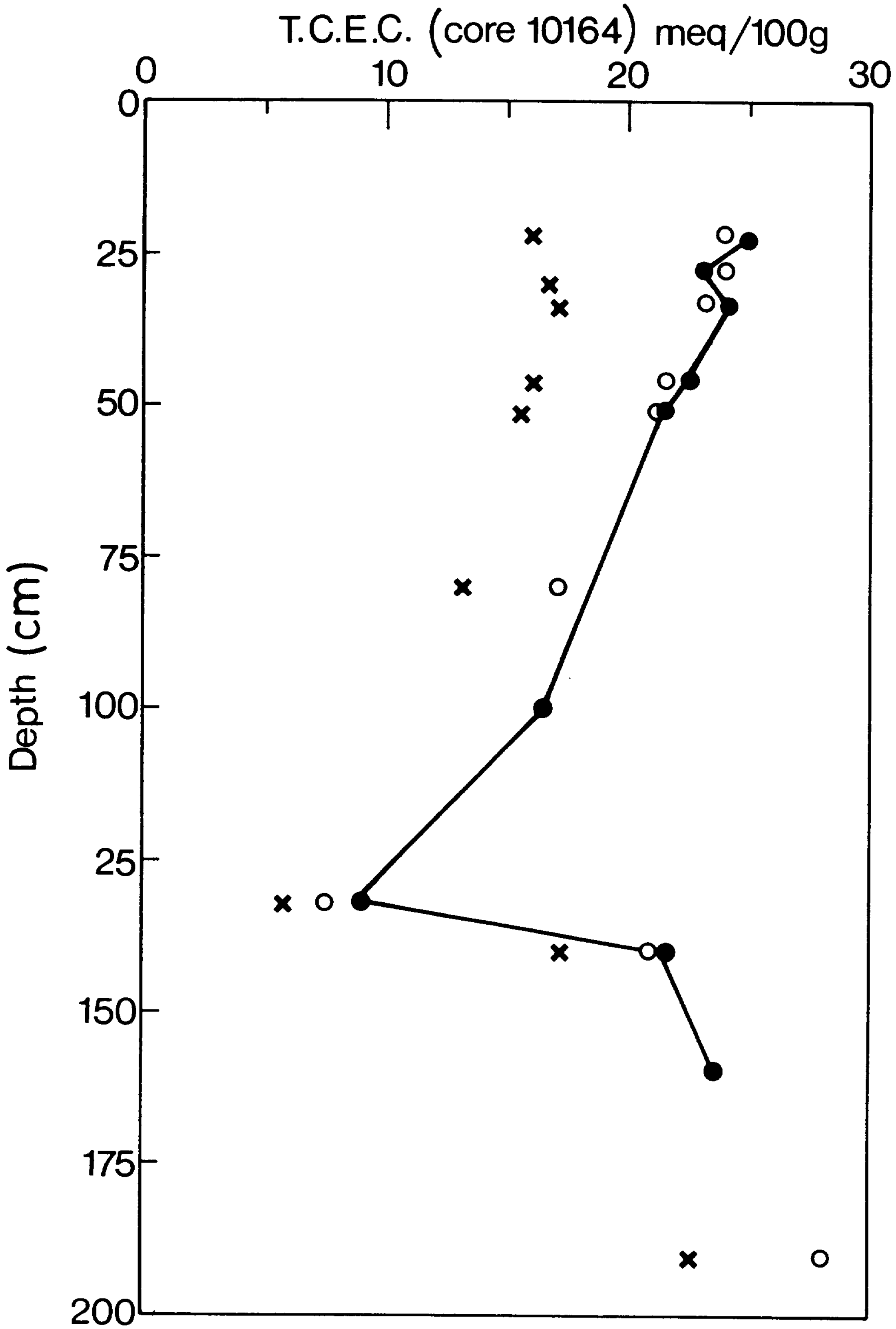

T.C.E.C. (core 10164) meq/100g
0
10
20
30
Depth (cm)
0
25
50
75
100
25
150
175
200

Fig. 9

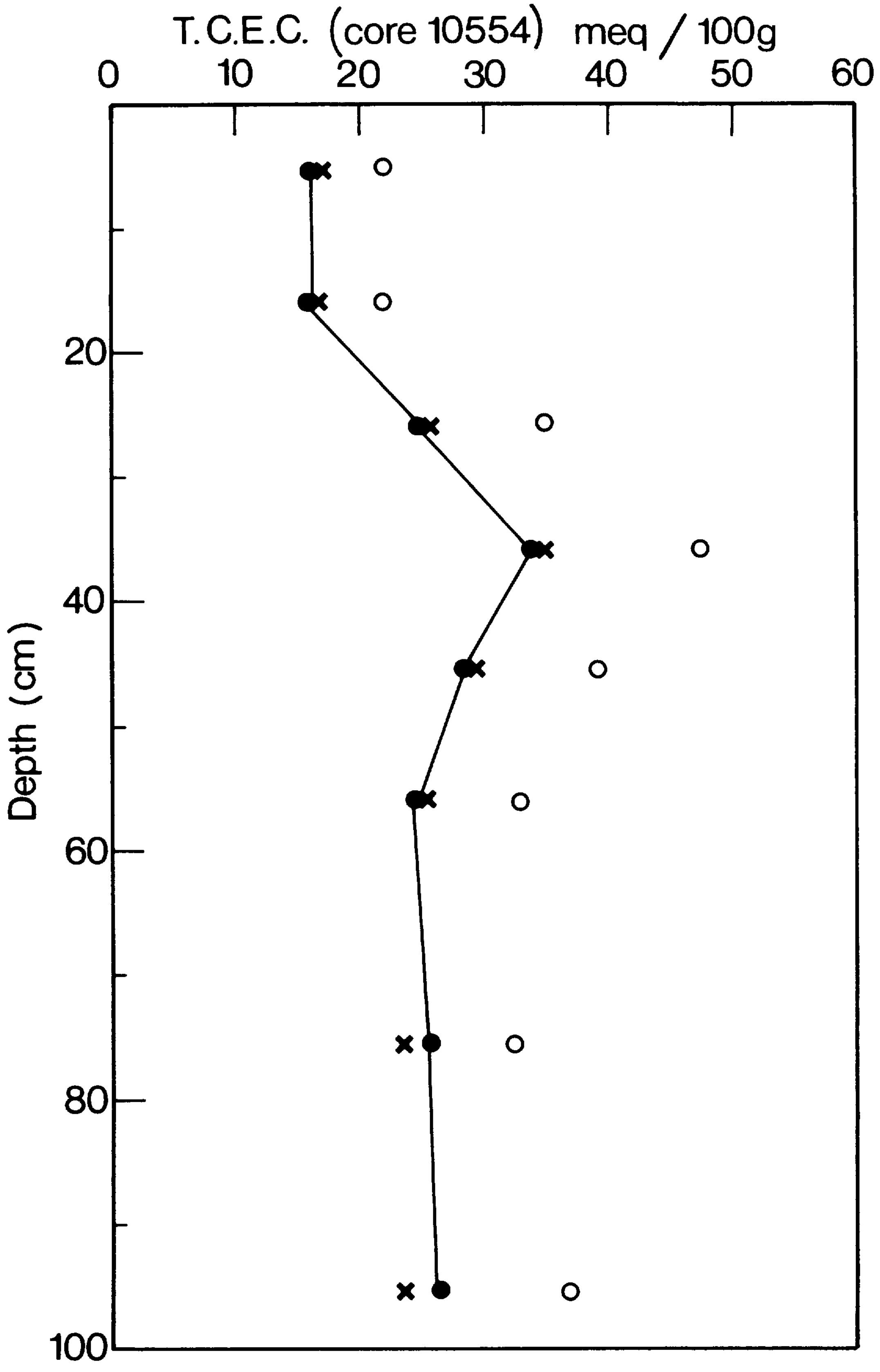

T.C.E.C. (core 10554) meq / 100g
0
10
20
30
40
50
60
Depth (cm)
20
40
60
80
100

Fig. 10

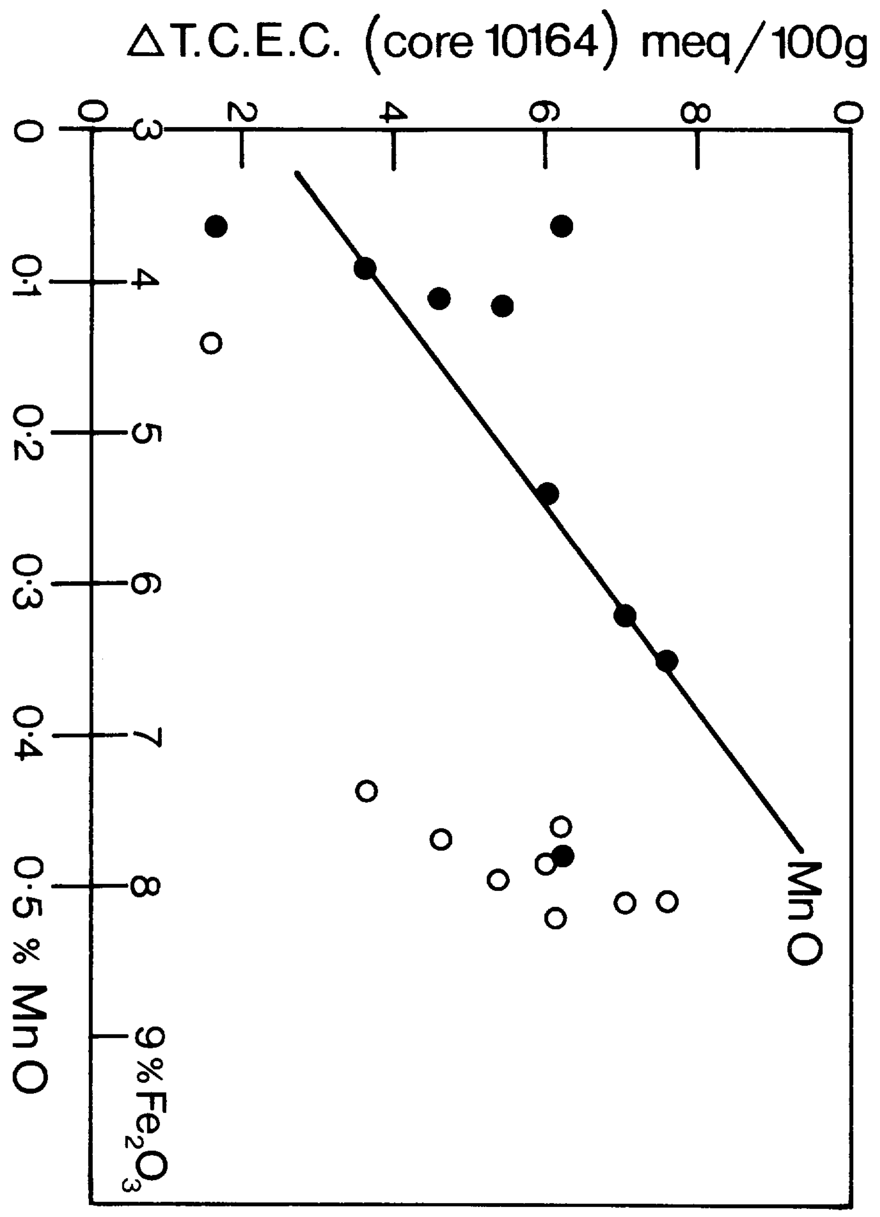

ΔT.C.E.C. (core 10164) meq/100g
0
2
4
6
8
0
MnO
0
0·1
0·2
0·3
0·4
0·5 % MnO
3
4
5
6
7
8
9 % Fe$_2$O$_3$

Fig. 11

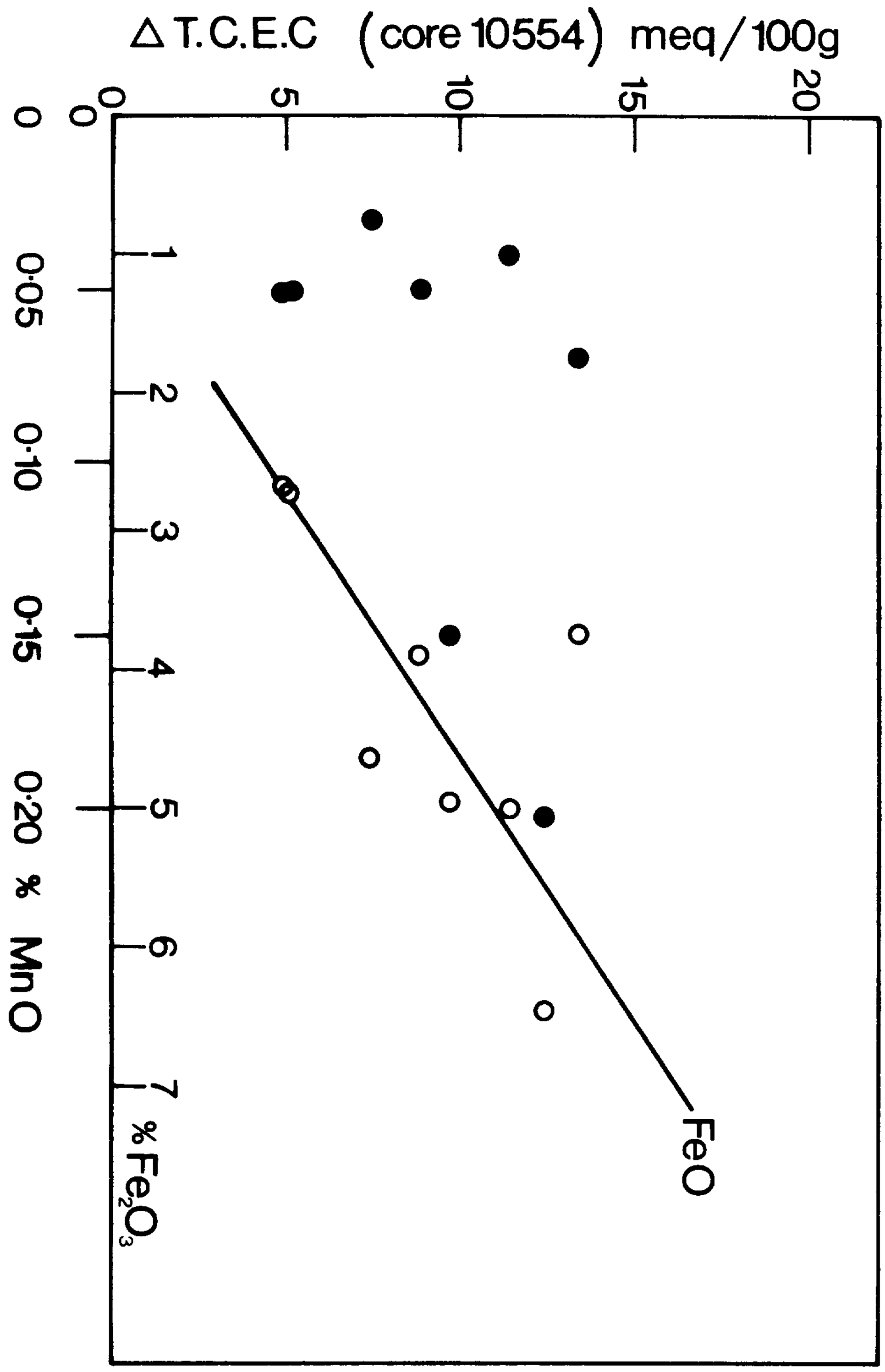

ΔT.C.E.C (core 10554) meq/100g
0
5
10
15
20
0
0·05
0·10
0·15
0·20 % MnO
0
1
2
3
4
5
6
7
% Fe_2O_3
FeO

Fig. 12