GEOCHEMISTRY AND MINERALOGY OF THE BEMBRIDGE AND HAMSTEAD BEDS (OLIGOCENE), ISLE OF WIGHT

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SUMMARY

Samples were collected from exposures of the Bembridge and Hamstead Beds in Whitecliff Bay, Hamstead Cliff and Bouldnor Cliff. Samples representative of various depositional environments were analysed for twenty-six major and trace elements. Mineralogical investigation by X-ray diffraction included quantification of the clay minerals, calcite and quartz.

Attempts to utilise geochemical indicators of palaeosalinity proved fruitless. Pyrite occurs in association with the two marine transgressions, suggesting that the source of sulphur was from solution. Alteration of pyrite to goethite and gypsum occured during Pleistocene weathering of the *Corbula* Beds and the movement of ions in solution associated with this affected the original exchangeable cation contents. An increase in zirconium content was found in samples deposited in high energy environments, although exceptions to this occur. The Oligocene sediments are enriched in lead, compared to average shales, due to lead fixation in clay minerals formed from the Cornubian granites. Aragonite occurs only in samples from the Bembridge Oyster Bed, in other samples only low-magnesium calcite was identified. The calcite in the Oligocene samples is poor in substituent trace elements.

The clay mineralogy is an illite/smectite/kaolinite assemblage, with traces of chlorite. The clay minerals are of a dominantly detrital origin, from Mesozoic and Tertiary sediments which lay to the north-west. The Lower Bembridge Beds in Whitecliff Bay show evidence for derivation from a kaolinite-poor, north-easterly source. There is evidence that transformation of smectite into illite and illite-smectite occurred, possibly following periods of more intense weathering in the hinterland. Two samples show evidence for the neoformation of smectite. One contains nontronite formed in a palaeosol, the other contains a smectite which is thought to have been formed from volcanic material. No variation in clay mineralogy was observed between marine and non-marine samples.

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1 INTRODUCTION

(A) Aims of the Thesis

(i) Area of study

Outcrops of strata of definite Oligocene age in England (MARTINI, 1970) are restricted to the Isle of Wight, with the exception of the small outlier of Creechbarrow Hill, Hampshire and possibly the Bovey Beds, Devon. In the Isle of Wight the beds occur on the northern limbs of the Brighstone and Sandown anticlines (which together form the Isle of Wight monocline). The Oligocene beds underly the northern half of the island, although exposures are limited to small, overgrown cliff sections.

Previous work in this Department by LIENGJARERN (1973) has been concerned with the micropalaeontology of the beds ascribed to the Oligocene by WHITE (1921), namely the Headon, Osborne, Bembridge and Hamstead Beds. The former author's results corroborated those of other workers who, using macro-invertebrate faunas, documented the presence of marine beds in a dominantly fluviatile succession. The collection of samples from a 200 metres thick succession at three localities by LIENGJARERN (1973) necessitated a large sampling interval. Consequently she omitted to sample certain thin beds, notably the Bembridge Oyster Bed, one of the few marine transgressions. DALEY (1973), in a study of depositional environments, limited his sampling to the Bembridge Marls and found evidence of cyclothems 0.1 to 3.3 metres in thickness. The need for a small sampling interval is, therefore, evident.

Sampling for this work was restricted to the Bembridge and Hamstead Beds. The section thus studied includes various depositional environments, well documented both palaeontologically and sedimentologically. It was thought that the samples collected would provide an opportunity to investigate possible relationships between mineralogy and/or geochemistry and palaeoenvironment.

(ii) The relationship of depositional environment and geochemistry

Much geochemical work has been devoted to attempts to obtain geochemical indicators of depositional environments. Unfortunately, the results obtained are not always unequivocal. Such a case is the relationship of boron with palaeosalinity. Boron in sediments occurs in detrital tourmaline and substituting in tetrahedral co-ordination in illite (MILLOT, 1970). DEGENS et al (1957) found an increase in the boron/gallium ratio between freshwater and marine shales. The same authors (1958) extended this method to include rubidium and found that the resulting triangular plot gave correct palaeosalinities for 80% of a set of analyses of fossiliferous Pennsylvanian shales. There is, however, a growing volume of evidence to suggest that the absorption of boron during sedimentation proposed by HARDER (1961) is not the only governing factor on boron concentration in sediments.SPEARS (1965) examined boron contents for some British Carboniferous sediments and concluded that the boron content of illite was fixed during weathering of the source rocks. WEDEPOHL (1971) found a typically marine boron content in some freshwater Pleistocene shales derived from marine Triassic sediments. HARDER (1961) mentioned that the absorption of boron was an irreversible reaction and this may be of particular relevance to this study, in which the source rocks are thought to have been dominantly marine sediments.

Other palaeosalinity indicators have been proposed, related to the difference in cation concentration between marine and freshwater conditions. MILLOT (1970) proposed that Rb, Ni and V should be concentrated in marine sediments, while Ga and Cr should be more representative of continental conditions. SPEARS (1973) showed that potassium was enriched in marine Carboniferous shales. He also showed that marine and non-marine sediments could be distinguished by a study of their exchangeable cation contents. An increased exchangeable Mg/Ca was found in marine sediments, supporting the observations of RUSSELL (1970). SPEARS (1973) also noted a decrease in cation exchange capacity (C.E.C.), although in laboratory studies this behaviour was shown only by 2:1 layer silicates.

The relationship of geochemistry and aspects of the depositional environment other than salinity has not received very much attention. PEARSON (1972) found that Zr content could be correlated with the energy of the depositional environment. This was due to the presence of Zr almost entirely in detrital zircon, the concentration of zircon decreasing with decrease in sediment grain size. This relationship would be expected to be applicable to most sediments, although COSGROVE (1973) showed that in conditions of intensive weathering, Zr was released from zircon and taken up by the clay minerals, leading to a concentration of Zr in finer-grained sediments.

Two other aspects of the depositional environment which may affect sediment geochemistry are pH and Eh. To a certain extent the variations in geochemistry between marine and non-marine sediments are due to the higher pH of marine waters. Variations within a large body of water are to be expected, leading to aerobic and anaerobic conditions. As examples of the kind of chemico-mineralogical variations to be expected, alkaline conditions will favour the formation of calcite, while reducing conditions may result in pyrite formation. These variations in mineralogy will, of course, result in variations in major and trace element geochemistry.

(iii) The relationship of depositional environment and mineralogy

In the preceding section the effect of pH and Eh on non-clay mineralogy has been mentioned. Certain non-clay minerals are of undoubted authigenic origin and are, therefore, directly indicative of aspects of the depositional environment. Thus the presence of pyrite indicates reducing conditions wth the availability of sulphur, while halite indicates hypersalinity. Large variations in sample geochemistry are always related to variations in sample mineralogy and even quite small geochemical changes may be due to mineralogical variation. Thus DEGENS et al (1957) reported that illite was enriched in marine sediments relative to kaolinite and this enrichment may explain the higher B, K and Rb contents in marine sediments.

Many workers have studied the relationship between clay mineralogy and palaeo-environment. The general conclusion that while kaolinite is stable in acid (freshwater) conditions, smectite and illite are more typical of higher pH environments, has been well documented. Thus JEANS (1971) found that marine sediments typically contained a smectite/illite assemblage. BROOKS and FERRELL (1970) similarly reported an increase in smectite and decrease in kaolinite content with increasing salinity. GILKES (1968) also recorded a smectite/illite assemblage in marine Tertiary sediments of the Hampshire Basin, compared with an illite/kaolinite assemblage in non-marine sediments. He did, however, conclude that this could have been due to differences in the source areas, as the distribution ofthe two assemblages was partially geographical.

Assuming that a relationship does exist between palaeosalinity and clay mineralogy, the question remains as to the cause of the relationship. Clay minerals have three possible modes of origin - inheritance, transformation and neoformation. JEANS (1971) concluded that most clay minerals in the geological past were of a neoformed origin. He considered that in the past, very subdued land relief was unable to supply detritus to the seas and that neoformation of clay minerals occurred from solutions or gels. At the present time, neoformation is only of quantitative importance in deep sea sediments (BISCAYE, 1965), that is, in areas far removed from any possible detrital supply. In epicontinental seas a transformed or inherited origin would be likely for most clay minerals. Transformations in the marine environment may result in the alteration of clay minerals (as for example, smectite being altered to illite, WEAVER, 1958), or in an increase in their crystallinity.

Two factors exist which may produce a relationship between mineralogy and palaeosalinity for inherited clay minerals. The first of these is a combination of the flocculation rates and average grain sizes of the clay minerals. GRIM (1953) reported average grain sizes as follows - kaolinite 0.3 to 4μ; illite 0.1 to 0.3μ; smectite 0.02 to 0.2μ. A combination of these different grain sizes with the varying tendency to flocculate of the clay minerals will produce mineral aggregates of varying size. The second factor is the density of these aggregates, which varies from 2.0g/cm^3 for hydrated smectites to 2.6g/cm^3 for kaolinite (DEER et al, 1962). Current sorting of the clay mineral aggregates will result in a lateral distribution of the clay minerals, with the heaviest aggregates being deposited first from water of decreasing velocity.

(iv) Statement of the aims of the thesis

The macro and micro-palaeontology of the Oligocene of the Isle of Wight have been comprehensively described by WHITE (1921) and LIENGJARERN (1973) respectively. Both of these authors also included descriptions of the depositional environments. The only mineralogical results available for the Oligocene are descriptions of the clay mineralogy by GILKES (1968 and 1978) and PERRIN (1971). The sequence studied presents, therefore, a chance to add to, the general level of geological knowledge.

The presence of well documented environmental changes in a sequence which appears to have undergone limited diagenetic change allows an opportunity to test the usefulness of geochemistry and mineralogy as palaeo-environmental indicators. Before this can be attempted there are certain problems which must be overcome. While methods of whole rock geochemical analysis are both accurate and precise, a problem exists with the determination of exchangeable cations in calcareous samples (SPEARS, 1973). Since most of the section studied contains fine-grained shell detritus, this could present problems in the use of exchangeable cations as palaeosalinity indicators.

If mineralogy, both clay and non-clay, is to be used for environmental investigations, methods of quantification must be developed. While successful methods have been reported for some non-clay minerals (e.g. quartz, by TILL and SPEARS, 1969), only semi-quantitative methods exist for clay minerals. X-ray diffraction (X.R.D.), the most widely available and commonly used method for determining clay mineralogy, has so far not been proven capable of producing quantitative results. One of the main reasons for this is that clay minerals are poor diffractors of X-rays, due to their small grain size and poor crystallinity. It is, therefore, usual to attempt to improve their diffracting capabilities either by concentrating the clay minerals, or by developing a preferred orientation in the sample. It is in these techniques that the problems for quantification arise. GIBBS (1965) considered that the method of sample preparation was of critical importance in quantitative work, while TOWE (1974) concluded that the size fraction used was more important. There are, thus, various considerations to be made in attempting to quantify clay mineralogy by X.R.D..

An alternative to the use of X.R.D. for mineral quantification is a recalculation of geochemical data, using X.R.D. to identify and partially quantify the mineralogy of the sample (SCHULTZ, 1964). Chemical analyses are of greater precision than most direct mineralogical quantifications, but commencing with data of high precision and accuracy does not guarantee results of similar accuracy. In geochemical recalculations, the main problem is the variability of mineral composition. This is especially marked in the clay minerals, but also occurs in some non-clay minerals. Geochemical recalculations need, therefore, to be approached with some care.

2 PREVIOUS WORK

(A) General Geology

(i) Geological setting

The Isle of Wight is separated from the Hampshire coast by the Solent and Spithead straits, the distance from the mainland varying between two and seven kilometres. It is shown in its entirety on the Ordnance Survey 1:50,000 sheet number 196. The abundance of fossiliferous deposits, coupled with the many cliff exposures, has attracted geological study for the past century. The geology of the island is shown on a Geological Survey special sheet and was described by WHITE (1921). The general stratigraphy of the Tertiary deposits is shown in figure 1.

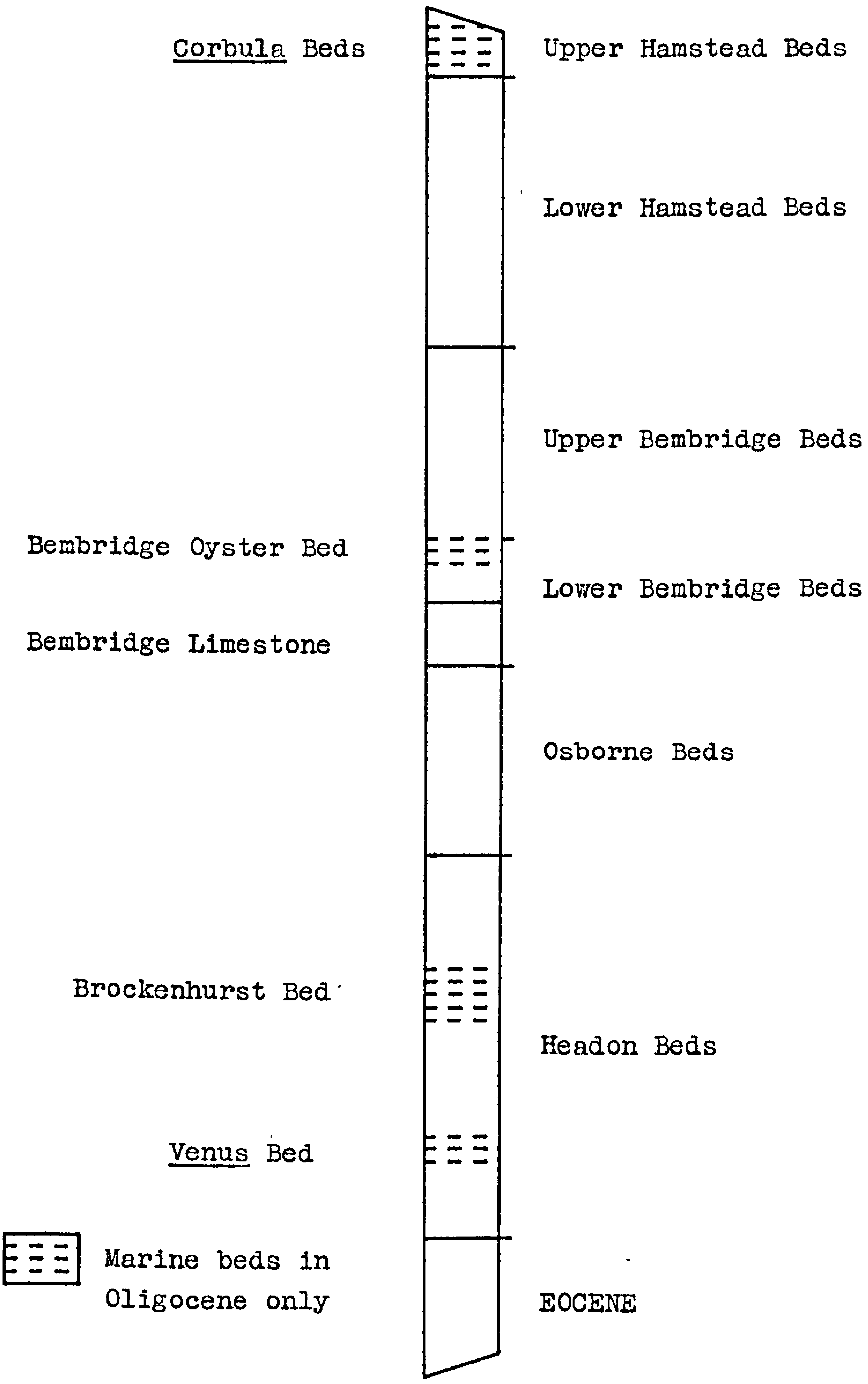
The outcrop of the Tertiary strata is determined by the geological structure and the island's topography. The dominant structural feature is the monocline, which is, in fact, two separate folds, slightly offset. Both folds have almost vertical northern limbs and gently dipping southern limbs. Thus the Cretaceous beds outcrop in the south of the island, while the Tertiary beds occupy the northern half. As the Eocene sediments and Headon Beds are almost vertical in most places, the Osborne, Bembridge and Hamstead Beds underly most of the northern half of the island. The distribution of the latter two is shown in figure 2, together with the shallow folds associated with the moncline, all of which plunge at a shallow angle to the north-west. The folding is obviously of post Corbula Bed age (Lower Stampian, CAVELIER, 1964) and is part of the Alpine orogeny. The general structure of the Bembridge and Hamstead Beds may be described as a shallow synclinorium plunging to the north-west. The effect of the topography on outcrop distribution is limited, as the northern half of the island is reasonably level, being mainly between twenty and fifty metres above sea level.

(ii) Location of the exposures

As was mentioned above, cliff exposures are plentiful in the Isle of Wight, but owing to the clayey nature of most of the Oligocene deposits, the cliff sections are often slumped and overgrown. The Bembridge Beds are named after the town of Bembridge and outcrop in nearby Whitecliff Bay. They attain their

Figure 1

Generalised stratigraphy of the Oligocene deposits in the Isle of Wight (after WHITE, 1921)



N.B. No vertical scale

Figure 2

Location map showing generalised geological structure

full thickness, however, only at Hamstead and in Thorness Bay. WHITE (1921) described the sections of the Bembridge Beds in Hamstead foreshore, Whitecliff Bay, Thorness Bay and Gurnard Bay. CHATWIN (1960) mentioned these exposures plus the section at St. Helens, while STINTON (1964) described the sections in Thorness and Gurnard bays as badly overgrown.

The Hamstead Beds are named after the cluster of farm buildings at the top of Hamstead Cliff (grid reference 400912). They attain their full thickness in Bouldnor Cliff and are only exposed elsewhere at the top of the cliffs in Thorness Bay. Even at the type locality the exposures are poor, with large scale slumping common. There is thus great difficulty in constructing a complete stratigraphic section of the Hamstead Beds. WHITE (1921) concluded that the Hamstead Beds were approximately eighty metres in thickness, but at the time of his work thirty-five metres of this were obscured.

Inland exposures of the Bembridge and Hamstead Beds are limited to quarries in the Bembridge Limestone at Tapnell (377863) and Prospect (385867). The beds exposed at these two localities are the limestone and some of the overlying clays (STINTON, 1964). WHITE (1921) obtained samples inland by auguring, but the value of such samples for a geochemical investigation and their stratigraphic location are questionable. The collection of samples for detailed work must, therefore, be limited to the cliff exposures. The best locations for exposures of the Bembridge and Hamstead Beds are Hamstead and Bouldnor cliffs and Whitecliff Bay, although even in these sections care needs to be taken to avoid sampling slumped material.

(B) Palaeontology and Sedimentology

(i) Age of the deposits

The base of the Oligocene in Europe is defined by a marine transgression in the section at Latdorf, in northern Germany. The equivalent of this transgression in the Hampshire Basin is not definitely known. WHITE (1921) placed the base of the Oligocene between the Barton and Headon Beds and most workers since him have accepted this datum. He did, however, mention doubt as to the validity of this decision and recent work has supported this uncertainty.

BHATIA (1955), in a study of the foraminiferal fauna of the

Palaeogene of the Isle of Wight, described the *Corbula* Beds as of Middle Oligocene age. The two underlying marine beds, the Bembridge Oyster Bed and the Brockenhurst Bed, he found to contain a transitional Eocene-Oligocene fauna. CAVELIER (1964), from molluscan evidence, concluded that the Hamstead Beds were all of Lower Stampian (Oligocene) age and that the underlying beds should be placed in the Eocene. CURRY (1966) reviewed the proposed correlations between European Tertiary deposits and mentioned that while molluscan and foraminiferal evidence suggested that the Brockenhurst Bed was of Lower Oligocene age, the mammalian remains suggested that the base of the Oligocene lay between the Bembridge Limestone and the Lower Hamstead Beds. He concluded that the Brockenhurst Bed should be taken as the base of the Oligocene. This conclusion was disputed by MARTINI (1970), who found Upper Eocene nannoplankton in the Brockenhurst Bed. MURRAY and WRIGHT (1974) summarised the preceding evidence and also mentioned that ostracods found in the Bembridge Marls and Hamstead Beds were comparable with those found in Lower Oligocene deposits in the Paris Basin. In general, the Hamstead Beds may be taken to be of definite Oligocene age, while most authors would agree that the underlying Bembridge Beds are of probable Oligocene age.

(ii) Depositional environments

Palaeontological and sedimentological evidence has been used by many workers to make deductions about the depositional environments of the Oligocene deposits of the Isle of Wight. WHITE (1921) gave an account of the major environmental changes, which were summarised by CURRY (1965). The Upper Headon, Osborne, Bembridge and Lower Hamstead Beds were regarded as a monotonous sequence of still and running freshwater deposits, with evidence of occasional brackish influences. Two beds within this sequence are worthy of note. The Bembridge Limestone was probably deposited over the whole of the Hampshire Basin, as is evidenced by the outlier of Creechbarrow Hill. The presence of land gastropods in the limestone at Yarmouth (STINTON, 1964) is, however, evidence of land close by. The limestone was deposited in still, freshwater to brackish conditions (salinities up to 10‰, MURRAY and WRIGHT, 1974). The second bed of interest is the Bembridge Oyster Bed, which was deposited by a sea transgressing from the east and does not occur to the west of Thorness. This bed was found to contain foraminiferids suggesting deposition in a shallow, hyposaline lagoon or estuary (salinity between 10 and 25‰) by MURRAY and WRIGHT (1974). These authors found sparse foraminiferids in two samples from near the base of the Bembridge Marls in Hamstead Cliff and none in samples from the Lower Hamstead Beds. LIENGJARERN (1973) reported sparse foraminiferids in samples from the top of the Bembridge Marls in Whitecliff Bay and from the base of the Lower Hamstead Beds in Hamstead Cliff. These results indicate that deposition of the Bembridge Marls and Lower Hamstead Beds was mainly in freshwater conditions.

The Upper Hamstead Beds are one of the more interesting parts of the sequence, as they show a transition from the brackish Cerithium Beds into the marine Corbula Beds. Typically such transgressions in the Palaeogene of the Hampshire Basin are marked by the development of brackish-marine sands (as for example the Bembridge Oyster Bed), but no such bed occurs in the Upper Hamstead Beds. Both LIENGJARERN (1973) and MURRAY and WRIGHT (1974) found foraminiferids in the Cerithium Beds indicative of deposition in a hyposaline lagoon, while the Corbula Beds were found to contain an open marine fauna. The diversity of species found in the Corbula Beds was low, but this was reported to be due to the muddy nature of the substrate rather than the salinity (reported as 32 to 36‰).

Detailed sedimentological investigations have been undertaken for the Bembridge Marls, but not for the Hamstead Beds. DALEY (1967 and 1968) presented results obtained from the study of a non-marine bed in the Bembridge Marls. He found pseudomorphs of gypsum rosettes, together with erosional features and desiccation cracks, all indicative of very shallow water at the time of sediment deposition. In a broader study of the Bembridge Marls, DALEY (1973) identified fining-up cyclothems. He considered these to be developed in a floodplain with occasional brackish influences. The cyclothems commence with fluvial deposits (more rarely showing evidence for brackish conditions), which pass upwards into lacustrine and subaerial deposits. Possible causes of this cyclicity are climatic variation, fluctuating rates of subsidence and migration of the river channels associated with a constant rate of subsidence. None of these reasons seem capable of explaining all of the features seen, but the latter would seem to be the preferable cause, failing only to explain the rare brackish commencement to some of the cyclothems.

As regards climatic conditions during the Oligocene in the Hampshire Basin, DALEY (1972) concluded that during deposition of the Bembridge Marls a subtropical climate prevailed, with rainfall distributed throughout the year. Similar present day conditions are Eastern Margin Warm Temperate climates. The existence of such conditions on the western margin of a continent could have been due to different wind circulation patterns, or to the presence of a large sea area to the south-east. MURRAY and WRIGHT (1974) concluded that sea temperatures were between sixteen and eighteen degrees Centigrade, in agreement with the above climatic conditions.

DALEY (1972) considered that the existence of evaporite deposits in the Paris Basin contemporaneous with normal clastic sedimentation in the Hampshire Basin was evidence of alternating dry and pluvial periods. From an examination of the palaeogeography of the two basins there seems to be no reason to invoke climatic variation. According to MURRAY and WRIGHT (1974) the Hampshire Basin was a bay opening to the south-east and fed by rivers from the north and west throughout the Palaeogene. The Paris Basin, conversely, took the form of a shortened bottle with the neck open to the sea, following the formation of small anticlines during the Middle Eocene. During the Oligocene the Paris Basin would, therefore, have had a large surface area subject to evaporation, with only a small potential for recharge from normal sea water. This may also have been coupled with a larger influx of freshwater in the Hampshire Basin. There seems, therefore, to be no reason for proposing climatic variations during the Oligocene.

(C) Mineralogy and Geochemistry

(i) Mineralogy

Mineralogical studies of the Oligocene sediments of the Hampshire Basin have usually been included in broader studies of the Tertiary deposits. The heavy minerals of the Palaeogene were the subject of a study by BLONDEAU and POMEROL (1968), who found garnet, epidote, zoisite and staurolite to be the commonest heavies in the Oligocene. They found that sediments in Alum Bay contained a greater content and diversity of heavies than those in Whitecliff Bay and took this to represent derivation from westerly and northerly sources. WALDER (1964) found a similar suite of heavies in Eocene sediments from the Isle of Wight and suggested three source areas, Brittany, Cornubia and the English Midlands.

Reworking of heavies from pre-existing sediments was probably of more importance than derivation from the metamorphic and granitic rocks of Brittany and Cornubia.

A summary of the clay mineralogy of the Oligocene was included by PERRIN (1971) in his report on the clay mineralogy of British sediments. He found that in the Bembridge and Hamstead Beds mica (cf. illite) was usually the dominant clay mineral, with smectite and kaolinite present in smaller quantities. Variations from this norm were observed, such as one sample from the Bembridge Marls which contained 90% smectite. GILKES (1968) found an illite/smectite/kaolinite assemblage in the Oligocene, together with minor amounts of mixed-layer illite-smectite and halloysite. The same author (1978) produced more detailed results for Upper Eocene and Oligocene sediments and showed that the division into western illite/kaolinite and eastern smectite/illite/kaolinite assemblages which existed in the Lower Eocene did not persist into the Oligocene. This division was considered to be either geographical or related to palaeosalinity. He considered that some of the illite in the Oligocene was neoformed, possibly in calcareous lakes, leading to a higher average illite content in the Oligocene than in the Eocene samples. The clay minerals in the Oligocene were thought to be mainly reworked from exposed, surrounding Lower Eocene sediments. Nontronite was reported to be present in the Bembridge Oyster Bed in Whitecliff Bay by BLONDEAU and POMEROL (1968).

(ii) Geochemistry

There have been no reports of geochemical analyses of Oligocene samples from the Hampshire Basin. This thesis should therefore go some way towards filling a gap in our knowledge and also towards providing more detail on the mineralogical variations reported by other workers.

3 FIELD WORK

(A) Sample Collection

(i) Sampling aims

Sampling was restricted to the Bembridge and Hamstead Beds, since these are taken by most workers to be of Oligocene age and also because the Bembridge Limestone provides an easily recognisable base to the succession. The Bembridge and Hamstead Beds are exposed in Hamstead and Bouldnor cliffs, while the Bembridge Beds are also exposed on the other side of the island in Whitecliff Bay.

The main aim in sampling was to collect sufficient samples representative of the different depositional environments. Sampling tended, therefore, to be concentrated around the thin marine beds and to be rather sparse throughout the Bembridge Marls and Lower Hamstead Beds. Since the marine influence during the Oligocene is known to have increased eastwards, the collection of samples from two sites, one on the north-west and one on the south-east coasts of the island, should allow an identification of possible changes in geochemistry and mineralogy with increase in distance from the source area.

(ii) Sampling technique

Since any errors or lack of care in sample collection will be carried through to all later conclusions, great care was taken to ensure that all samples collected were as fresh and representative of the bed sampled as possible. Exposures were scraped clean with a stainless steel trowel and the sample collected ten centimetres inwards from the surface thus obtained. Approximately 300 grams of sample was collected and stored in labelled, self-sealing polythene bags.

(iii) Location and description of the outcrops

Samples were collected during August, 1974, when the exposures were in a dehydrated state, due to the low rainfall of the preceding months. This meant that recent slumping was limited and few fresh exposures in the back walls of rotational slumps were found. One of the few was found at the top of Bouldnor Cliff

(388907), where the horizontally bedded Upper Hamstead Beds were well exposed. A general view of the outcrop is shown in plate 1(a), while in plate 1(b) part of the Corbula Beds is shown in more detail. It was possible to construct an almost complete section through the Corbula, Cerithium and underlying Hamstead Beds, representing the upwards change from freshwater to marine conditions. Samples 28 to 55 were collected at this locality. Slightly further westwards an exposure of the Lower Hamstead Beds was found on a stack standing off the cliff face (383904). Plate 2 shows this exposure, with apparently cross-bedded sediments towards the top of the stack. That this is in fact slumping rather than cross-bedding can be seen by the truncated bases of the more steeply dipping beds. Towards the base of the stack evidence of cyclothemic deposition, similar to that reported by DALEY (1973) for the Bembridge Marls, was found. Samples 56 to 72 were collected from this outcrop.

The remaining Lower Hamstead Beds occupy the majority of Bouldnor and Hamstead cliffs, but unfortunately both cliffs were very badly overgrown, so that exposures were rare. Poor, scattered exposures were found above high tide level between 382906 and 377903 and samples 73 to 87 were collected from them. A good exposure of part of the Lower Hamstead Beds and the last exposure before Yarmouth was found at 376902. Here the main feature was the presence of rythmically deposited sediments, shown in plate 3. Samples 88 to 109 were collected from this locality.

The full sequence of the Bembridge Beds is developed at Hamstead (CHATWIN ,1960), but unfortunately this was only shown in the foreshore (plate 4(a)). The beds were less well exposed in the cliff itself, from where samples 1 to 27 were collected. The Bembridge Limestone was poorly exposed in the cliff, but it was possible to collect a sample from a thin, clayey horizon with rootlets interbedded with the limestone (plate 4(b)). Examples of beds with rootlets were common in the Bembridge Marls, indicating deposition in shallow water. That such rootlets were not present day features was shown by their rapid, upwards truncation (plate 5). Table 1 lists the section of the Bembridge and Hamstead Beds exposed in Hamstead and Bouldnor cliffs, together with the sampled levels.

The type locality of the Bembridge Beds is in Whitecliff Bay. There, the effect of the Alpine orogeny is readily apparent, the Bembridge Limestone at 639861 dipping at 30/022°, while half a kilometre north-east along the shoreline the dip is 04/020°. At

Plate 1(a)

General view of the *Corbula* Beds, Bouldnor Cliff (388907)

Plate 1(b)

Close-up of part of the *Corbula* Beds, showing concretions

Plate 2

Section of the Hamstead Beds (383904)

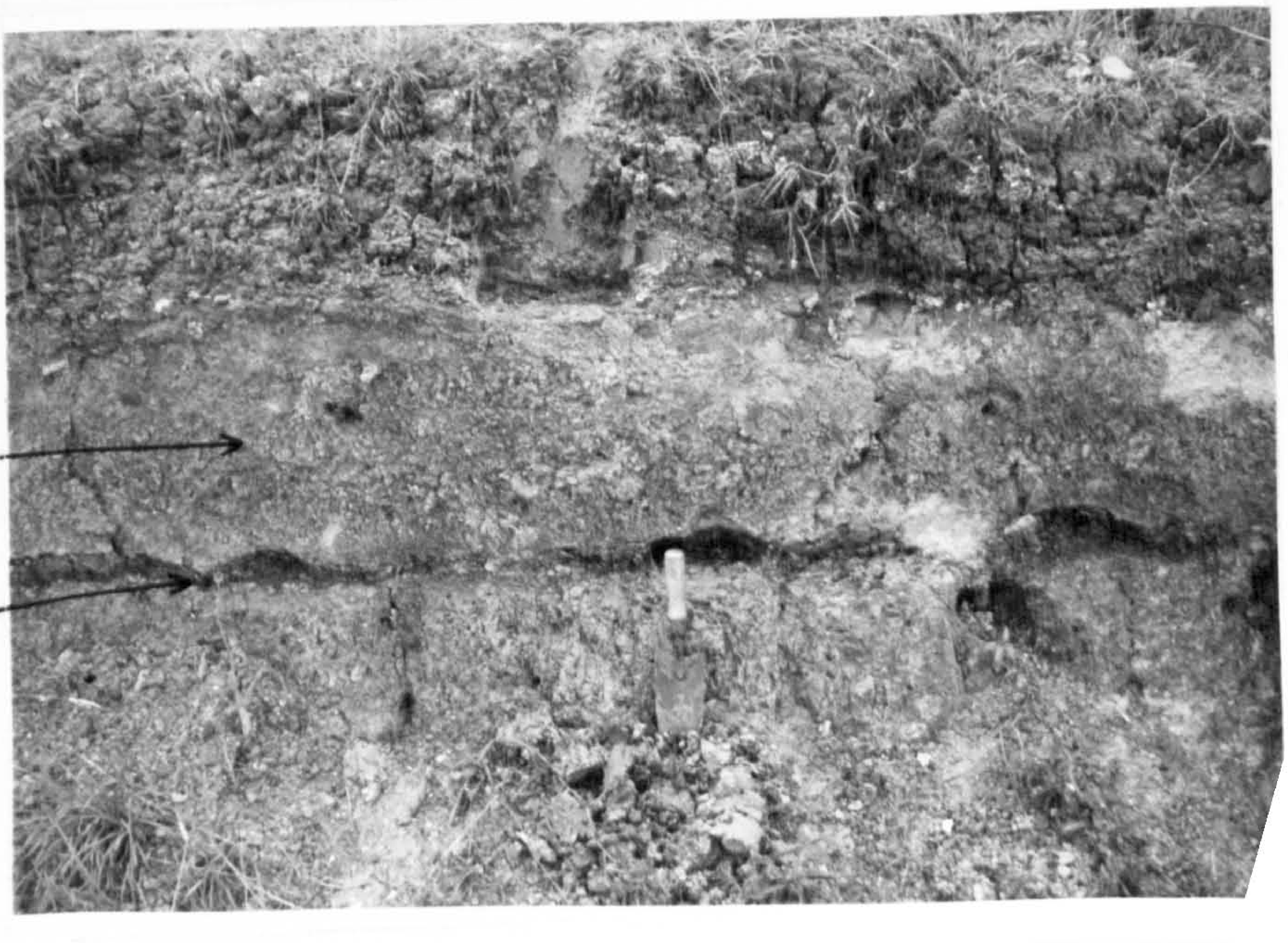
Rucksack approximately one metre in height

.ate 4(a)

Section of the Bembridge Marls in Hamstead foreshore

Plate 4(b)

The Bembridge Limestone in Hamstead Cliff (405920)



Limestone,
sample 3

Black marl,
sample 2

Plate 5

A bed in the Bembridge Marls showing rootlets

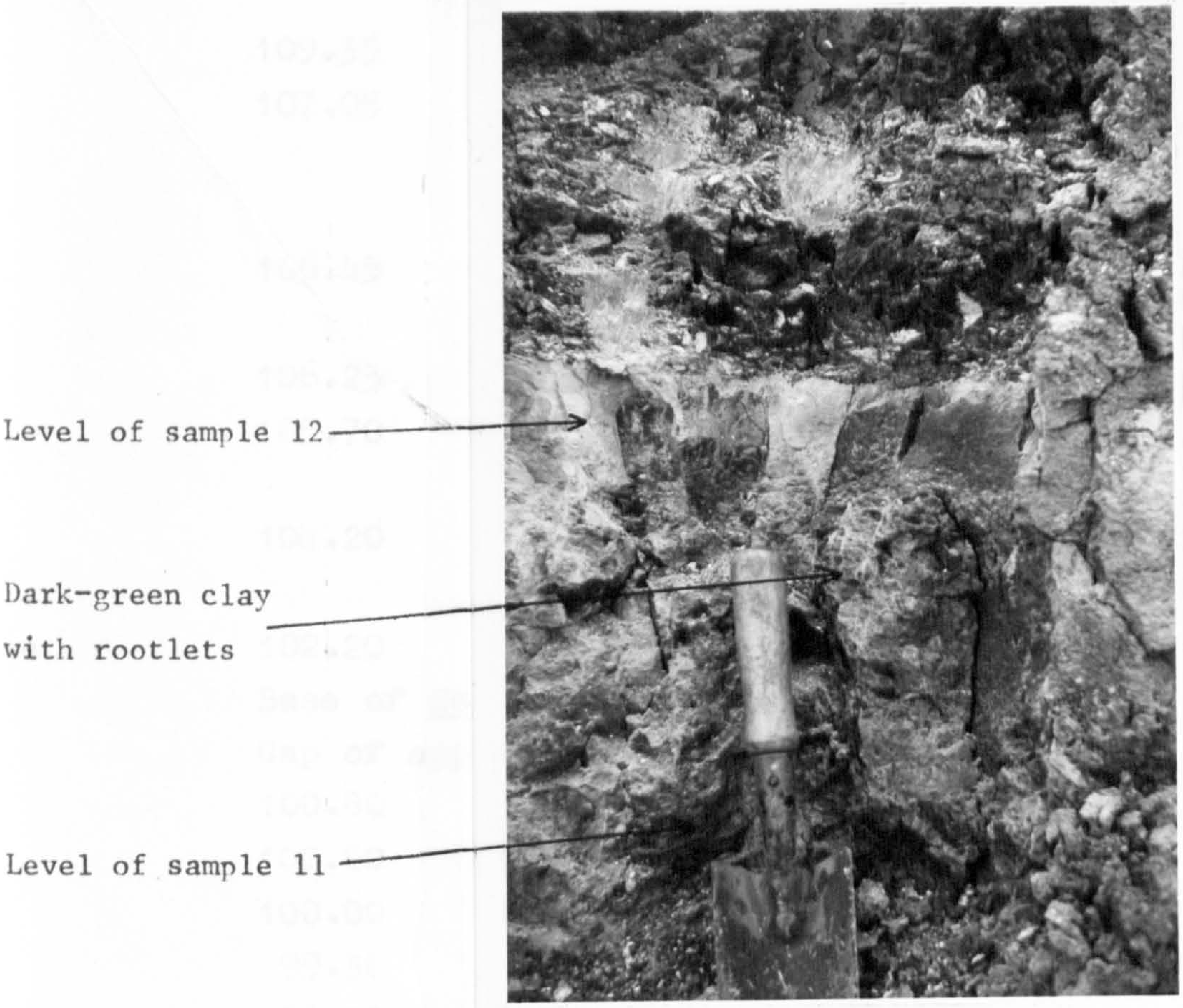


Table 1

Stratigraphic succession of the Bembridge and Hamstead Beds in Hamstead and Bouldnor cliffs, showing sampled beds

Stratigraphic level	Lithology	Sample nos.
109.35	Plateau Gravel.	
107.05	Grey clay with carbonaceous blebs and gypsum towards base. Layer of iron stained calcareous concretions at base.	28, 29 30
106.45	Black laminated clay with *Corbula*. Shell bed at base.	31, 32
106.25	Black clay with shell bed at base.	33
105.70	Dark-grey clay with *Corbula*. Layer of iron stained calcareous concretions at base.	34, 36
104.20	Black-grey clay with *Corbula*. Layer of iron stained calcareous concretions at base.	37, 38 40
102.20	Black-grey marl with *Corbula*.	39
Base of *Corbula* Beds		
Gap of approximately one metre		
100.80	Grey gypsiferous clay.	41
100.60	Black fossiliferous marl.	42, 43
100.00	Grey clay with shell bed at base.	44, 45
99.30	Grey clay with shell bed at base.	46
98.05	Dark-grey clay becoming lighter and with carbonaceous blebs towards base.	48, 49
97.95	Carbonaceous clay.	50
Base of *Cerithium* Beds		
97.80	Light-grey clay.	51
97.25	Black-grey clay with pelecypods and shell bed at base.	52
97.00	Laminated black-grey clay.	53
94.55	Stiff blue clay.	54, 55
Gap of approximately one metre		
93.35	Grey clay.	56
93.30	Sandy limestone.	57
93.25	Grey clay with gypsum.	58
93.20	Black clay.	59
92.95	Grey clay.	60
92.40	Grey marl.	61, 62

Table 1 (contd.)

Stratigraphic level	Lithology	Sample nos.
92.25	Black carbonaceous clay.	63
91.25	Grey marl grading downwards into mottled red/grey clay.	64, 65
91.00	Grey clay.	66
90.95	Red parting.	67
90.70	Grey clay grading downwards into mottled red/grey clay.	68, 69
89.60	Grey marl with occassional darker partings.	70, 71
89.30	Dark-grey clay.	72
Gap of approximately fifteen metres		
71.95	Dark-grey clay with impersistent lighter bands.	73, 74 75
71.55	Dark-grey clay with carbonaceous blebs.	77, 78
Gap of approximately ten metres		
58.05	Grey-green iron stained marl.	80, 81, 82, 83, 84, 85, 86, 87
Gap of approximately five metres		
52.05	Grey-green marl.	88
51.95	White marl.	89
50.30	Grey-green marl with red mottling towards base.	90, 91
46.30	Laminated grey and white marl.	92, 93
Gap of approximately five metres		
38.80	Finely laminated black clay with *Polymesoda convexa* and small gypsum crystals.	94, 95 96
Gap of approximately one metre		
37.30	Grey gypsiferous marl with plant remains.	97, 98
37.25	Fine-grained sand.	99
37.05	Laminated grey and white clay with shell bed at base.	100
36.95	Grey clay.	101
36.55	Black gypsiferous clay with plant remains	102, 103
36.40	Light-grey clay with shell bed at base.	104
35.90	Light-grey marl.	105

Table 1 (contd.)

Stratigraphic level	Lithology	Sample nos.
Gap of approximately ten metres		
23.90	Laminated white and grey clay.	106, 107, 108, 109
Base of Hamstead Beds		
Gap of approximately five metres		
18.70	Dark-grey marl.	
18.65	Grey marl with small gastropods.	
17.05	Dark-grey marl with carbonaceous blebs and shell bed at base.	27
16.40	Dark-grey clay with layer of iron stained calcareous concretions at base.	26
15.80	Grey marl with shell bed at base.	25
13.95	Grey marl grading downwards into blue-grey marl with shell bed at base.	23, 24
13.30	Laminated black marl.	22
13.00	Dark-green gypsiferous marl.	21
12.20	Green marl with molluscan partings and shell bed at base.	19, 20
11.75	Dark-green marl with shell bed at base.	18
11.65	Green marl with shell bed at base.	17
11.55	Black clay.	
11.50	Grey gypsiferous marl.	16
11.40	Black marl.	15
10.90	Light-grey clay.	14
10.20	Laminated dark-green clay with shell bed at base.	13
9.95	Light-green marl.	12
9.90	Dark-green marl with rootlets.	
9.65	Dark-green marl.	11
9.50	Dark-green fossiliferous marl.	10
9.40	Light-green marl.	9
9.30	Green marl with rootlets.	8
7.50	Dark-green marl with shell bed at base.	7
6.05	Blue fossiliferous marl.	5, 6
6.00	Laminated brown marl.	4
Base of Bembridge Marls		
5.65	Limestone with rootlets at base.	3
5.60	Black marl with rootlets.	2

Table 1 (contd.)

Stratigraphic level	Lithology	Sample nos.
0.00	Limestone.	1
Base of Bembridge Beds		

N.B. Stratigraphic level is given as height of base of bed (in metres) above base of the Bembridge Limestone.

this last locality samples 110 to 126 were collected from the Bembridge Limestone, interbedded marls and overlying Bembridge Oyster Bed and marls. Higher in the cliff, at 643864, samples 127 to 138 were collected. Unfortunately , this outcrop was very dehydrated, so that while most of the features described by DALEY (1973) as indicative of cyclothemic deposition could be seen, it was not possible to collect samples from each lithotype within any one cyclothem. The thin limestone bed described by DALEY (1968) was seen and the sedimentary structures shown were identified and measured. These included runnel casts and ripples and showed that water movement was in a north-west to south-east direction. Table 2 lists the section of the Bembridge Beds in Whitecliff Bay together with the sampled levels.

(B) Features Associated with Slumping

(i) Large-scale slumping

Hamstead and Bouldnor cliffs showed evidence for extensive large-scale slumping. Plate 6(a) shows a view of Hamstead Cliff in which the rotational nature of the slumps is clearly visible by the 'toe' outcropping in the foreground. The back wall of a similar slump is shown in figure 1(a). Smaller-scale features associated with slumping were found at the base of Bouldnor Cliff (376902). Plate 6(b) shows quite intensely folded Lower Hamstead silts and clays, while plates 7(a) and (b) show features associated with the plane of movement of a slump. The light-coloured marls have slipped over the black clays and due to their more compact nature have gouged out areas of the clays. The injection structure in plate 7(b) is of particular interest in that it is a large-scale equivalent of a flame cast and, therefore, gives an indication of the direction of movement. This was to the south-west, or parallel to the cliff face, which is at right angles to the expected direction of slump movement. A likely explanation is that an obstruction caused an alteration of the course of the mudflow and such an obstruction could also have been responsible for the folding shown in plate 6(b). The black clay shown in plates 7(a) and (b) was found as the plane of movement over a distance of 100 metres, indicating that this bed must have been in a plastic state at the time of slumping.

Table 2

Stratigraphic succession of the Bembridge Beds in Whitecliff Bay showing sampled beds

Stratigraphic level	Lithology	Sample nos.
21.30	Laminated light-grey marl with many molluscan partings and ironstone concretions at base.	137, 138, 139
20.55	Dark-grey marl.	135, 136
19.95	Laminated light and dark-grey marl with runnel casts and ripple marks.	134
18.35	Dark-green marl with molluscan partings and microlaminations in places.	131, 132
18.15	Light-green limestone.	130
17.35	Green marl.	128, 129
17.10	Red/green mottled marl.	127
Gap of approximately six metres		
10.70	Black-grey marl.	126
10.50	Light-grey limestone.	125
10.15	Black marl.	124
9.90	Grey sands with *Ostrea vectensis*.	122, 123
9.70	Green marl with *Ostrea vectensis*	120, 121
9.30	Dark-green marl.	119
9.00	Dark-grey marl.	118
8.60	Light-grey fossiliferous marl.	117
8.45	Black-grey marl.	116
7.70	Light-grey marl.	114, 115
Base of Bembridge Marls		
4.70	White limestone with many shell casts.	113
4.00	Grey marl.	112
3.00	Black marl.	111
0.00	White limestone with many shell casts.	110
Base of Bembridge Beds		

N.B. Stratigraphic level is given as height of base of bed (in metres) above base of the Bembridge Limestone.

Plate 6(a)

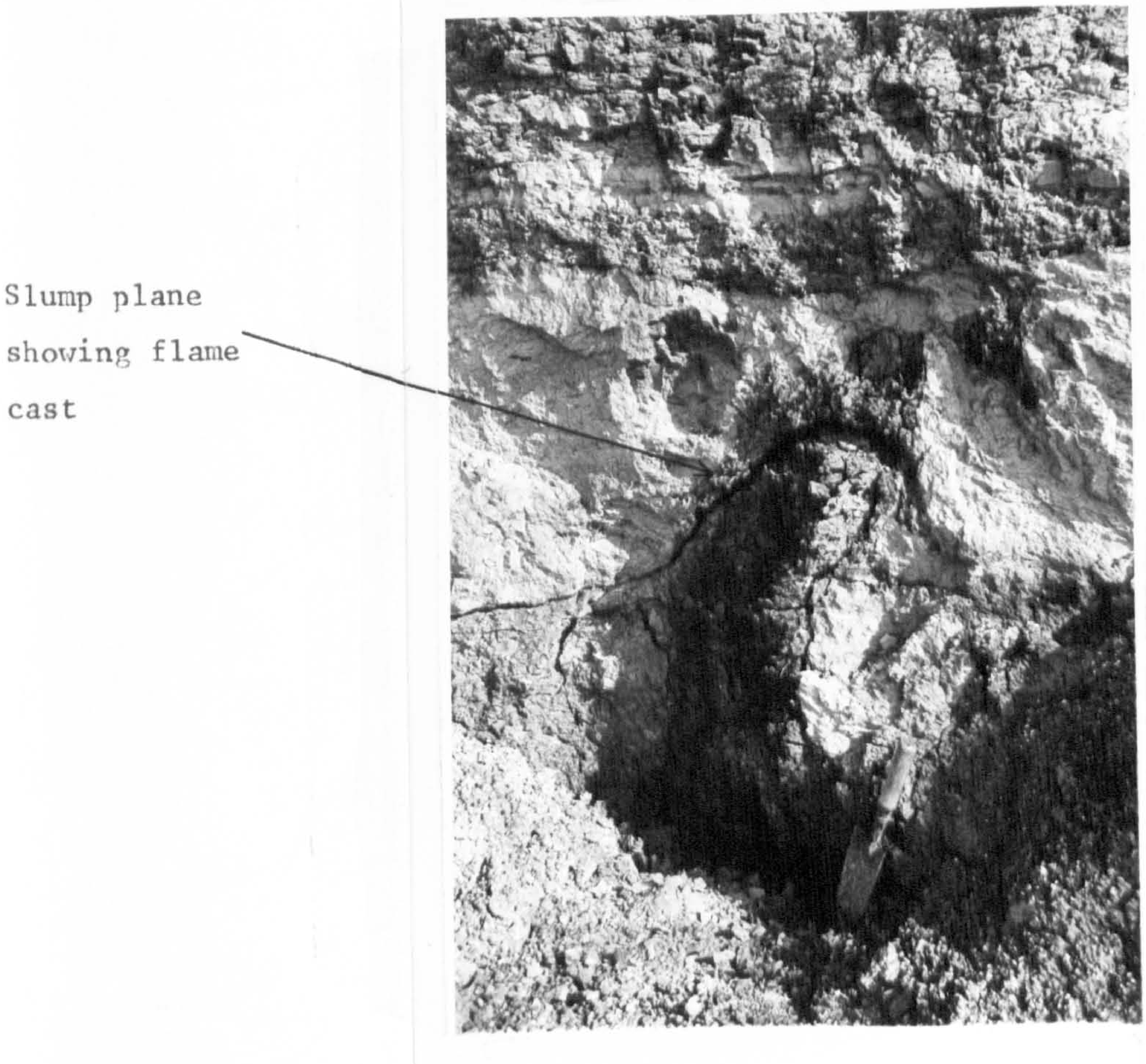
Slumping in Hamstead Cliff (403918)

Plate 6(b)

Folds produced in the Hamstead Beds by slumping

Plates 7(a) and (b)

Features associated with a slump plane (376902)



(ii) Incompetence of the Corbula Beds

Features which may not be due to slumping, but which are here considered with slump features, were displayed at the top of Bouldnor Cliff. Here the Corbula Beds were overlain unconformably by Plateau Gravel, as shown in plate 8(a). WHITE (1921) considered the Plateau Gravel to be a degraded river gravel of Pleistocene age. Plate 8(b) shows two features worthy of note, firstly the presence of a mass of Plateau Gravel within the Corbula Beds and secondly the injection of the Corbula Beds into the overlying gravel. CHATWIN (1960) mentioned that some Plateau Gravels in the Hampshire Basin showed 'contortions usually associated with the movement of frozen soil'. While the injection feature could be explained by the presence of a layer of permafrost, the foundering of a mass of gravel into the underlying clays has no obvious explanation. It seems, however, most likely that this feature may be associated with freezing and thawing during the Pleistocene glaciation.

Plate 8(a)

Unconformity between the Corbula Beds and Plateau Gravel (388907)

Plate 8(b)

Features associated with incompetence of the Corbula Beds (388907)

4 GEOCHEMISTRY

(A) Major Element Analyses

(i) Sample preparation

Of the 138 samples collected in the field, it was decided to analyse approximately one half, these being chosen to represent the various lithologies and palaeo-environments. Approximately thirty grams of apparently unweathered, representative material was chosen for each sample and dried for three hours at 110°C. The sample was then hand-ground with an agate mortar and pestle to a talc-like consistency, dried for a further hour and then stored in a labelled Beatson powder bottle. This material was used for major and trace element analyses and for mineralogical analysis by X.R.D..

To quantify the effect of unrepresentative subsampling two separate subsamples were chosen for samples 74, 116 and 124. In addition, two further subsamples of 124 were selected to represent the apparently weathered and unweathered portions of the sample, in an attempt to identify the possible effect of surface weathering on the geochemistry and mineralogy.

(ii) X-ray fluorescence

SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, K_2O, MnO, P_2O_5 and SO_3 were determined by X-ray fluorescence (X.R.F.), using a Philips 2kW spectrometer with a Cr tube. Samples were analysed in the form of glass discs, prepared by the method of NORRISH and HUTTON (1969). Oxide concentrations were determined by comparison with a ratioing glass standard, FS 48, supplied by Dr. Norrish of the C.S.I.R.O.. The results obtained are shown in table 3. The values shown for loss on ignition (L.O.I.) were measured during the glass preparation procedure and may be taken to be the sum of H_2O, CO_2 and C, less a weight gain due to the oxidation of reduced elements (Fe^{2+}, $S^{=}$). The presence of $NaNO_3$ during the fusion process should have prevented the loss of sulphide sulphur by ensuring its complete oxidation.

As a measure of the precision of the method, the figures shown in table 4 were obtained from the analysis of three glass discs prepared from U.S.G.S. standard rock G1, each disc being analysed twice. The results show that the coefficient of

Table 3

Major element contents %

Sample No.	SiO_2	AL_2O_3	TiO_2	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	SO_3	L.O.I.	Total
2	43.02	14.07	0.32	15.93	0.34	2.13	7.94	0.18	2.73	0.03	0.09	0.27	12.87	99.96
5	54.15	18.03	0.92	6.58	0.37	1.81	3.89	0.20	2.68	0.03	0.08	0.34	11.26	100.39
7	31.32	11.15	0.50	4.92	0.83	1.55	28.83	0.18	1.85	0.22	0.13	0.29	23.59	100.45
8	29.79	10.52	0.44	3.82	0.68	1.56	25.57	0.18	1.96	0.23	0.12	0.27	25.20	100.51
10	53.71	20.56	0.85	6.51	0.59	1.89	2.86	0.27	3.93	0.03	0.14	0.12	8.58	100.11
19	57.84	12.17	0.83	3.96	0.50	1.43	9.13	0.16	2.32	0.08	0.15	0.37	11.26	100.26
22	47.45	17.69	0.76	6.01	0.70	2.06	6.12	0.20	3.08	0.05	0.10	1.04	15.01	100.35
24	42.11	17.47	0.69	5.23	0.73	1.78	12.40	0.21	2.50	0.12	0.16	0.79	15.82	100.10
27	47.64	15.87	0.82	3.50	0.73	1.49	12.22	0.18	2.30	0.05	0.14	0.60	15.01	100.62
28	58.51	21.07	0.97	5.15	0.30	1.95	0.63	0.26	3.43	0.05	0.07	0.05	7.77	100.25
29	57.01	18.20	0.92	6.10	0.18	1.79	2.60	0.21	2.99	0.13	0.07	2.92	7.51	100.65
31	57.40	18.20	0.90	4.84	0.55	1.83	2.72	0.22	3.07	0.05	0.10	2.16	7.77	99.87
32	54.73	18.54	0.89	6.67	0.68	1.98	1.07	0.22	3.00	0.07	0.08	3.93	7.77	99.71
33	56.45	18.14	0.88	6.25	0.75	2.09	1.23	0.22	3.15	0.04	0.07	4.13	6.97	100.43
36	60.80	17.73	0.98	4.94	0.54	1.39	1.78	0.18	2.67	0.04	0.06	3.01	5.63	99.81
37	60.68	18.17	0.98	4.62	0.63	1.56	1.97	0.20	2.77	0.04	0.07	2.25	6.43	100.44
39	58.84	18.55	0.96	4.46	0.61	1.69	2.21	0.20	2.84	0.05	0.09	2.34	7.77	100.68
42	52.35	15.84	0.80	6.21	0.55	1.80	5.81	0.19	2.49	0.08	0.07	5.51	8.58	100.33
45	58.99	18.70	0.90	4.58	0.90	1.90	0.67	0.20	3.01	0.07	0.08	0.98	9.12	100.20
47	53.01	20.19	0.98	7.33	0.70	2.12	0.57	0.20	2.91	0.07	0.11	5.53	6.17	99.96
49	56.22	18.20	1.02	4.34	0.65	1.61	4.15	0.21	2.66	0.10	0.10	1.32	9.12	99.76
50	56.77	11.48	0.98	4.42	0.67	0.79	1.28	0.16	1.84	0.02	0.06	0.37	20.91	99.82
51	69.05	13.63	1.29	3.56	0.30	1.27	0.39	0.15	2.59	0.07	0.06	1.58	6.70	100.67
52	54.55	15.90	0.89	7.03	0.41	1.17	1.02	0.21	2.31	0.07	0.05	5.81	9.92	99.39
54	50.62	19.26	0.76	6.27	0.55	1.62	5.47	0.30	3.63	0.14	0.10	0.73	9.92	99.44
55	56.65	19.32	0.96	10.32	0.29	1.17	0.64	0.28	3.55	0.04	0.08	0.13	6.17	99.62
58	48.28	20.22	0.73	6.45	0.23	1.85	5.77	0.32	3.08	0.06	0.10	1.82	10.99	99.92
62	45.95	21.74	0.69	6.04	0.22	1.59	7.31	0.31	3.09	0.28	0.08	0.16	13.14	100.61
64	50.69	18.77	0.86	8.93	0.24	1.57	5.05	0.34	3.22	0.24	0.09	0.10	10.46	100.58
65	52.30	22.91	0.86	9.18	0.21	1.53	0.65	0.34	3.27	0.02	0.11	0.17	8.31	99.87
67	51.47	21.92	0.77	8.59	0.20	1.77	1.46	0.43	2.68	0.06	0.13	0.12	10.72	100.35
68	46.33	18.65	0.67	6.70	0.37	1.59	8.75	0.27	2.82	0.14	0.09	0.17	14.21	100.68
74	65.68	17.59	1.46	3.69	0.69	1.25	0.59	0.25	2.71	0.04	0.05	0.16	5.90	100.13
74II	66.99	17.01	1.50	3.71	0.66	1.18	0.50	0.23	2.58	0.05	0.05	0.10	5.63	100.26
76	64.27	17.79	1.25	4.96	0.64	1.30	0.56	0.24	2.68	0.04	0.07	0.09	6.17	100.13
77	57.04	19.59	1.14	8.62	0.71	1.48	0.61	0.23	2.81	0.04	0.15	0.14	7.51	100.13

Table 3 continued

Sample No.	SiO_2	AL_2O_3	TiO_2	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	SO_3	L.O.I.	Total
82	57.64	19.06	1.01	5.71	0.27	1.53	2.42	0.27	3.44	0.06	0.07	0.06	8.85	100.42
86	51.45	17.55	0.87	5.53	0.28	1.98	6.94	0.25	3.38	0.09	0.10	0.12	11.26	99.81
88	54.85	19.36	0.93	6.73	0.27	1.68	3.21	0.30	3.49	0.05	0.09	0.07	8.85	99.91
91	55.26	21.50	0.93	7.72	0.29	1.85	0.88	0.32	3.47	0.05	0.07	0.07	7.24	99.68
93	50.16	12.17	0.69	3.64	0.28	1.75	12.65	0.20	2.22	0.15	0.13	0.27	15.82	100.18
95	55.98	20.67	0.96	5.79	0.54	1.90	1.14	0.30	2.99	0.04	0.12	0.64	9.12	100.25
98	49.77	17.14	0.83	5.41	0.25	1.74	8.41	0.26	2.51	0.06	0.11	0.19	13.40	100.10
102	69.58	14.12	1.12	4.07	0.19	0.95	0.53	0.22	2.43	0.03	0.04	0.24	6.17	99.71
105	84.74	6.16	1.19	2.34	0.13	0.48	0.25	0.22	1.57	0.03	0.12	0.33	2.14	99.71
106	67.88	14.59	1.45	3.58	0.40	1.28	0.44	0.40	2.42	0.05	0.05	0.14	6.97	99.69
109	71.96	13.09	1.41	3.33	0.36	1.12	0.39	0.30	2.35	0.03	0.04	0.11	4.83	99.35
111	53.53	16.73	0.62	5.27	0.28	2.12	7.01	0.49	2.76	0.03	0.06	0.19	11.26	100.37
112	23.62	8.07	0.29	2.89	0.30	1.68	32.35	0.26	1.28	0.05	0.06	0.24	28.69	99.81
113	1.28	0.40	0.02	0.31	0.17	1.23	51.99	0.51	0.09	0.07	0.10	0.32	43.43	99.94
114	7.65	2.80	0.07	1.47	0.27	1.18	46.81	0.10	0.41	0.11	0.08	0.19	40.21	101.38
116	49.97	16.03	0.50	7.10	0.45	2.74	7.39	0.30	4.21	0.03	0.07	0.15	11.26	100.24
116II	48.47	15.63	0.49	6.85	0.47	2.67	8.51	0.29	4.10	0.08	0.08	0.13	12.60	100.42
119	41.64	11.71	0.47	5.06	0.41	1.91	16.48	0.23	2.45	0.06	0.07	0.17	18.77	99.47
121	44.76	12.66	0.43	4.81	0.49	1.81	15.36	0.49	3.09	0.02	0.27	0.27	16.35	100.86
122	80.98	3.64	0.20	1.11	0.09	0.35	6.23	0.22	0.92	0.02	0.03	0.05	6.17	100.02
123	56.20	13.72	0.66	4.60	0.42	1.79	7.16	0.28	2.44	0.06	0.07	1.75	10.46	99.65
124	50.48	16.61	0.72	6.38	0.49	2.18	6.42	0.25	2.91	0.09	0.10	2.52	11.53	100.72
124II	52.22	16.23	0.74	6.33	0.48	2.14	6.42	0.26	2.95	0.04	0.10	2.64	9.65	100.25
124IN	49.79	16.49	0.72	6.14	0.55	2.10	6.84	0.26	2.94	0.04	0.11	2.25	11.26	99.54
124EX	51.09	17.63	0.76	6.35	0.52	2.35	6.15	0.25	3.04	0.08	0.10	2.18	9.65	100.21
126	43.75	16.22	0.64	8.46	0.50	2.05	8.35	0.24	2.76	0.05	0.14	7.12	9.65	99.98
129	53.37	14.15	0.68	5.06	0.45	1.76	7.91	0.22	3.04	0.10	0.18	0.20	12.33	99.50
133	54.62	13.52	0.85	3.49	0.59	1.71	9.69	0.24	2.43	0.08	0.14	0.35	12.87	100.64
134	57.47	5.44	0.74	1.21	0.63	0.74	16.65	0.31	1.13	0.18	0.14	0.12	15.55	100.36
136	54.54	21.35	0.91	5.39	0.71	1.61	1.83	0.30	3.36	0.03	0.08	0.19	9.12	99.48
138	77.05	9.43	1.12	1.88	0.26	0.73	2.37	0.27	1.68	0.04	0.11	0.20	5.09	100.26

Table 4

Precision of the X.R.F. analyses as determined by three duplicate analyses of U.S.G.S. standard rock G1

Oxide	Mean content %	Standard deviation	Coefficient of variation %
SiO_2	69.225	0.248	0.36
Al_2O_3	15.192	0.033	0.22
TiO_2	0.490	0.005	1.02
Fe_2O_3	2.641	0.016	0.61
MgO	0.787	0.009	1.14
CaO	1.926	0.003	0.16
K_2O	4.427	0.004	0.09
P_2O_5	0.138	0.003	2.17
S	0.015	0.005	33.33

variation for each oxide present in amounts exceeding 1% is less than 1%. It is evident that the method used has a high level of precision

To determine the accuracy of the method, in table 5 analyses of four U.S.G.S. standard rocks are listed, together with the average compositions for the same rocks, given by FLANAGAN (1969). It can be seen that the two sets of results show very close agreement. The most marked difference is in the values for MgO, where the values obtained by the method used here are always higher than the cited averages. The difference between the two sets of results tends to increase with increasing concentration, but as the samples studied here all contain less than 3% MgO, the difference is not thought to be too significant. A similar slight overestimation of P_2O_5 can also be seen, but, with the constant low P_2O_5 contents of the Oligocene samples, this is thought to be unimportant.

(iii) Wet chemistry

Wet chemical techniques were used to determine those major element oxides not determined by X.R.F., namely Na_2O, FeO and H_2O. Na_2O was determined by atomic absorption spectrophotometry following dissolution of 0.1g of rock powder in a mixture of hydrofluoric and perchloric acids. FeO was determined by titration against potassium dichromate, using sodium diphenylamine sulphonate indicator, of a hydrofluoric and sulphuric acid digest of 0.5g of sample. Some difficulty was experienced with samples containing organic carbon, as this remained in suspension and obscured the titration end-point. It was possible to obtain a satisfactory end-point for all samples except sample 50, the one with the highest organic carbon content. One drawback with this method of determining FeO is that pyrite is insoluble in the acids used and FeO present in pyrite is, therefore, reported as Fe_2O_3. Na_2O and FeO contents are included in table 3.

Total water was determined by the method of PENFIELD (1894). Adsorbed water (H_2O^-) was determined by weight loss of the sample after drying overnight at 110°C. This was then subtracted from the total water content to give a value of combined water (H_2O^+). DEER et al (1962) stated that although clay minerals lose most of their adsorbed water at 110°C, some may be retained until 300°C. It seems, therefore, that the H_2O^- contents may be slightly low and the H_2O^+ values correspondingly high. The determined H_2O^+ and

Table 5

Accuracy of the X.R.F. analyses as determined by analyses of four U.S.G.S. standard rocks - G 2, GSP 1, AGV 1 and BCR 1

	G 2		GSP 1		AGV 1		BCR 1	
Oxide	1	2	1	2	1	2	1	2
SiO_2	69.19	69.23	67.27	67.33	58.99	59.54	54.48	54.45
Al_2O_3	15.34	15.19	15.11	15.01	17.01	17.15	13.65	13.41
TiO_2	0.53	0.49	0.69	0.67	1.08	1.07	2.23	2.28
Fe_2O_3	2.68	2.64	4.33	4.23	6.78	6.71	13.58	13.44
MgO	0.78	0.79	0.95	1.02	1.49	1.71	3.28	3.61
CaO	1.98	1.93	2.03	2.02	4.98	5.00	6.95	7.02
K_2O	4.51	4.43	5.48	5.44	2.89	2.94	1.68	1.71
P_2O_5	0.14	0.14	0.28	0.30	0.48	0.53	0.36	0.40
S	0.02	0.01	0.06	0.04			0.03	0.04

N.B. The values in column 1 are from FLANAGAN (1969), those in column 2 were obtained using the X.R.F. method outlined on page 26.

H_2O^- contents are shown in table 6.

It was originally intended to determine CO_2 using the method of MOLNIA (1974), in preference to the evolution-absorption technique commonly in use at Sheffield. This method involves measuring the weight loss of a sample on a Millipore filter after treatment with dilute HCl and is reported to be both rapid and accurate. It was found, however, that in samples containing less than 75% calcite the method was very time-consuming and also inaccurate, as no allowance could be made for soluble salts in the samples, or the removal of exchangeable cations. CO_2 determinations were, therefore, not attempted, quantification of the carbonate minerals being considered a more rapid and accurate determination (see chapter 5(A)(iii)b)).

(iv) Duplicate precision

The oxide contents for the three duplicate samples are included in tables 3 and 6. From these it is possible to calculate the contribution of subsampling variation to the oxide concentrations listed. GARRETT (1973) gave the following formula for the calculation of the variance of duplicate determinations -

$$\text{Variance} = \frac{\sum_{i=1,n} (x_{1i} - x_{2i})^2}{2N}$$

Where, N = no. of duplicates

x_1 = first determination of variable x

x_2 = second determination of variable x

The standard deviation may then be calculated as the square root of the variance. The results obtained, listed in table 7, show that for only two oxides - SiO_2 and CaO, is the standard deviation greater than 1%. This is to be expected for SiO_2, the dominant oxide, while the high standard deviation for CaO may be explained as sample inhomogeneity with respect to shell fragments. In general it may be said that geochemical variations due to subsampling are very small.

Comparison of the results for the weathered and unweathered portions of sample 124 also shows only minor differences. These again may be explained as due to the presence of more shell material in one subsample. It is, therefore, safe to conclude that the variations in oxide concentrations shown in tables 3 and 6 are representative of real differences between the samples, rather than to analytical precision, subsample variation or the effect of

Table 6

H_2O^+ and H_2O^- contents

Sample no.	H_2O^+ %	H_2O^- %	Sample no.	H_2O^+ %	H_2O^- %
2	4.91	6.09	76	5.27	2.03
5	6.76	4.61	77	6.30	2.44
7	4.22	2.44	82	6.34	3.47
8	3.79	2.42	86	6.10	3.47
10	6.23	3.68	88	5.96	3.96
19	4.16	1.37	91	6.38	4.54
22	6.34	4.15	93	4.71	2.85
24	5.66	2.14	95	6.96	4.40
27	4.56	2.53	98	6.02	4.02
28	5.88	3.89	102	5.77	2.39
29	6.59	4.25	105	2.20	0.79
31	6.09	3.70	106	4.86	2.65
32	6.39	2.88	109	4.01	2.25
33	6.50	3.36	111	4.22	3.42
36	5.09	2.62	112	2.98	2.86
37	5.51	3.31	113	1.07	0.34
39	6.01	3.46	114	1.39	1.11
42	5.96	3.51	116	4.67	4.40
45	6.93	3.84	116 II	4.71	4.41
47	7.14	4.20	119	4.41	3.55
49	5.73	3.46	121	3.62	1.73
50	6.76	3.91	122	1.45	0.76
51	4.74	2.90	123	4.76	3.53
52	7.18	4.60	124	6.11	4.69
54	6.14	3.73	124 II	5.59	4.40
55	6.01	3.80	124 In	5.95	4.36
58	7.12	4.81	124 Ex	5.90	4.28
62	6.73	4.37	126	5.99	4.14
64	6.45	3.69	129	5.13	2.84
65	6.33	3.84	133	4.77	1.72
67	5.95	7.36	134	1.77	0.66
68	6.37	3.51	136	6.42	3.82
74	5.06	2.68	139	6.42	3.82
74 II	4.92	2.61			

Table 7

Standard deviations for the major element determinations on duplicate subsamples

Oxide	Standard deviation
SiO_2	1.05
Al_2O_3	0.39
TiO_2	0.02
Fe_2O_3	0.26
FeO	0.04
MgO	0.11
CaO	1.12
Na_2O	0.02
K_2O	0.17
MnO	0.07
P_2O_5	0.01
SO_3	0.14
H_2O^+	0.54
H_2O^-	0.30

surface weathering.

(B) Trace Element Analyses

(i) Preparation and analysis

In order to avoid undue repetitive analyses, it was decided to decrease the number of samples analysed for trace elements. Since the duplicate samples showed that the subsampling variation was small, they were left out of the following analyses. Also, where two samples showed very similar major element contents, only one was chosen for trace element analysis. This resulted in 47 samples being chosen for trace element study.

The samples were analysed in the form of powder pellets with a boric acid backing. These were prepared by pressing the samples in a mechanical press, at ten to fifteen tons per square inch pressure for three minutes. Quartz-rich samples (numbers 51, 102, 109, 121, 122, 134 and 138) needed the addition of five drops of polyvinyl alcohol to the powder before pressing, to prevent cracking of the pellet following release of the pressure. Sample 2 was found to expand on release of the pressure and so was prepared without a boric acid backing. These slight variations in sample preparation procedure should have no effect on the resuts obtained, as all pellets were of infinite thickness to the X-radiation used.

The trace elements determined were Ba, Co, Cr, Cu, Mn, Ni, Pb,Rb, Sr, V, Y, Zn and Zr, all of which were determined by X.R.F. using a Philips 2kW spectrometer with a W tube. Elemental concentrations were determined by comparison with a glass disc, prepared in Sheffield by Dr. R.K.Sotiriou, allowance being made for variations in sample mass absorption. Mass absorption coefficients for each sample were calculated from the major element results. The elemental concentrations obtained are shown in table 8.

One possible source of inaccuracy to the values in table 8 is that the calibration constants used were derived from igneous rock types. Since the samples were analysed in powder form sample mineralogy may affect the results obtained, as the mass absorption of a mineral will be different from that for the whole sample. Other workers at Sheffield have examined this possible source of error and concluded that the inaccuracy was less than five percent. It is apparent, therefore, that the trace element results are of an acceptable accuracy.

Table 8

Trace element contents ppm

Sample No.	Zn	Cu	Pb	Ba	Ni	Co	Mn	V	Cr	Rb	Sr	Y	Zr
2	93	101	171	231	165	86	302	282	112	182	295	10	134
7	51	25	25	241	30	11	1951	85	75	90	270	21	79
10	82	35	27	385	50	16	254	144	128	182	162	30	146
22	98	34	42	351	53	19	439	134	122	152	190	24	131
24	77	23	33	475	40	15	845	125	108	143	312	27	110
27	97	40	46	457	40	15	639	121	118	132	239	27	132
28	141	17	37	459	82	30	452	158	141	191	102	63	181
29	101	17	52	386	51	35	882	146	128	157	102	34	188
31	99	21	51	367	48	16	242	145	126	170	125	35	183
32	121	26	66	378	52	16	534	136	121	161	114	28	181
33	123	32	81	337	58	18	360	136	126	159	136	28	187
36	91	22	63	353	40	14	255	143	127	156	119	27	216
37	93	20	54	363	38	12	277	139	121	156	130	30	212
39	90	25	45	393	39	10	312	138	121	151	140	39	204
45	122	29	56	380	58	22	273	136	132	154	101	32	200
47	132	25	61	381	67	16	412	147	129	156	103	41	156
51	51	19	55	375	24	2	147	100	98	122	87	40	243
52	107	24	65	347	45	7	396	123	103	133	119	35	181
54	121	41	58	375	88	45	924	142	116	172	198	35	140
55	122	33	39	409	52	18	192	144	117	186	110	31	165
62	105	23	40	390	40	13	1966	145	127	175	215	32	114
64	113	31	31	393	51	16	1707	132	119	171	146	39	145
65	126	19	45	407	64	20	236	164	140	201	142	34	145
67	132	12	31	355	50	21	338	124	134	103	133	27	127
68	102	27	37	433	49	14	1285	125	120	156	203	25	126
74	80	29	38	494	40	11	143	130	121	159	131	63	257
77	104	26	61	431	71	18	200	155	128	173	137	56	203
82	108	29	49	389	43	21	279	136	127	169	141	40	196
88	123	22	40	392	52	15	418	136	127	165	141	32	167
93	67	18	19	301	31	5	1275	92	93	100	264	33	171
98	101	23	63	380	49	16	343	126	120	140	174	42	162
102	53	17	56	443	25	4	91	111	110	122	104	39	310
109	76	23	30	393	37	13	198	100	107	115	81	58	371
111	85	47	27	247	45	12	174	123	116	208	181	14	157
112	37	6	30	123	18	4	565	58	56	91	349	7	57
113	14	4	10	78	4	1	490	12	17	8	1124	-7	5
116	103	13	16	158	35	9	192	80	102	312	193	20	108
119	52	9	30	223	29	11	493	100	91	127	229	22	90
121	84	9	20	229	29	10	129	92	96	142	639	23	136
122	31	2	26	188	12	3	86	31	39	44	198	1	124
123	81	8	97	290	52	18	411	101	102	136	222	32	264
124	77	67	58	298	43	18	270	125	117	168	209	23	128
126	79	20	102	270	57	22	419	128	108	157	247	21	108
129	68	28	24	591	39	10	817	107	103	130	192	33	221
134	50	14	21	220	11	4	1372	43	83	50	151	40	301
136	90	35	52	420	67	30	197	154	138	184	170	24	155
138	56	13	21	335	19	8	142	68	85	85	110	43	370

an acceptable accuracy.

(ii) The use of acid pretreatment in determining the locations of the trace elements

a) Method and results

To supplement the results shown in table 8, two samples were chosen for acid pretreatment, in an attempt to identify the locations of the trace elements. The samples chosen were numbers 31 and 74, three 8g aliquots of each being treated with 100ml of 1N HCl for one, three and five hours respectively. The weight loss of each sample was determined after the samples had been centrifuged, washed and dried, in order that the results obtained could be directly compared with the original determinations. The results thus obtained are listed in table 9. Certain of the elements' results are also shown graphically in figures 3 and 4.

b) Interpretation

Since a dilute acid was used at room temperature, dissolution of the samples should be limited to calcite and gypsum, both of which were present in sample 31. In addition there is a possibility that partial dissolution of chlorite may have occurred, as this mineral is soluble in hot, dilute HCl (BRINDLEY, 1961). Removal of exchangeable cations will also have occurred, both from clay minerals and organic complexes. It is doubtful whether the acid used was strong enough to dissolve iron oxide coatings, although some solution could be expected.

From the results shown in table 9, it is evident that in neither sample was Co, Cr, Rb or Zr removed by the acid treatment. It may be assumed, therefore, that these elements do not occur in any of the minerals listed above. The lack of any Co removal suggests that dissolution of the iron oxides was not occurring in the acid used.

In both samples approximately 40ppm Ba was removed in the first hour of acid treatment, suggesting that this is present in exchangeable locations. This was followed by no further removal. The same removal pattern is shown by Sr in figure 4, but in figure 3 approximately 60ppm Sr was removed in the first hour, indicating that Sr is also present in calcite.

Approximately 10ppm V was removed from both samples during

Table 9

The effect of various periods of acid pretreatment on the trace element

Sample 31

Element	Untreated	After 1 hr.	After 3 hr.	After 5 hr.
Ba	366.7	329.8	330.0	332.6
Co	16.4	15.1	14.4	14.6
Cr	126.4	120.7	118.9	122.5
Cu	20.8	14.1	16.2	12.4
Mn	242.4	149.2	133.0	135.6
Ni	48.2	40.4	37.4	38.6
Pb	51.1	34.3	31.1	33.8
Rb	170.3	164.5	164.0	164.8
Sr	125.1	67.8	69.6	74.7
V	144.6	128.8	127.2	130.6
Y	35.2	23.1	24.0	19.3
Zn	99.0	79.7	79.1	74.6
Zr	183.0	180.3	184.0	184.7

Sample 74

Element	Untreated	After 1 hr.	After 3 hr.	After 5 hr.
Ba	493.6	454.1	454.0	454.9
Co	11.2	14.9	11.8	14.9
Cr	121.3	116.1	124.6	121.0
Cu	28.9	17.3	15.8	13.9
Mn	142.6	134.4	133.1	133.1
Ni	39.6	41.8	39.1	40.4
Pb	37.9	23.4	23.9	27.0
Rb	158.5	157.3	164.5	158.3
Sr	130.8	86.9	85.5	85.0
V	129.6	120.9	122.0	122.5
Y	62.5	45.6	42.1	48.9
Zn	79.7	76.9	77.6	78.4
Zr	256.8	255.9	261.5	253.9

Figure 3

The effect of acid pretreatment on the trace element contents of sample 31

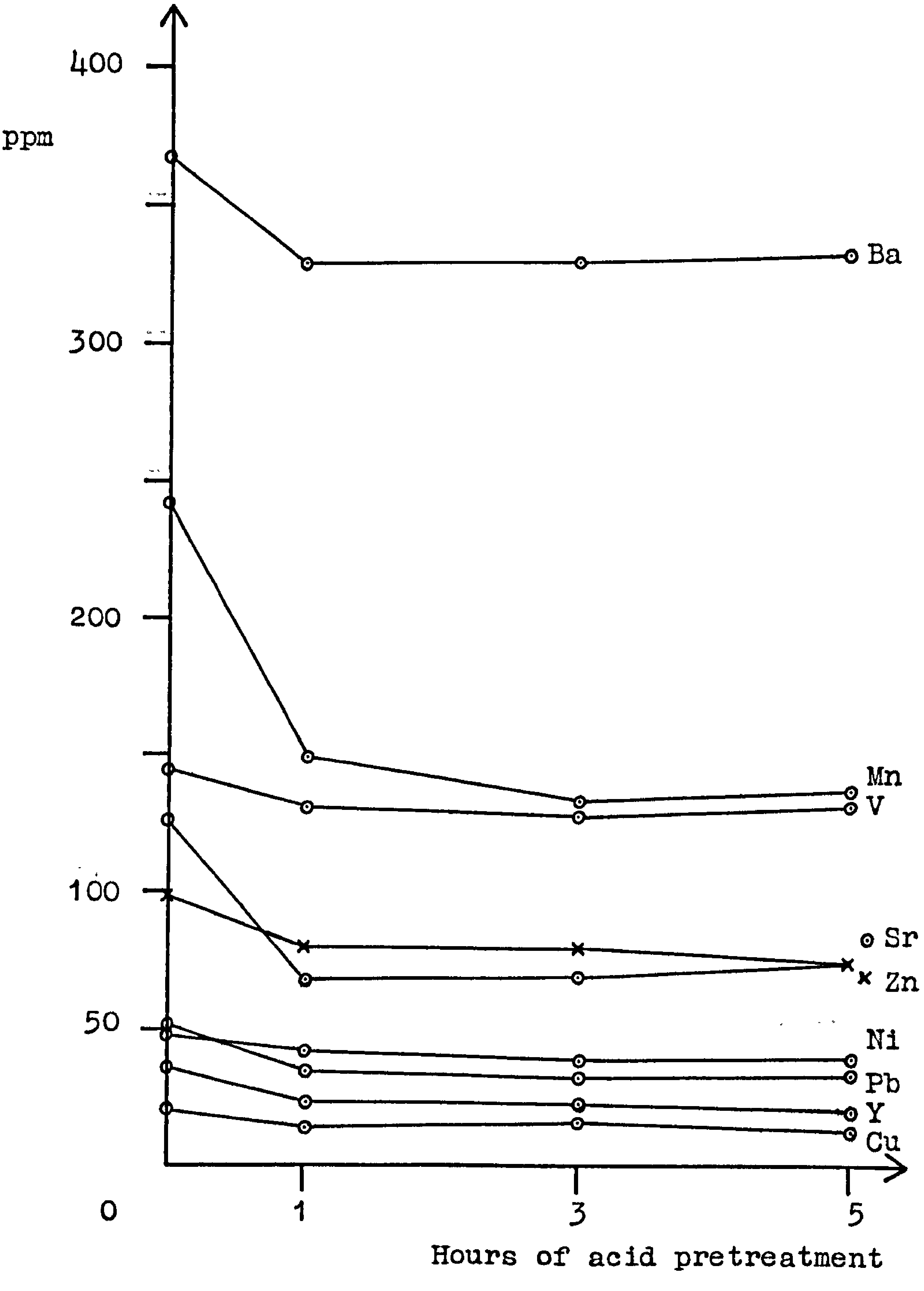
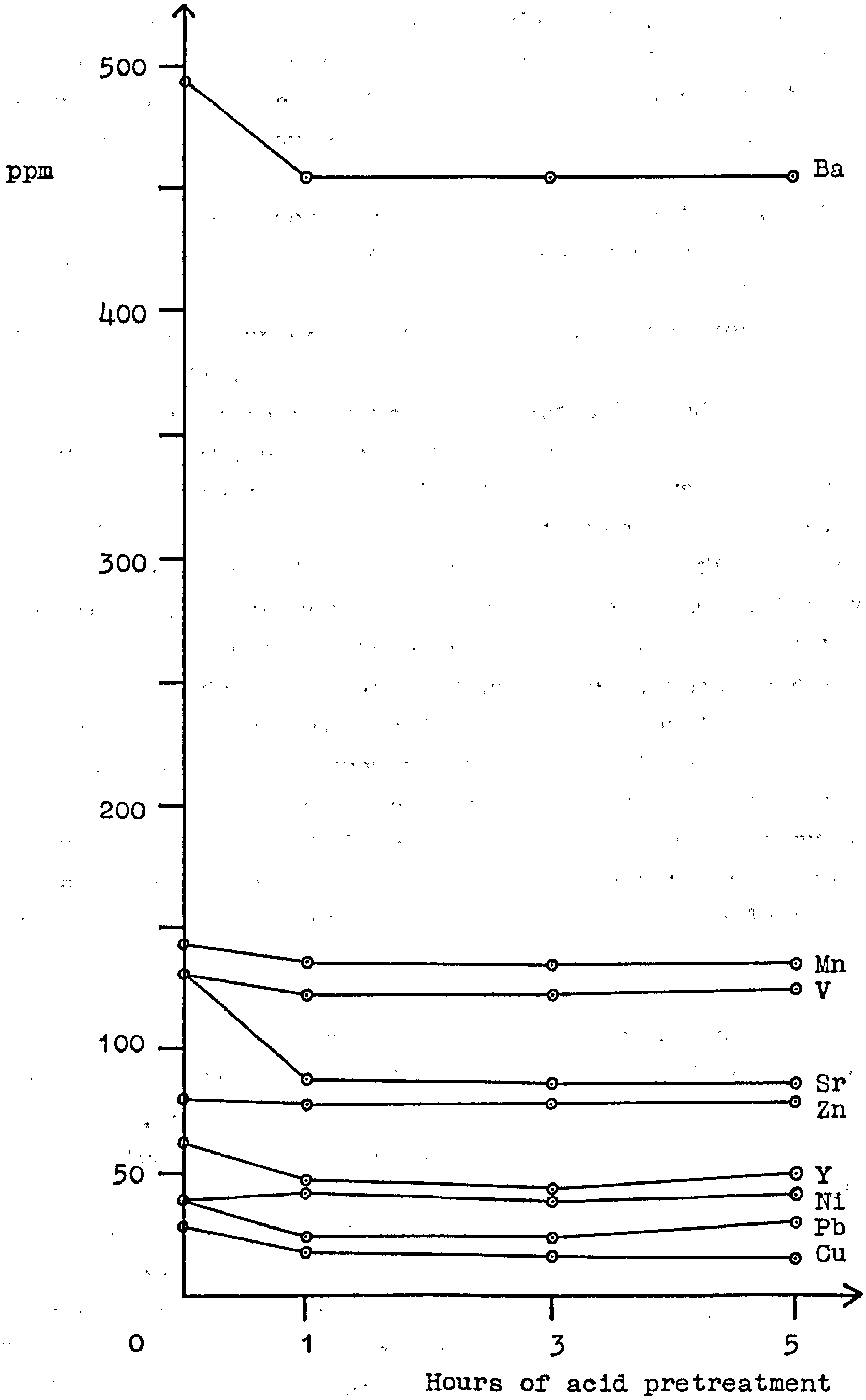


Figure 4

The effect of acid pretreatment on the trace element contents of sample 74



the first hour of acid treatment. A similar amount of Mn was removed from sample 74 and it is thought that this amount of Mn and V is present as fine grained coatings on the clay minerals. In sample 31, 100ppm Mn was removed by acid treatment, indicating that Mn is a more important substituent in calcite than is Sr.

Approximately 10ppm Cu and 15ppm Pb were removed from both samples within the first hour of acid treatment, no further removal then occurring. KRAUSKOPF (1956) showed that smectites were effective removers of Zn, Cu and Pb from solution, so an exchangeable location for Cu and Pb is to be expected. Y was also removed from both samples on first acid treatment, but it is less likely that Y is occurring as an exchangeable cation on the clay minerals. Instead it seems possible that Y is partially present in the organic content of the samples, as was mentioned by WEDEPOHL (1974).

The two remaining trace elements, Ni and Zn, show the same removal pattern, no removal from sample 74 and partial solution in the first hour from sample 31. While Ni was reported by WEDEPOHL (1971) to be a common substituent in calcite, Zn was not, so it is not possible to fully explain the different behaviour of the two samples by variations in calcite content. The two samples are different in respects other than their calcite contents. Sample 31 is from the marine Corbula Beds, which contain organic matter, pyrite and iron oxides produced from the alteration of pyrite. Sample 74 is from the non-marine Lower Hamstead Beds and does not contain pyrite or appreciable quantities of organic matter. FLEISCHER (1955) reported that in sedimentary pyrite Ni was a common substituent, so it seems reasonable to conclude that the soluble Ni present in sample 31 was originally held in the pyrite structure and was released on oxidation of the pyrite. The Ni thus released into solution was taken up by clay minerals and organic matter into exchangeable locations. Again it is not thought that this can explain the presence of acid soluble Zn in sample 31, as FLEISCHER (1955) reported that Zn was not as common a substituent as Ni in pyrite.

It was mentioned above that smectites are effective removers of Zn from solution and RASHID (1974) showed that organic matter was also capable of removing Zn from solution. The presence of exchangeable Zn in sample 74 would, therefore, have been expected. RASHID (1974) showed, however, that organic matter removed Cu preferentially to Zn from solutions of equal concentrations of the two metals, but that the same organic matter removed eight times as much Zn as Cu from seawater. It may be expected that smectites would show similar behaviour. It seems possible, therefore, that the different behaviour of Zn in samples 31 and 74 is due to one being of marine and the other of freshwater origin. Whereas Zn has a similar concentration in river and sea water, Cu is approximately five times as concentrated in river water. Organic matter and possibly clay minerals, would remove Cu preferentially to Zn from river water, while in sea water the opposite would occur. Further supporting evidence for this is that the freshwater sample, 74, contains more exchangeable Cu than does the marine sample. It appears, therefore, that exchangeable Cu and Zn contents may be potential palaeosalinity indicators, although further work is obviously needed to confirm the preliminary results presented here.

It can be seen that acid pretreatment is useful in identifying trace element locations. More information could be obtained by using acids of varying strength, as well as different temperatures and lengths of exposure to acid.

(C) Organic Geochemistry

(i) Organic contents

Due to the difficulties involved in accurate organic carbon determinations and the generally low organic carbon contents in the Oligocene samples, it was decided not to determine organic carbon contents. Organic carbon was merely recorded as present or not, as seen by the presence of carbonaceous material in suspension during the ferrous iron titration. It is possible to estimate organic content from the loss on ignition value as follows -

Organic content = L.O.I. - $(CO_2 + H_2O) + FeO/10 + 1.5 \times S^=$

A visit was made to the Organic Geochemistry Unit at Newcastle University, where initial investigation of five samples was undertaken. The content of extractable organic compounds was determined by Soxhlet extraction of the ground sample with distilled dichloromethane. Refluxing was continued for twelve hours and the extract was then dried, first in a rotary evaporator under partial vacuum and finally air dried. The weight of the residues obtained, expressed as a percentage of the original sample weight are shown in table 10, together with the total organic content estimated by the above expression.

Table 10 Extractable organic contents

Sample no.	Extractable organic %	Total organic %
22	0.164	2.6
31	0.028	0.4
32	0.151	0.9
42	0.049	0.6
50	0.164	12.3

From table 10 it is apparent that the extractable organic content forms a small part of the total organic content. While the latter values are thought to be of poor accuracy, they are thought to be usually underestimations, since H present in organic matter would be reported as H_2O^+ in the water determination. The low proportion of extractable organic matter would, therefore, be emphasised. In the hand specimens, the organic matter was seen to be present as leaf remains, or in a peat-like form, both of which would be insoluble in dichloromethane.

(ii) Reflectivity measurements

Small pieces of the samples were cast in 'Metset' resin and ground down under alcohol to produce a smooth surface. The samples were then studied microscopically, using x600 magnification under oil immersion. Reflectivity was measured on vitrinite particles, using a light wavelength of 546nm and polished glass reference standards. Values obtained from six particles from sample 50 ranged between 0.25 and 0.27% Ro, with a mean of 0.26%. In sample 31, three fragments gave reflectivities in the range 0.26 to 0.28% Ro, while a fourth gave a value of 0.65%. Excepting the last value, it can be seen that reflectivities of 0.25 to 0.28% Ro are typical of the Upper Hamstead Beds. This range is in the eodiagenesis zone of FOSCOLOS et al (1976), corresponding to loss of pore water, but no clay dehydration or hydrocarbon generation. The higher reflectivity for one particle from sample 31 undoubtedly represents detrital organic matter. The reflectivity obtained falls within the lower mesodiagenesis zone of FOSCOLOS et al (1976), which is the region of maximum hydrocarbon generation. Since hydrocarbon generation is known to have occurred in the Upper Jurassic and Lower Cretaceous sediments of the Hampshire Basin, it seems reasonable to conclude that these may have been the source of the particle seen.

(D) Exchangeable Cations

(i) Relationship with palaeosalinity

The positions occupied by exchangeable cations are the most chemically reactive sites in a clay mineral and cations occupying these sites readily equilibrate with the prevailing chemical environment. KELLEY and LIEBIG (1934) showed that a Ca saturated clay replaced its Ca by Mg and Na when immersed in sea water. Similarly RUSSELL (1970) showed a decrease in exchangeable Ca and increase in Mg, Na and K in recent marine sediments, when compared with non-marine sediments. SPEARS (1973) found that Carboniferous shales could be identified as marine or non-marine by their exchangeable Mg/Ca value.

(ii) Statement of the problem

The measurement of exchangeable cations is relatively straightforward, unless a carbonate mineral is present in the sample. Most, if not all, potential exchange solutions also dissolve carbonates to a certain extent, thus releasing into solution the cations present in the carbonate (commonly Ca and Mg). Three possible methods of overcoming this problem exist. Firstly, the separation of a carbonate-free phase, which was proved to be unlikely for the Oligocene sediments, as calcite was still shown by X.R.D. to be present in the $<2\mu$ fraction. Secondly, the use of an exchange solution which does not affect the solubility of carbonates. Again this is improbable, as previous work has not, so far, produced such an exchange solution. The final and only possible method is that of evolving a method capable of distinguishing exchangeable from carbonate Ca and Mg.

(iii) Development of the method

Two factors limit the choice of exchange solution, the anion chosen must have easily soluble Ca and Mg salts, while the cation must be monovalent, or a strong-base forming divalent one (BOWER and TRUOG, 1940). As regards the choice of anion, SPEARS (1973) reported that acetates greatly increased the solubility of calcite, by a process of complex formation. As chlorides are thought to be similar complex formers, it was decided to use a nitrate. Since it is usual to determine exchangeable Na and K, the use of a Na or

K salt as the exchange solution would necessitate the use of a further exchange solution to determine Na or K. It was decided, therefore, that $Ba(NO_3)_2$ would be the best salt to employ.

The method used for the determination of exchangeable cations was an amendment of that outlined by SPEARS (1973). Two aliquots of approximately 0.2g of unground sample were weighed accurately into centrifuge tubes. Twenty millilitres of distilled water were added and the tubes stoppered and shaken mechanically for ten minutes. After standing for one hour the suspensions were centrifuged and the resistivity of the supernate measured. The supernate was then discarded and a further washing performed. Once similar resistivities were obtained for two successive washings, one aliquot of sample was treated with twenty millilitres of 0.1N $Ba(NO_3)_2$, the other with twenty millilitres of distilled water. The former solution contained the exchangeable cations, while the latter gave an indication of water soluble cations. The solutions were analysed for Na, K, Ca and Mg using a Perkin-Elmer 303 atomic absorption spectrophotometer. If a measurement of C.E.C. was required, the aliquot treated with $Ba(NO_3)_2$ was washed through three times with twenty millilitres of distilled water, the final washing being retained. The sample was then treated with twenty millilitres of 0.5N KCl and the two solutions thus obtained were analysed for Ba.

To test the accuracy and precision of this method, exchangeable cations and C.E.C. were determined for eight portions of a non-calcareous sample, number 74. The means and standard deviations obtained are shown in table 11, after subtraction of water soluble values.

Table 11 Mean and standard deviation for the exchangeable cations and C.E.C. of sample 74 (meq/100g)

	Na	K	Ca	Mg	Total	C.E.C.
Mean	0.00	0.10	10.67	4.63	15.40	15.98
Standard deviation	-	0.01	0.39	0.40	0.68	0.76

It can be seen from table 11 that the method used has a high level of precision, especially when it is remembered that no attempt at sample homogenisation had been made. The small difference between the total exchangeable cations and C.E.C. indicates that other exchangeable cations occur in the sample, but that they are of minor importance. It can therefore be safely concluded that, C.E.C. = Na + K + Mg + Ca.

To investigate the effects of various exchange solutions on a calcareous sample, four aliquots of sample 74 were spiked with ten percent by weight of calcium carbonate and a further four spiked with ten percent of sample 113 (from the Bembridge Limestone). After washing to a relatively constant supernate resistivity, one aliquot was treated with distilled water, one with 0.1N $Ba(NO_3)_2$, one with 0.5N NH_4OOCCH_3 and the final one with 0.5N NH_4NO_3. C.E.C. was determined for the aliquot treated with $Ba(NO_3)_2$ by the method mentioned above. The results obtained are listed in table 12, after the subtraction of water soluble values. The results are expressed as meq/100g of sample 74, ignoring the amount of carbonate present, so as to be directly comparable with those in table 11.

Table 12 Exchangeable cations determined for spiked aliquots of sample 74

	Exchange solution	Na	K	Ca	Mg	Total	C.E.C.
74 + 10% $CaCO_3$	0.1N $Ba(NO_3)_2$	0	0.10	18.57	2.10	20.77	9.66
	0.5N NH_4NO_3	0	0.08	112.08	1.78	113.96	
	0.5N NH_4OAc	0	0.11	128.12	1.75	127.98	
74 + 10% 113	0.1N $Ba(NO_3)_2$	0.04	0.07	26.96	2.65	29.72	10.69
	0.5N NH_4NO_3	0.02	0.06	93.72	3.70	97.53	
	0.5N NH_4OAc	0.02	0.04	103.93	3.68	107.72	

Several points are worthy of note in table 12. Most apparent is the large variation in exchangeable Ca values, showing that the exchange solutions used dissolve calcite to different extents. That all of the exchange solutions are at least partially dissolving calcite is shown by the higher total exchangeable cation values in table 12 than in table 11. The exchangeable Ca and Mg values for any one exchange solution are different for the sample spiked with the Bembridge Limestone and that spiked with $CaCO_3$. This indicates that the degree of dissolution of calcite is not constant for any exchange solution, but varies with the nature of the calcite present in the sample. Finally, the exchangeable Mg and C.E.C. values are lower than those in table 11.

The final point may be understood by a consideration of equilibrium chemistry. Calcite exists in three states in the presence of water -

$$\begin{array}{lll} CaCO_3 = & CaCO_3 & = Ca^{++} + CO_3^{=} \\ \text{solid} & \text{dissolved,} & \text{dissolved,} \\ & \text{unionised} & \text{ionised} \end{array}$$

The cations released by the small amount of calcite which dissolves will equilibrate with the exchangeable cations on the clay minerals. Since all of the Oligocene samples contain low-Mg calcite (see chapter 5(A)(iii)b)), the Mg/Ca value for the carbonate is always lower than that for the exchangeable cations. During each washing prior to the treatment with the exchange solution, Ca will tend to migrate from the carbonate to the exchangeable locations, with a reverse movement of Mg occurring. This latter prduces the low exchangeable Mg values. In effect, the following equilibrium is being moved to the right -

$$\text{Clay-Mg} + Ca^{++} + CO_3^{=} + CaCO_3 = \text{Clay-Ca} + Mg^{++} + CO_3^{=} + CaCO_3$$

The decrease in C.E.C. observed between tables 11 and 12 may be explained by similar reactions to the above. The reactions taking place during cation exchange in a calcareous sample may be summarised as follows -

$$\text{Clay-M} + Ba^{++} + nCaCO_3 = \text{Clay-Ba} + M^{++} + mBaCO_3 + n\text{-}mCaCO_3$$

where M = the exchangeable cation

The first washing of the Ba saturated clay will still contain much $Ba(NO_3)_2$ in solution, but in succeeding washings resistivity measurements suggest that the Ba concentration in solution decreases rapidly. Once the Ba concentration falls below the total concentration of other ions in solution, exchange will occur between these ions and the exchangeable Ba, thus leading to low determined Ba contents and, hence, C.E.C..

The C.E.C. results shown in table 12 were determined after six washings. To test the above hypothesis, further carbonate spiked portions of sample 74 were prepared and Ba saturated. These samples were washed only twice before removal of the Ba with 0.5N KCl. The results obtained are shown in table 13, together with the Ba content of the last washings.

Table 13 C.E.C. of calcite spiked aliquots of sample 74

		Ba meq/100g
74 +	Last washing	3.01
10% $CaCO_3$	0.5N KCl	16.22
74 +	Last washing	3.69
10% 113	0.5N KCl	17.25

While the Ba contents removed by 0.5N KCl are similar to the C.E.C. in table 11, after removal of the last washing value they would be too low. It is thought that this is due to the large amount of $Ba(NO_3)_2$ still present in the second washing. It can, however, be seen that minimising the number of washings after Ba saturation can lessen the removal of Ba from the exchange positions.

To return to the problem of determining exchangeable Ca and Mg in calcareous samples, it was shown in table 12 that the exchange solutions used were dissolving calcite to different extents. Plotting a graph of the exchangeable Ca and Mg determined by the three exchange solutions results in a straight line, the slope of which is the Ca:Mg ratio in the carbonate, slightly amended by partial equilibration with the Ca:Mg ratio of the exchangeable cations. It was shown above that the four determined cations account for over 95% of the C.E.C. and, therefore, subtracting the total of Na and K from the determined C.E.C. leaves a good estimate of the sum of Ca and Mg. If a point is located on the graph of exchangeable Ca against Mg where Ca plus Mg equals this sum, the values obtained are the values of exchangeable Ca and Mg. This is shown graphically in figure 5, the C.E.C. value used being that from table 11.

The Ca and Mg values obtained from the graphs in figure 5 may be seen to be different from the exchangeable Ca and Mg values in table 11. The Ca values are both higher, while the Mg values are lower than the originals. This is, of course, due to the exchange of carbonate Ca for exchangeable Mg during the washing procedure. The extent of this exchange may be seen from the upper graph in figure 5. The sample in this case was spiked with A.R. $CaCO_3$ and, thus, the graph should have a vertical or very slightly positive slope, indicating a negligible Mg content in the sample. Instead the graph has a negative slope indicating a negative Mg content.

In conclusion, it may be said that while the determination of exchangeable cations in non-calcareous samples is both precise and accurate by the method outlined on page 35, their accurate determination in calcareous samples is not yet possible. While the accurate determination of C.E.C. in calcareous samples is possible by other methods, the washing procedures employed will result in high exchangeable Ca and low exchangeable Mg values being obtained for samples containing low-Mg calcite.

Figure 5

Graphs of exchangeable Ca against Mg for calcite spiked aliquots of sample 74


Sample 74 + 10% A.R. CaCO$_3$

Sample 74 + 10% sample 113

(iv) Results obtained

The methods developed above were used to determine the exchangeable cation contents of several marine and non-marine samples. The results are shown in table 14.

Table 14 Exchangeable cation contents of some marine and smectite rich samples (meq/100g)

Sample no.	Na	K	Ca	Mg	Total	Mg/Ca
30	0	0	10.90	3.50	14.40	0.32
32	0	0	5.90	1.00	6.90	0.17
33	0	0	10.52	0.48	11.00	0.05
37	0	0	12.80	0	12.80	-
67	0.02	0.29	28.26	11.53	40.10	0.41
121	0	0	6.7	2.3	9.0	0.34
2	0	0	30.05	1.98	32.03	0.07

Samples 2 and 121 are the only calcareous samples in table 14 and their exchangeable Ca and Mg contents were determined from a graph plotted of the exchangeable Ca and Mg released by 0.5N NH_4OOCCH_3, 0.5N $Ba(NO_3)_2$ and 0.1N $Ba(NO_3)_2$.

Samples 30, 32, 33 and 37 are all from the marine Corbula Beds, although they do not show the same exchangeable Mg/Ca as did those of SPEARS (1973). To identify the cause of this difference the first washings of samples 32, 33 and 37 were retained and analysed, as a measure of groundwater composition. They contained an average of 3,500 μg/ml Ca and gave an Mg/Ca value of 0.15 to 0.29, comparable to the exchangeable Mg/Ca values. It is evident, therefore, that the exchangeable cations had equilibrated with the groundwater. The reason for the very high Ca content of the groundwater is the presence of gypsum in the Corbula Beds, formed from the solution of calcite and oxidation of pyrite. Inspection of table 1 shows that these four samples were collected from a stratigraphic thickness of only one metre, yet in that distance the exchangeable Mg/Ca falls uniformly from 0.32 to zero. This suggests that sample 30 was collected from near the top of the gypsum producing environment and, therefore, was not subjected to the same volume of gypsiferous solution as were the samples below. It seems reasonable to conclude that, from the evidence of the exchangeable cation contents, the oxidation of pyrite in the Corbula Beds occurred while the Corbula

Beds were of their present thickness and, may, therefore, have been contemporaneous with deposition of the overlying Plateau Gravel (of Pleistocene age, WHITE, 1921).

Sample 121 was collected from the brackish-marine Bembridge Oyster Bed, but again the exchangeable Mg/Ca is typical of a non-marine sample (SPEARS, 1973). This sample contains shell fragments and it is thought that, to a large extent, the exchangeable Mg/Ca had equilibrated with the Ca:Mg ratio in the carbonate. This could have occurred during groundwater movement, or during the determination of the exchangeable cations. To support the former, KELLEYand LIEBIG (1934) showed that outcropping marine sediments frequently showed non-marine exchangeable Mg/Ca values. This they said was due to the movement of waters charged with calcium bicarbonate. It is possible that in more lithified samples the original exchangeable cation contents may be retained even after surface exposure, especially if care is taken in the collection of fresh samples.

The final two samples in table 14 are both non-marine, but were shown by X.R.D. to be very smectite rich (see chapter 5(B)(iii)b)). The determined exchangeable cation totals support this observation, being more than double those of other samples studied. They are, however, less than half the C.E.C. of pure smectite given by DEER et al (1962) of 100meq/100g. This suggests that the samples contain between thirty and fifty percent smectite.

5 MINERALOGY

(A) Determination of non-clay minerals by X.R.D.

(i) Sample preparation and analysis

Of the samples used for major and trace element analysis, nine were not used for mineralogical analysis, as they contained only small quantities of clay minerals. The non-clay minerals were determined on portions of the ground sample from the Beatson powder bottles. The powder was used to backfill an aluminium powder holder with a cavity two by one centimetres in area. Care was taken to avoid producing preferred orientation, while also ensuring that sufficient powder was in the holder so that the sample surface was level with the holder surface.

Samples were analysed on a Philips diffractometer, using Ni filtered Cu Kα radiation produced at 36kV and 26mA. A goniometer speed of 1° 2θ per minute was used, with a corresponding time constant of one second. The first samples were scanned from 4 to 44°2θ, but as the (001) clay reflections were scarcely discernible from the background, following samples were only scanned from 10 to 44°2θ. This range is, however, suitable for the identification of all common non-clay minerals. Some samples were also scanned from 56 to 63°2θ, in order to cover the most intense pyrite peak and the (060) clay peaks. For the latter very poor results were obtained due to the poor crystallinity and small grain size of the clay minerals. It was, therefore, not possible to identify the clay minerals as dioctahedral or trioctahedral.

(ii) Mineral identification

The diagnostic lattice spacings used to identify the minerals found in this study are shown in table 15. The lattice spacing of a mineral is easily found from its diffraction peak angle by the Bragg equation -

$$n\lambda = 2d \sin\theta$$

where λ = 1.5405Å for Cu Kα
d = lattice spacing
θ = diffraction angle

Figure 6 shows the diffraction trace for sample 36 and includes many of the non-clay minerals identified in this study. Peaks corresponding to lattice spacings of 7Å, 3.5Å and 5Å were

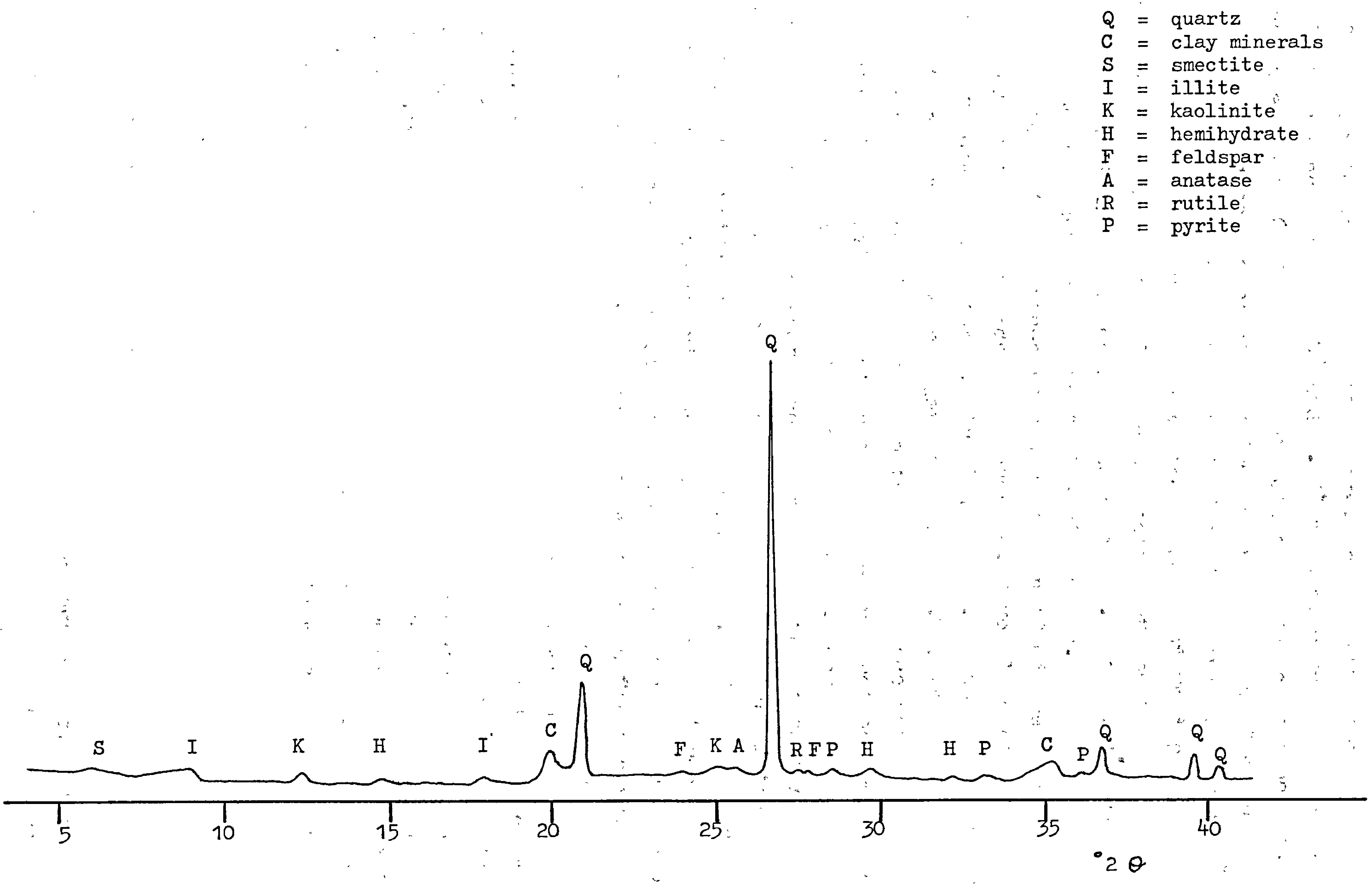
Table 15

Diagnostic lattice spacings of non-clay minerals identified by X.R.D.

Mineral	Lattice spacings (Å) in order of decreasing intensity					
Quartz	3.34	4.26	2.46	2.28	2.24	2.13
Calcite	3.03	2.28	2.09	2.49	3.86	
Hemihydrate	5.99	3.00	2.80	3.47		
Pyrite	1.63	2.71	2.42	2.21	3.13	
Goethite	4.18	2.69	2.45	2.19	4.98	2.49
Anatase	3.51	2.38				
Rutile	3.24	2.49				
Aragonite	3.40	3.27	2.70	2.37	2.48	2.34
Hematite	2.69	2.51	2.20			
Jarosite	3.08	5.09	3.11			

Figure 6

X-ray diffractogram of sample 36



identified in most samples. These are respectively the (001) and (002) kaolinite and (002) illite peaks. Broad assymetric peaks due to lattice spacings of 4.45Å and 2.55Å were also regularly seen. These are due to {hk0 and {hkl reflections of the clay minerals. The peak broadness is related to the superimposition of several peaks. Small peaks in the regions 3.28 to 3.16Å and 3.78 to 3.74Å were seen in a few samples due to the presence of feldspars. The peaks were too small to allow identification of the type of feldspar. Similar small peaks in the region 2.85 to 2.81Å are thought to represent small quantities of apatite.

In table 16 the non-clay minerals identified are arranged semi-quantitatively in order of abundance. Several points are worthy of note in this table. Firstly, gypsum, which is present in many of the samples was not identified by X.R.D.. Instead, hemihydrate, a mineral which is unstable at surface conditions, was found. It is evident that in the sample preparation procedure (page 26) gypsum was converted to hemihydrate. Secondly, hemihydrate and pyrite show a very similar distribution through the succession, due to the formation of gypsum following the weathering of pyrite (as mentioned on page 39). A further point of interest is that aragonite was only identified in three samples. BERNER (1971) showed that aragonite was a regular constituent of molluscan shells, but was unstable on exposure to freshwater. It may be significant that the three aragonite bearing samples are all from the Bembridge Oyster Bed, suggesting that the aragonite was retained in the robust Ostrea shells, but altered to calcite in the other more delicate shells. Finally, two titanium dioxide minerals occur in the Oligocene sediments, anatase and rutile. Anatase seems to be dominant over rutile, suggesting a possible authigenic origin, although derivation from pre-existing sediments is just as likely. WALDER (1964) showed that in Eocene sediments in the Hampshire Basin, both anatase and rutile were of partial derived and partial authigenic origin.

(iii) Quantification

a) General considerations

Quantification of a sediment's mineralogy can provide a great deal of information about the sediment's history. Direct methods of quantification, such as point-counting, are not possible for fine-grained sediments, so it is usual to utilise indirect

Table 16

Non-clay minerals identified by X.R.D.

Sample no.	Minerals identified in order of decreasing abundance							
2	C	Q	G					
7	C	Q	G					
10	Q	C	An	G	Ar			
27	Q	C	An					
28	Q	An	R					
29	Q	Hy	G	F	P?			
31	Q	C	Hy	An	Hm?	P?		
32	Q	P	Hy	An	R	F		
33	Q	Hy	P	F				
36	Q	Hy	P	An	R	F		
37	Q	Hy	P	An	R	C		
39	Q	P	C	R				
45	Q	P	F	Hy?				
47	Q	Hy	P	An	F			
49	Q	C	An	P	Hy?			
51	Q	An	G	R	J	F		
52	Q	Hy	J	R	An	F	C	P?
54	Q	C	An	G	P			
55	Q	An	G					
64	Q	C	An	G	R			
65	Q	G	An					
67	Q	An	Hm	C	R	F		
74	Q	An	R	F	S?			
77	Q	An	G	F				
95	Q	An	R	F				
102	Q	An	R	F				
111	Q	C	R					
112	C	Q						
116	Q	C	An					
119	C	Q						
121	Q	Ar	C					
122	Q	Ar	C	R				
123	Q	C	G	Ar	R	P		
124	Q	C	P	An	F			
126	Q	C	P	Hy	An			
129	Q	C	An					

Table 16 (contd.)

Sample no.	Minerals identified in order of decreasing abundance					
134	$\underline{\text{Q}}$	$\underline{\text{C}}$	R?	F?	Ap?	
136	$\underline{\text{Q}}$	$\underline{\text{C}}$	$\underline{\text{An}}$	$\underline{\text{R}}$	G	F

N.B. Q = quartz; C = calcite; Ar = aragonite; Ap = apatite; An = anatase; R = rutile; Hy = hemihydrate; Hm = hematite; P = pyrite; F = feldspar; G = goethite; J = jarosite; S = sphene.

$\underline{\text{X}}$ = mineral X positively identified
X = mineral X tentatively identified
X? = mineral X questionably identified

methods such as X.R.D.. Unfortunately, clay minerals are frequently poor diffractors of X-rays, so while the quantification of non-clay minerals by X.R.D. is possible, clay mineral quantification is more difficult. An alternative method for quantifying clay mineralogy is recalculation of the sample's geochemistry, as was used by SCHULTZ (1964).

The diffracted peak intensity of any mineral in a sample may be considered to be the product of the following factors - the percentage of that mineral in the sample; the mass absorption coefficient of the sample; the crystallinity and grain size of the mineral; diffractometer variability; and a factor related to the orientation of the mineral in the sample holder. Quantification of mineralogy by X.R.D. must either quantify or remove variation in all of the above factors except diffracted peak intensity and the percentage of the mineral in the sample, so that a direct relationship exists between the two. In this work mass absorption coefficients for Cu Kα for all samples had already been calculated during the trace element analyses. For non-clay minerals, the factors of crystallinity and grain size may be taken to be constant. Similarly it is thought that orientation may be considered constant, as the sample preparation procedure should produce randomly oriented samples. The only remaining variable is, therefore, diffractometer variability. This was measured daily by means of counting the peak intensity obtained from a silicon disc. A coefficient of variation in the range of five to ten percent was obtained. Although this seems to be a large potential source of error, it was found that the main contributor to this was positioning of the disc in the sample holder. Since this problem does not exist with the aluminium powder holders, a coefficient of variation significantly less than five percent is suggested for diffractometer variability. If all of the above assumptions are valid, the relationship between diffracted peak area and mineral content may be expressed as follows -

$$\mathrm{Area}_I = \%_I \times (\mathrm{M.A.C.}_Y/N) \times F_I$$

where Area_I = peak area of mineral I in sample Y

$\%_I$ = percentage of mineral I in sample Y

$\mathrm{M.A.C.}_Y$ = mass absorption coefficient of sample Y for Cu Kα radiation

N = a constant M.A.C., taken to be 50.0

F_I = calibration constant for mineral I at M.A.C. of N

Calculation of the calibration constant in the above equation is possible from samples containing a known quantity of mineral I and whose mass absorption coefficient is known. This method of mineralogical quantification is similar to that used by SCHULTZ (1964), except that he calculated calibration constants by spiking artificial samples. Also he did not allow for variations in sample mass absorption, which in these samples would lead to large errors, as sample mass absorption varies from 41.9 to 67.8 for Cu Kα. The main advantage of this means of quantifying non-clay mineralogy is that it is very efficient in diffractometer machine time.

An alternative method of quantification which has found widespread usage, involves using internal standards. While this method overcomes variations in sample mass absorption and diffractometer response, its main drawbacks are that it uses more diffractometer time and that the possibility exists for inhomogeneity between the sample and the internal standard.

b) Calcite contents

The quantification of calcite contents has been attempted by SCHULTZ (1964) and mentioned by MILLIMAN (1974). The latter author stated that peak area was partially dependent on $MgCO_3$ content. He gave five graphs relating the $(1\bar{1}04)$ calcite spacing to mole% $MgCO_3$ in the calcite and suggested use of the one produced by GOLDSMITH et al (1961) (shown in figure 7). Mole% $MgCO_3$ was calculated for all calcareous samples using this graph and using the $(1\bar{1}01)$ quartz peak as an internal standard during measurement of the calcite $(1\bar{1}04)$ peak position. The results obtained shown in table 17, show that the calcite in the Oligocene samples is a low-Mg variety, the maximum $MgCO_3$ content being only 5.1 mole%. To check the accuracy of the values in table 17, the value for sample 113, from the Bembridge Limestone, may be examined. This sample contains approximately 95% calcite and gave a $(1\bar{1}04)$ spacing of 3.026Å. This corresponds to 2.7 mole% $MgCO_3$, which gives a MgO content for the calcite of 1.04%, compared with a whole rock value of 1.23%. The close agreement of these two figures suggests that the $MgCO_3$ values in table 17 are accurate.

The small range in $MgCO_3$ contents should have no effect on the calcite peak areas. It, therefore, remains necessary only to calculate a calibration constant to enable quantification of the calcite contents in these samples. In order to do this five samples with varying calcite contents were chosen as standards. For four

Figure 7

Graph of mole % $MgCO_3$ against d $(1\bar{1}04)$ spacing for calcite (from GOLDSMITH et al, 1961)

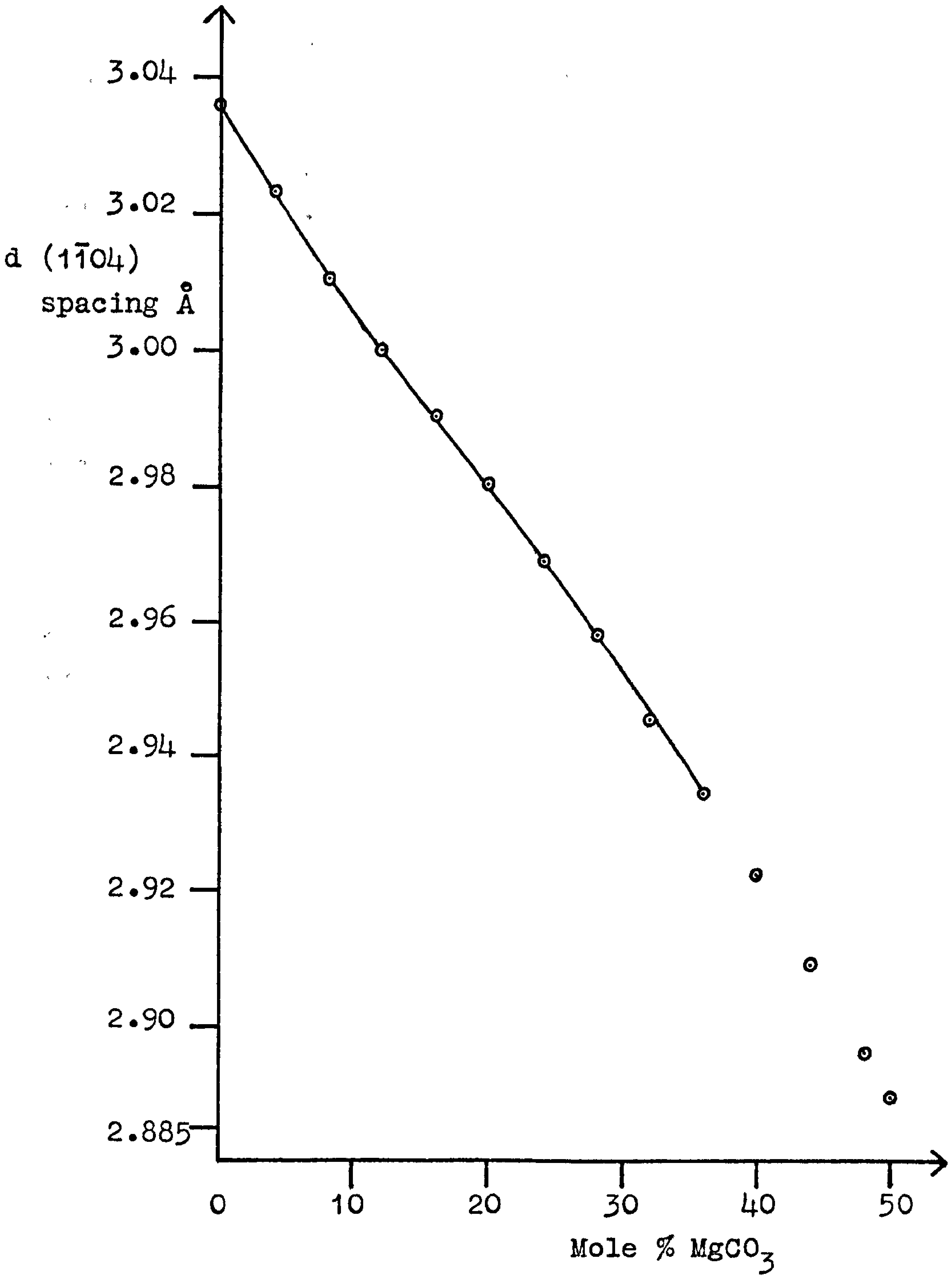


Table 17

Calcite d $(1\bar{1}04)$ Å and mole% $MgCO_3$ for calcareous samples

Sample no.	d $(1\bar{1}04)$ Å	Mole% $MgCO_3$
2	3.034	0.3
7	3.019	5.1
10	3.019	5.1
27	3.028	2.2
31	3.033	0.7
37	3.030	1.5
39	3.034	0.3
49	3.034	0.3
54	3.021	4.4
64	3.026	2.9
111	3.032	0.9
112	3.028	2.1
116	3.027	2.4
119	3.027	2.4
121	3.026	2.7
122	3.029	1.9
123	3.027	2.4
124	3.026	2.7
126	3.023	3.8
129	3.031	1.5
134	3.022	4.1
136	3.021	4.4

of these, CO_2 contents were determined by wet chemistry, while for the fifth, calcite content was determined by a geochemical recalculation. An evolution-absorption technique was used for the determination of CO_2, involving liberation of CO_2 with orthophosphoric acid and absorption in tubes filled with soda-asbestos and $CaCl_2$. The CO_2 contents obtained are shown in table 18.

Table 18 CO_2 contents determined by wet chemistry

Sample no.	CO_2%
7	18.59
54	3.64
112	24.75
134	11.69

As the only carbonate mineral present in these samples is calcite, calcite contents may be easily determined from the CO_2% and mole% $MgCO_3$. Due to the very high calcite content in the fifth standard (sample 113), a simple geochemical recalculation gives a sufficiently accurate calcite content. The calcite contents for the five standards are listed in table 19, together with the corresponding $(1\bar{1}04)$ calcite peak area.

Table 19 $(1\bar{1}04)$ calcite peak areas and determined calcite % for five samples

Sample no.	Calcite %	$(1\bar{1}04)$ peak area kc
7	41.81	6.90
54	8.20	1.64
112	55.93	9.38
113	95.15	14.63
134	26.35	5.89

The peak areas shown in table 19 were measured from a superimposed $1mm^3$ net and are expressed in thousands of X-ray counts (kc) to allow for variations in diffractometer settings. (At a full scale deflection of $1x10^3$, 1kc equals $1.2cm^3$). All peak areas are the average of at least three readings, the precision of these readings being usually less than three percent.

After correction of the peak areas in table 19 to allow for variations in sample mass absorption from the assumed value of

50.0, they may be plotted on a graph against calcite content. This is shown in figure 8. It can be seen that four samples lie very close to a straight line, but that the fifth (134) lies some way off. As this sample is non-gypsiferous and contains a low content of clay minerals, almost all of the CaO present in the sample must be present in calcite. A geochemical recalculation gives a calcite content of 29.5%, compared with 26.4% obtained from the determined CO_2%. This indicates that the CO_2 determination was in error. Using the former calcite content, sample 134 would also plot close to the straight line in figure 8.

The calibration constant obtained from figure 8 is 4.87% calcite/kc and using this, calcite contents for all of the samples examined by X.R.D. were determined. These are listed in table 20, together with the CaO, MgO and CO_2 calculated to be present in the calcite. To obtain an estimate of the accuracy of the calcite contents, table 21 lists the total CaO contents of calcareous samples, together with the calculated CaO present in calcite and the estimated CaO present in other minerals. It must be stressed that the latter values are very approximate, except for the few samples for which exchangeable cations had been determined (2, 31 and 121). The values in the final column in table 21 are the remainders after subtraction of CaO present in calcite and other minerals from total CaO. If the calcite values and estimated CaO in other minerals were accurate, the figures in this column should be close to zero. The range of figures seen is small and is thought to be mainly due to errors in estimating the CaO present in other minerals. It may be concluded that the method of calculating calcite contents is of a reasonable accuracy.

c) Quartz contents

Several workers have attempted the quantification of quartz contents in sediments by X.R.D.. TILL and SPEARS (1969) used boehmite as an internal standard for the 4.26Å quartz peak, after igniting the sample at 950°C, to destroy interfering clay mineral peaks. COLLINS (1976) used fluorite as an internal standard for the 1.82Å quartz peak, while COSGROVE and SULAIMAN (1973) used a method similar to that used above to determine calcite contents.

One important contributory factor to quartz peak area is orientation. ESLINGER et al (1973) showed that preferred orientation altered the ratio of the $(1\bar{1}00)$ and $(1\bar{1}01)$ quartz peak areas and that secondary quartz gave a more intense $(1\bar{1}00)$

Figure 8

Graph of calcite % against calcite (1$\bar{1}$04) peak area

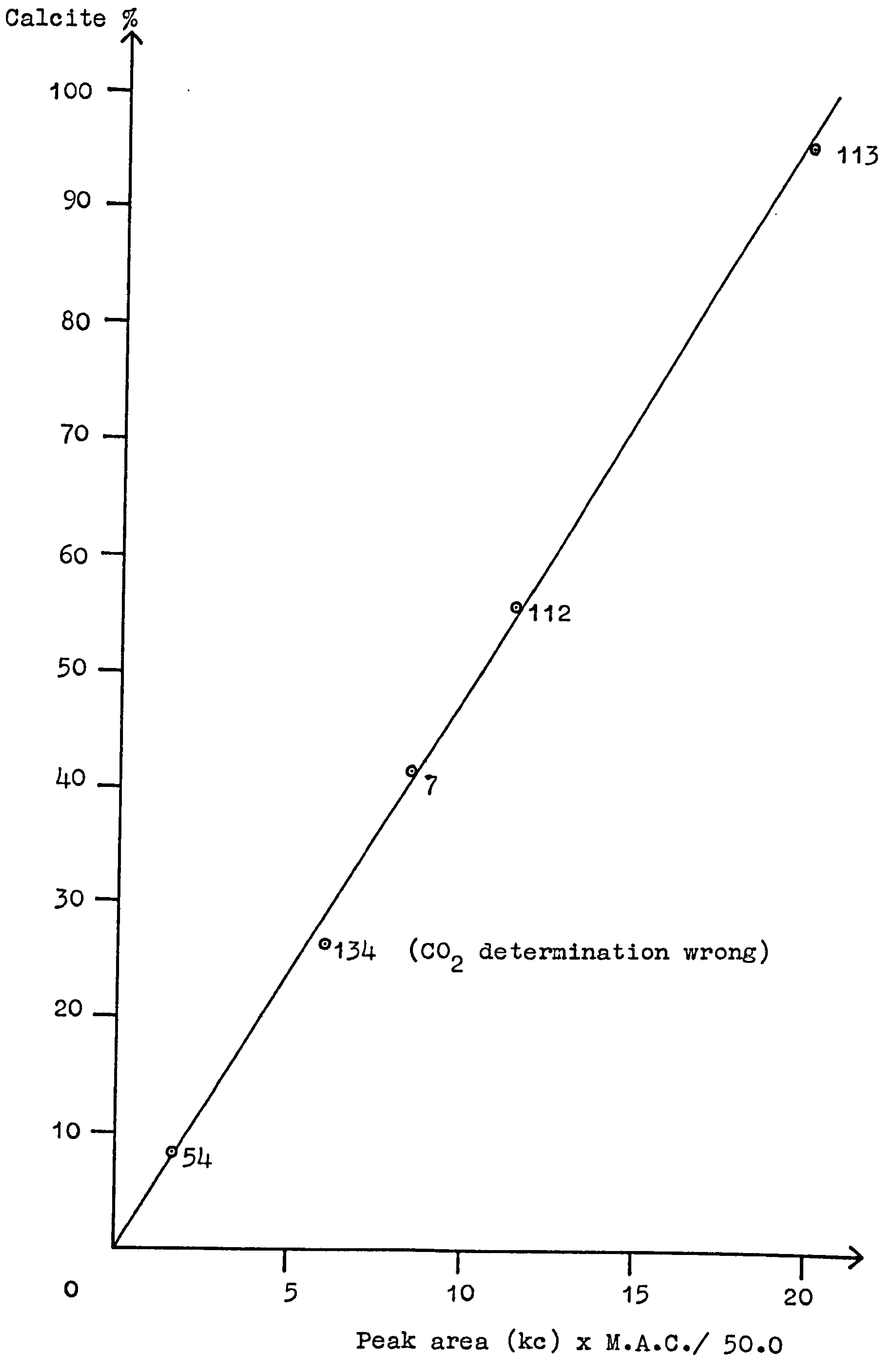


Table 20

Calculated CaO, MgO and CO_2 % present in calcite

Sample no.	CaO %	MgO %	CO_2 %	Calcite %
2	7.79	0.02	6.13	13.94
7	21.89	0.84	18.11	40.84
10	0.96	0.04	0.79	1.79
27	10.52	0.17	8.44	19.13
31	2.10	0.01	1.65	3.76
39	0.79	0.00	0.62	1.41
49	3.03	0.01	2.38	5.42
54	4.51	0.15	3.67	8.35
64	4.63	0.10	3.73	8.46
111	5.40	0.04	4.28	9.72
112	30.47	0.47	24.44	55.38
116	6.73	0.12	5.42	12.27
119	16.92	0.30	13.60	30.82
121	0.48	0.01	0.39	0.88
122	1.85	0.03	1.48	3.36
123	5.90	0.10	4.74	10.74
124	4.99	0.10	4.01	9.10
126	6.88	0.20	5.62	12.70
129	7.67	0.08	6.11	13.86
134	15.85	0.49	12.97	29.31
136	0.99	0.03	0.81	1.83

Table 21

Comparison of CaO % calculated to be present in calcite and total CaO %

Sample no.	Total CaO %	CaO % in calcite	CaO % in other minerals	Remnant CaO %
2	7.45	7.79	0.8	-1.14
7	23.50	21.89	0.4	1.21
10	2.80	0.96	0.6	1.24
27	12.12	10.52	0.5	1.10
31	2.61	2.10	1.5	-0.99
39	2.15	0.79	0.8	0.56
49	4.02	3.03	0.7	0.29
54	5.25	4.51	0.6	0.14
64	4.86	4.63	0.6	-0.37
111	6.95	5.40	0.6	0.95
112	31.66	30.47	0.3	0.89
116	7.13	6.73	0.5	-0.10
119	15.92	16.92	0.4	-1.40
121	15.18	0.48	15.2	-0.50
122	6.18	1.85	4.2	0.13
123	6.96	5.90	0.5	0.56
124	6.17	4.99	0.5	0.68
126	7.77	6.88	0.6	0.29
129	7.76	7.67	0.4	-0.31
134	16.70	15.85	0.1	0.75
136	1.79	0.99	0.6	0.20

N.B. CaO % in other minerals for 121 includes 14.8% in aragonite. In 122, CaO % in other minerals includes 4.1% in aragonite.

reflection than detrital quartz. It was obvious, therefore, that before quantification of quartz contents could be attempted, an investigation of the relationship between orientation and quartz peak area was needed. To achieve this end, an unground portion of sample 122 was sieved to remove the $<53\mu$ fraction and digested in warm dilute HCl. Microscopic examination showed that the residue was over 99% quartz and, could, therefore, be used as a quartz standard. This standard material was ground to a talc-like consistency and three aliquots were mounted in aluminium sample holders, with attempts being made to produce different degrees of orientation. The peak areas obtained for the two main quartz peaks are shown in table 22.

Table 22 Effect of orientation on quartz peak areas

Aliquot no.	$(1\bar{1}00)$ peak area	$(1\bar{1}01)$ peak area	$(1\bar{1}00)/(1\bar{1}01)$
1	8.155	41.486	0.197
2	8.351	38.890	0.215
3	8.816	40.947	0.215

The results for aliquot 1, which was very loosely packed, should be ignored, as the sample sank in the sample holder, producing a marked shift in peak position, from 26.66 to 26.54°2θ. The results for the other two aliquots show that number 3, which was more firmly packed than the others, gave more intense diffraction peaks, but an identical orientation value (expressed as $(1\bar{1}00)/(1\bar{1}01)$ as number 2. This suggests that the density of packing of the samples could be a factor in determining the peak area, although the sample holders used should contain enough sample to be of infinite thickness to the radiation used. It should be noted that the orientation values obtained are considerably lower than the theoretical value of 0.35 and also lower than the average values obtained by ESLINGER et al (1973) of 0.24. This suggests the presence of secondary quartz.

It was decided to use the peak areas for the averagely prepared quartz standard (aliquot 2 in table 22) for calculation of the quartz calibration coefficient. It can be seen from the results in table 22 that the calibration coefficient calculated is likely to be in error by up to five percent. The best peak to use for quartz quantification is the $(1\bar{1}00)$ as this is relatively free from interfering peaks. Although the {hk0 and {hkl clay mineral peaks occur between 4.5 and 4.3Å, no common mineral has a peak directly underlying the 4.26Å quartz peak (see figure 9). On the other hand, the $(1\bar{1}01)$ quartz peak directly overlies the (003) illite peak and is, therefore, useless for quantification. Using the $(1\bar{1}00)$ peak areas for aliquot 2 in table 22, a calibration coefficient of 16.82% quartz/kc is obtained. The quartz contents determined using this calibration coefficient are listed in table 23.

A check on the accuracy of the values in table 23 may be obtained by examining the values for samples with low Al_2O_3 contents. SiO_2 in the samples studied here is present as free silica and combined silica, mainly in the clay minerals. Samples with low Al_2O_3 contents will, therefore, have most of their silica present as free silica (mainly as quartz, but possibly also as amorphous silica). Such samples are numbers 112, 122 and 134. In table 24 the Al_2O_3% and calculated combined SiO_2 values for these samples are listed.

Table 24 Comparison of calculated quartz % and SiO_2% for three samples

Sample no.	Total SiO_2%	Quartz%	Combined SiO_2%	Al_2O_3%
112	23.1	3.4	19.7	7.9
122	80.3	66.4	13.9	3.6
134	57.6	49.1	8.5	5.5

DEER et al (1962) published analyses showing that the ratio of SiO_2 to Al_2O_3 in most common clay minerals was between 1:1 and 3:1. The calculated combined $SiO_2:Al_2O_3$ for samples 112 and 134 fall within this range, suggesting that the quartz contents may be accurate, but the value for 122 is outside the range, suggesting that the quartz content in this sample was underestimated. It may be concluded that the quartz contents in table 23 are accurate to about ± 5%.

d) Other minerals

No non-clay minerals other than quartz and calcite regularly occur in quantities exceeding one percent in the samples studied. Anatase and rutile are present in most samples, but usually in quantities of one percent or less, as shown from the TiO_2% in table 3. Hemihydrate and pyrite occur in only a few samples, but in quantities up to ten percent. The problem in quantifying these

Figure 9

Diffractogram of sample 45, showing overlap of non-basal clay mineral reflections and quartz $(1\bar{1}00)$ peak

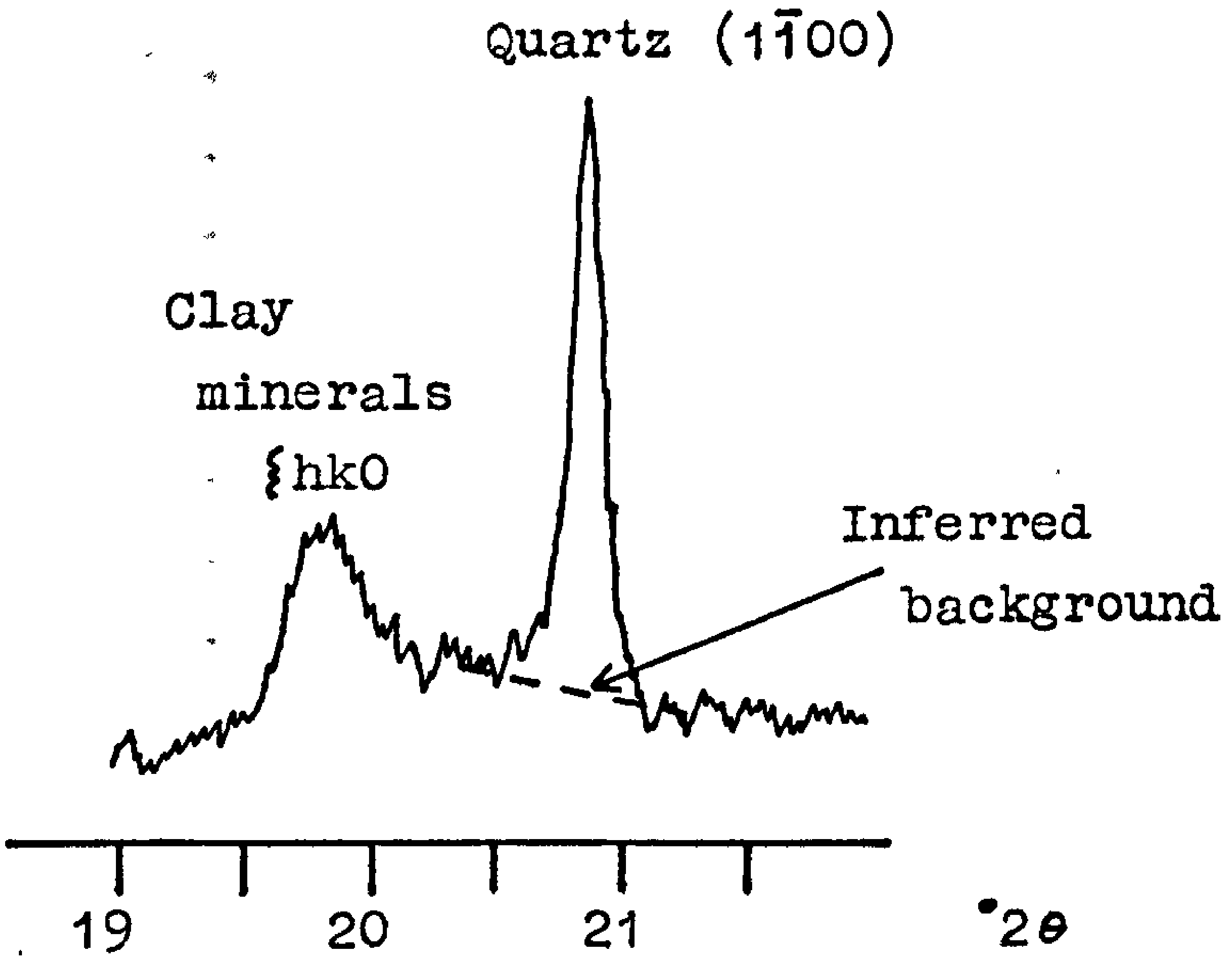


Table 23

Calculated quartz contents

Sample no.	Quartz %	Sample no.	Quartz %
2	9.6	64	12.3
7	11.2	65	9.4
10	11.2	67	9.4
27	21.0	74	37.3
28	20.0	77	18.3
29	27.4	95	16.6
31	25.0	102	47.5
32	24.0	111	12.8
33	24.6	112	3.4
36	32.7	116	8.2
37	22.6	119	18.3
39	32.0	121	13.2
45	29.0	122	66.4
47	17.9	123	33.3
49	22.2	124	17.5
51	44.1	126	9.0
52	28.0	129	28.6
54	13.7	134	49.1
55	17.8	136	16.4

minerals lies in calculating a calibration coefficient. To do this a sample must be found which contains only one of the two minerals, so that the SO_3 content of the sample may be used to calculate the hemihydrate or pyrite content. It was possible to do this for certain samples, but the calibration coefficients obtained were found to vary wildly. It is thought that this was due to the small size of the diffraction peaks. SCHULTZ (1964) reported that the determination of pyrite and gypsum in quantities less than three percent was very variable by X.R.D.. It was decided, therefore, not to proceed with the quantification of other non-clay minerals.

(B) Determination of Clay Minerals by X.R.D.

(i) Sample preparation and analysis

a) Size fraction used

As it was found to be virtually impossible to identify the clay mineral peaks in the diffractograms obtained from the sample powders, it was obvious that a different method of sample preparation was necessary to identify and quantify the clay minerals. The clay fraction of sedimentary rocks is usually taken to be the less than two micron equivalent settling diameter fraction ($<2\mu$ e.s.d.). This is comprised mainly of clay minerals, with a few non-clay minerals. All of the clay minerals are not necessarily of $<2\mu$, many clay particles, especially of kaolinite, are above this size. In this work the $<2\mu$ fraction was separated for clay mineral analysis, but as a check on the possible relationship of clay mineralogy with size fraction examined, the $<5\mu$ fraction was also separated for five samples.

The usual method of separating fine-grained size fractions is settling through water. JACKSON (1969) gave calculated tables of settling velocity against grain size for spherical particles of density $2.65 g/cm^3$, settling through water. From these it can be seen that the $<2\mu$ fraction will have settled five centimetres or more in three hours and fifty-three minutes, at surface grvitational attraction, while the $<5\mu$ fraction will take thirty-five minutes to settle the same distance.

The procedure used to separate the size fractions was to prepare an approximately 10:1 suspension of the samples in water by mechanically shaking the lump samples with distilled water for fifteen minutes. If the suspension thus obtained flocculated, it was centrifuged, the liquid decanted, fresh water added and the sample resuspended. This procedure was repeated until a non-flocculating suspension was obtained. This was then stood for the required lengths of time, stated above, before the upper five centimetres were pipetted off and stored in a stoppered glass bottle. The size fractions thus obtained probably contained larger particles than the theoretical maximum, due to the platy nature of the clay minerals and their lower densities than the average used by JACKSON (1969). The actual grain size of the size fraction is relatively unimportant, of more importance is possible segregation of the clay minerals due to their vaying densities. Thus fine-grained size fractions may be unnaturally enriched in smectite, due to its lower density and this will result in quantitative results obtained from the size fraction being different from those for the whole sample. The analysis of two size fractions for certain samples should enable an estimation of this possible source of error.

b) Sample preparation

The size fractions obtained were prepared for X.R.D. analysis by the method known as dropper-on-slide. This involves spreading a thin film of clay suspension on a glass slide and allowing the water to evaporate. This leads to a very high degree of preferred (001) orientation. A possible drawback to the method is that segregation of the clay minerals may occur, leading to a smectite rich upper layer. This was shown to occur by GIBBS (1965), leading him to conclude that the method should not be used for quantitative clay mineral analysis. STOKKE and CARSON (1973) investigated further the relationship between apparent clay mineral content and clay layer thickness. They found that clay layers over 7.7μ thick gave overestimeted smectite contents, due to the presence of a smectite enriched upper layer, from which most of the X-ray pattern at low angles is derived. Clay layer thicknesses less than 3.9μ gave diminished smectite contents, due to the poor development of (001) orientation. When samples were prepared with clay layers between 3.9 and 7.7μ in thickness, the results obtained were comparable with those by other methods.

PIERCE and SIEGEL (1969) performed an analysis of variance on the quantification of clay mineralogy by X.R.D. and found that while variations in the calculation procedure were significant at the 1% level, differences in the method of sample preparation were only significant at the 5% level of probability. It seems, therefore, that if care is taken in the preparation of slides by the dropper-on-slide method, especially in controlling sample thickness, reasonable results may be obtained. In order to monitor the thickness of the samples produced, a set of standard slides with clay thicknesses of between 1.5 and 10μ were produced. The thickness of each sample was then determined by visual comparison with these standards. Table 25 shows the thicknesses estimated for the prepared slides. It can be seen that the range in thicknesses is small and is within, or just below, that found by PIERCE and SIEGEL (1969) to give accurate clay mineral results.

c) Method of analysis

The samples were prepared on microscope slides, approximately 5x4 cm in size. As far as possible the sediment was kept to one half of the slide, the uncovered half being held in the diffractometer sample holder. The diffractometer conditions used were the same as those given on page 41. The untreated samples were scanned from 3 to 30°2θ, samples after treatment with ethylene glycol or heat treatment being scanned fron 3 to 13°2θ and 24 to 30°2θ. The separate charts thus obtained were superimposed by hand, using different coloured inks for the different treatments.

Peak area was measured from a superimposed $4mm^2$ net. The results were expressed as kc, to two decimal places. The use of a larger mesh net than for the non-clay minerals made the peak area measurement much more rapid and did not affect accuracy due to the larger peak areas involved. Peak area was taken as the average of at least three measurements and a precision of ± 3% was usual.

(ii) Mineral identification

a) Methods of sample pretreatment

The examination of a single X-ray diffraction trace of a sediment is not usually sufficient to positively identify the clay minerals present. It is, instead, usual to make use of various pretreatment techniques. In this study the pretreatments used were ethylene glycol saturation and heating to 300 and 550°C. All samples were analysed in their natural state of cation saturation. From the exchangeable cation results, it is evident that Ca is the

Table 25

Estimated thickness of clay mineral layer on sedimented slides

Sample no.	Thickness µ	Sample no.	Thickness µ
2	4	65	4
7	6	66	4
10	5	67	3
27	4	74	3
28	3	77	3
29	4	95	6
31	5	102	3
32	3	111	3
33	5	112	4
36	3	116	2.5
37	2.5	119	2.5
39	3	121	5
45	3	122	3
47	3	123	3
49	3	124	3
51	4	126	5
52	3	129	3
54	5	134	3
55	5	136	5
64	4		

dominant exchangeable cation.

The ability of certain clay minerals, notably the smectites, to absorb polar organic liquids has long been known. HOFFMANN and BRINDLEY (1961) reported that smectites absorbed two layers of ethylene glycol, to give a (001) spacing of 16.85Å. The method used to glycollate the oriented clay samples was that of BRUNTON (1955). This involved placing the slide with its dried clay film over a bowl of ethylene glycol in a desiccator, which was then placed in an oven at 60°C for one hour. The samples were analysed immediately after removal from the desiccator.

Clay minerals vary greatly in their thermal stability. SCHULTZ (1964) showed that heating to 300°C contracted the (001) spacing of smectites to 10Å, while not affecting illite, kaolinite or chlorite. Heating to 550°C for one hour was found by MOLLOY and KERR (1961) to destroy kaolinite while not affecting illite. At this temperature a decrease in the (002) chlorite peak was observed with a concomitant increase in the (001) peak. Other workers have shown that some types of chlorite may be destroyed at this temperature.

To ensure maximum reproducibility of the diffractometer traces, the same sedimented slide was used for all pretreatments. This was analysed first in its natural state and then after ethylene glycol saturation by the method mentioned above. The slide was then heated in a furnace at 300°C for one hour before further analysis and finally heated in a furnace at 550°C for one hour and scanned. The samples were analysed as soon after removal from the furnace as possible, to prevent rehydration, although it is thought that this is unlikely to occur, especially after heating to 550°C.

b) Diagnostic properties of the clay minerals

The reactions of the clay minerals identified in the samples studied to the various pretreatments are shown in table 26. Illite is used in the original connotation of GRIM et al (1937) as a general term for the micaceous constituent of fine-grained sediments. It is characterised by a series of basal reflections at approximately 10, 5 and 3.3Å, unaffected by glycollation or heat treatment up to 550°C. From the unoriented powder samples, the presence of a peak at 2.58Å and the absence of one at 2.80Å shows that the illite is of a 1Md variety (MAXWELL and HOWER, 1967). The (001) reflection of the untreated samples is usually asymmetric

Table 26 Diagnostic X.R.D. Properties Of Clay Minerals

MINERAL	UNTREATED	AFTER GYLCOLLATION	AFTER HEATING AT 300°C	AFTER HEATING AT 550°C
Illite	(001) 10Å	(001) 10Å	(001) 10Å	(001) 10Å
	(002) 5Å	(002) 5Å	(002) 5Å	(002) 5Å
	(003) 3.3Å	(003) 3.3Å	(003) 3.3Å	(003) 3.3Å
	N.B. (001) spacing usually asymmetric		N.B. Symmetry and sharpness usually increases	
Kaolinite	(001) 7.1Å	(001) 7.1Å	(001) 7.1Å	All peaks completely destroyed
	(002) 3.6Å	(002) 3.6Å	(002) 3.6Å	
Smectite	(001) 15Å	(001) 16.8Å	(001) 10Å	(001) 10Å
	N.B. Peak position variable	(002) 8.4Å	(003) 3.3Å	(003) 3.3Å
		(005) 3.4Å		
Chlorite	(001) 14.2Å	(001) 14.2Å	(001) 14.2Å	(001) 13.4Å
	(002) 7.1Å	(002) 7.1Å	(002) 7.1Å	N.B. Other peaks markedly decreased
	(003) 4.7Å	(003) 4.7Å	(003) 4.7Å	
	(004) 3.5Å	(004) 3.5Å	(004) 3.5Å	
Illite-smectite	(001) 10 - 14Å	(001) 10 - 16Å	(001) 10Å	(001) 10Å
	N.B. Spacing depends on relative proportions of constituents			

towards a higher lattice spacing. This asymmetry is not shown by the glycollated sample and is thought to be due to partial hydration of the illite interlayers, because of a deficiency of potassium in the interlayer sites and a corresponding charge increase in the octahedral and tetrahedral layers. The degree of hydration is obviously insufficient to allow entry of the larger ethylene glycol molecule into the interlayers.

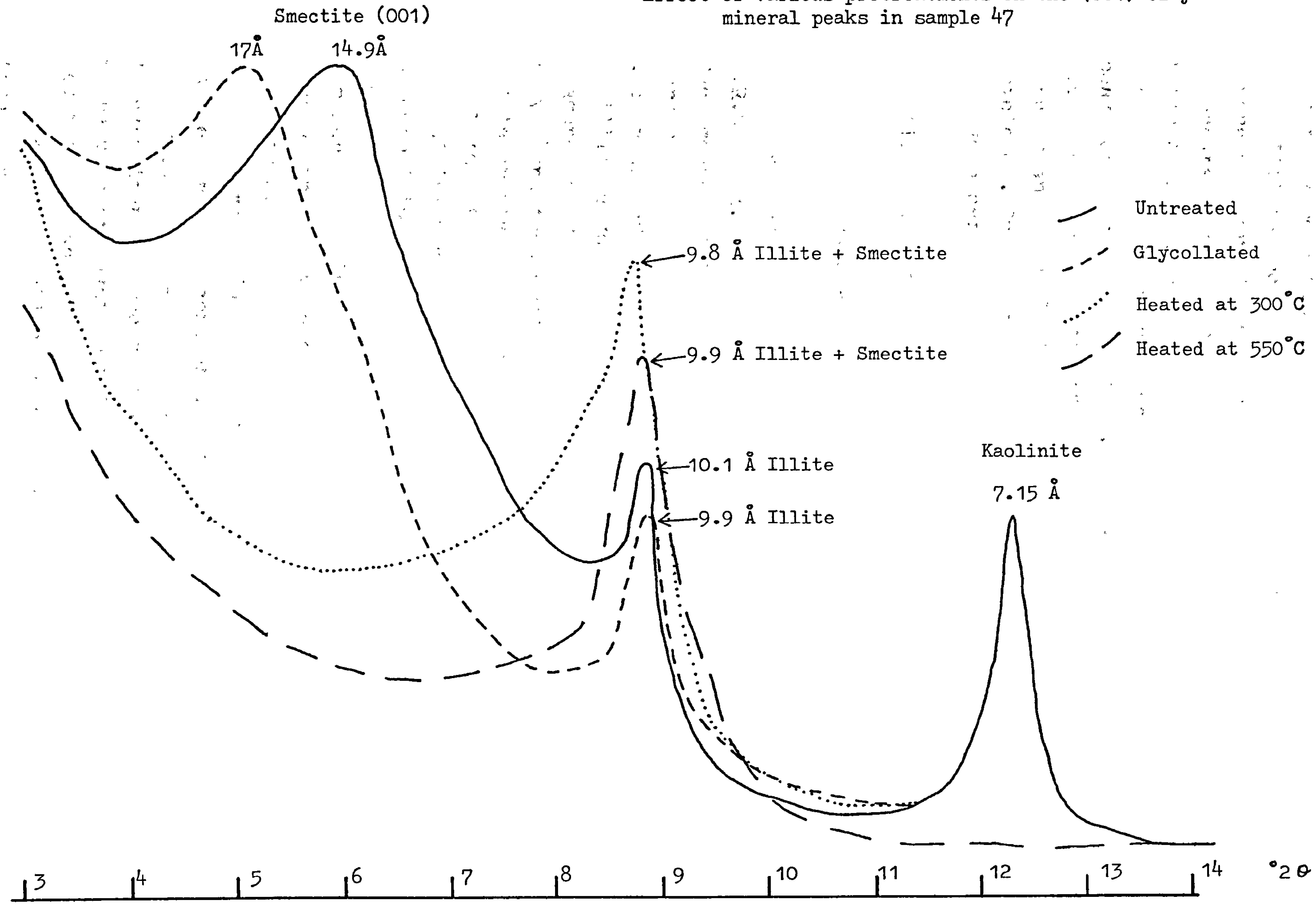
Kaolinite is the commonest member of the kandite family of clay minerals and is characterised by basal reflections at 7.12 and 3.56Å. These are unaffected by glycollation or heating to 300°C, but are completely destroyed after heating to 550°C.

The smectites (BRINDLEY and PEDRO, 1975) are a very variable group of clay minerals, due to chemical substitutions in the octahedral and tetrahedral sites of the structure. The (001) spacing of the untreated sample is dependent on the degree of hydration of the mineral, which is in turn dependent on the exchangeable cation (with Ca the (001) spacing is approximately 15Å). On exposure to ethylene glycol, the smectites expand to give a basal spacing of 16.8Å (HOFFMANN and BRINDLEY, 1961). In both the untreated and glycollated states, the (001) peak is frequently the only one identifiable. On heating to 300°C, the interlayer water of the smectites is driven off and the basal spacing contracts, to give an illite-like set of reflections at 10, 5 and 3.3Å. The (001) reflection is commonly broad and asymmetric to a higher lattice spacing, suggesting the presence of poorly developed brucite layers replacing the exchangeable cations (SCHULTZ, 1964). The peak crystallinity increases after heating to 550°C. The effect of these various pretreatments on the three clay minerals is shown in figure 10.

Chlorite was identified in small quantities in a few samples. It shows a set of basal reflections at 14.1, 7.1, 4.7 and 3.6Å, the relative intensity of them being dependent on the Mg:Fe ratio in the chlorite. Thus Mg chlorites have strong (001) and (003) reflections. Unfortunately in the Oligocene samples the quantities of chlorite present were too small to allow estimation of the Mg and Fe contents. The chlorite peaks are unaffected by glycollation and heating to 300°C, but after heating to 550°C show a marked increase in the (001) peak and corresponding decrease in the other peaks. Due to the superimposition of the chlorite peaks on the (001) smectite and (001) and (002) kaolinite peaks, chlorite is a difficult mineral to identify when present in small quantities. It is possible, therefore, that chlorite may exist in more samples

Figure 10

Effect of various pretreatments on the (001) clay mineral peaks in sample 47



than those reported in table 30.

Illite-smectite is the term applied to the series of minerals intermediate in composition between illite and smectite. It occurs in only two samples and in those shows only a (001) reflection, suggesting an irregular structure. The relative contents of illite and smectite in the struture govern the (001) peak position (MACEWAN et al, 1961). On glycollation, a shift in (001) peak position occurs, representing an increase in (001) spacing and a small discrete (001) glycol-smectite peak is developed. On heating to 300°C and above, the structure contracts to give a series of illite-like reflections.

(iii) Quantification

a) Measurements of crystallinity

The crystallinity of a mineral may be measured from its X.R.D. peak, by measuring the peak width at half peak height. Such measurements for clay minerals have been shown by various workers to be related to mineral provenance and degree of diagenesis of the sample. FOSCOLOS et al (1976) found an increase in illite crystallinity related to an increase in the degree of diagenesis of their samples. At low diagenetic levels, however, they found that provenance was more important in determining illite crystallinity, a conclusion supported by DUNOYER DE SEGONZAC (1970). The latter author also considered that illite crystallinity could be related to climatic conditions at the time of deposition. WEAVER (1960) showed that illite peak sharpness (defined as peak height at 10Å divided by height at 10.5Å) could similarly be related to diagenetic level. Increases in kaolinite crystallinity have also been noted with increase in degree of diagenesis.

The values of kaolinite crystallinity for the Oligocene samples are very constant, varying only between 0.7 and 1.1cm, with most values in the range 0.9 to 1.1cm. This small range may be due to experimental precision as much as to actual variation. Since no results are available for clay mineral crystallinities in the South of England, it is not possible to suggest that the values reported here could represent derivation from certain geological formations.

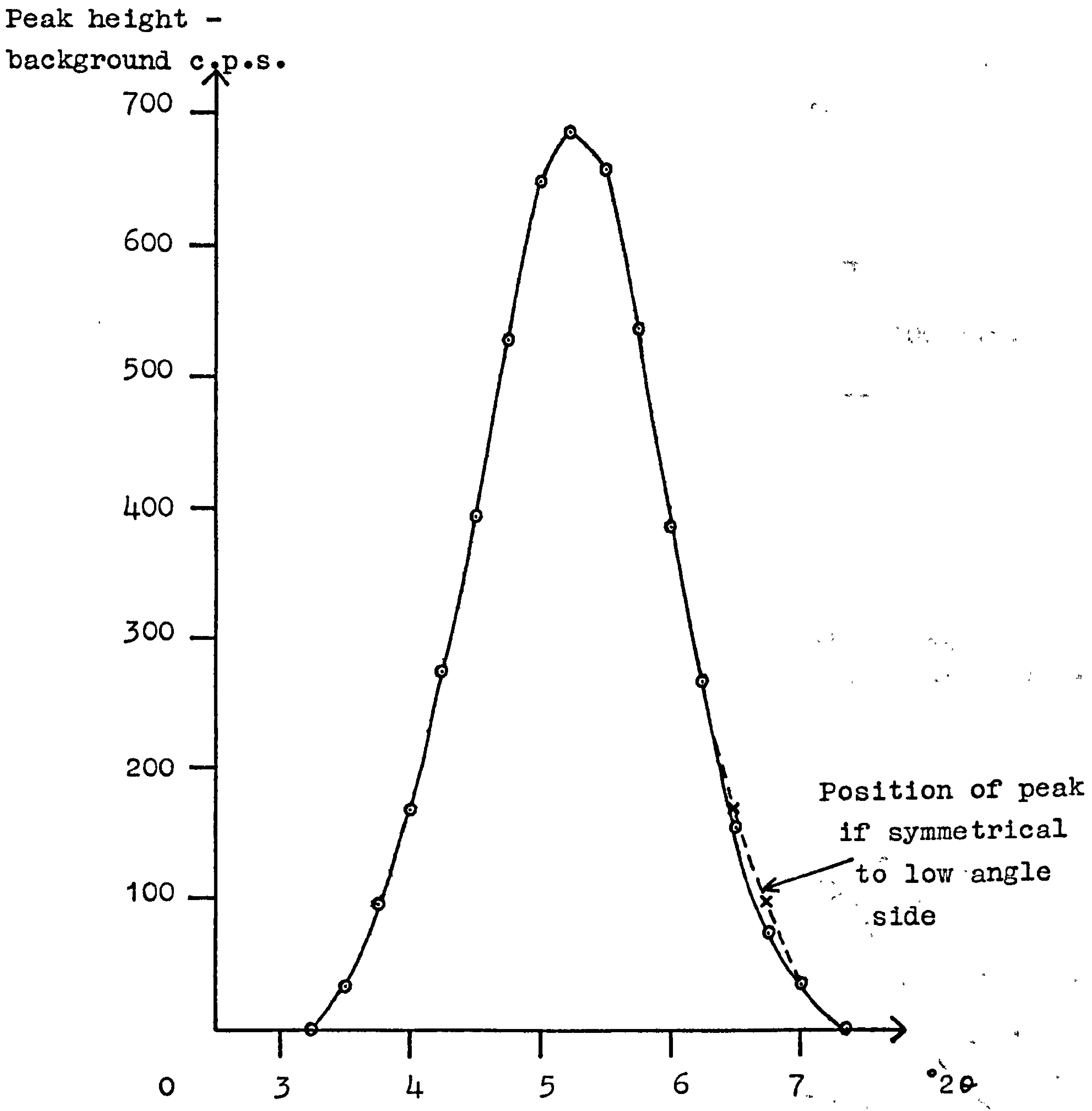
The measurement of illite crystallinity may be undertaken on the untreated or glycollated X.R.D. traces. Since it was mentioned that glycollation increased the illite crystallinity, it would seem that measurement of crystallinity on the untreated trace is to be preferred. This unfortunately presents one problem, overlap of the (001) smectite and illite peaks. In order to measure the illite half-width, the contribution of the (001) smectite peak to the low angle side of the illite peak must be known. Figure 11 shows the result of recalculating a (001) glycol-smectite peak to a flat background. The peak can be seen to be approximately symmetrical, the slight deviation from symmetry being due to Lorentz and polarisation factors (JOHNS et al, 1954). Since the (001) glycol-smectite peak is almost symmetrical, it seems reasonable to conclude that the (001) smectite peak is also symmetrical. It is, therefore, possible to recalculate the (001) smectite peak as being symmetrical to the interference-free low angle side. Subtraction of this peak from the combined (001) smectite and illite peaks leaves the (001) illite peak, for which the half-width can be measured. This procedure is shown in figure 12.

Untreated (001) illite peaks were recalculated by the above procedure for all samples containing smectite. Illite crystallinity was then measured as peak width at half peak height. The illite peaks obtained were frequently very asymmetric, as for example those shown in figure 13. It was mentioned on page 53 that this asymmetry was due to charge deficiency and corresponding hydration of the illite interlayers.

Table 27 gives the illite crystallinities for both the recalculated (001) illite peaks and the glycollated peaks. It can be seen that the recalculated values are consistently larger, indicating lower crystallinity. FOSCOLOS et al (1976) gave values of illite crystallinity and vitrinite reflectivity corresponding to increasing diagenesis. On page 33 it was mentioned that the vitrinite reflectivities obtained for the Oligocene samples corresponded to the eodiagenesis zone, which is characterised by illite crystallinities of 2.7cm and greater. It is apparent from table 27 that whereas the recalculated illite crystallinities correspond to these values, the glycollated crystallinities are consistently lower and would correspond to vitrinite reflectivities of 2%, higher even than that measured on a detrital fragment, given on page 33. It seems, therefore, that the method of recalculating the smectite and illite peaks is valid and that the recalculated crystallinities are correct. These show that the Oligocene sediments may be placed in the eodiagenesis zone of

Figure 11

Recalculation of (001) glycol-smectite peak from sample 95 to a flat background



Position of peak if symmetrical to low angle side

Figure 12

Recalculation of smectite and illite (001) peaks for sample 112

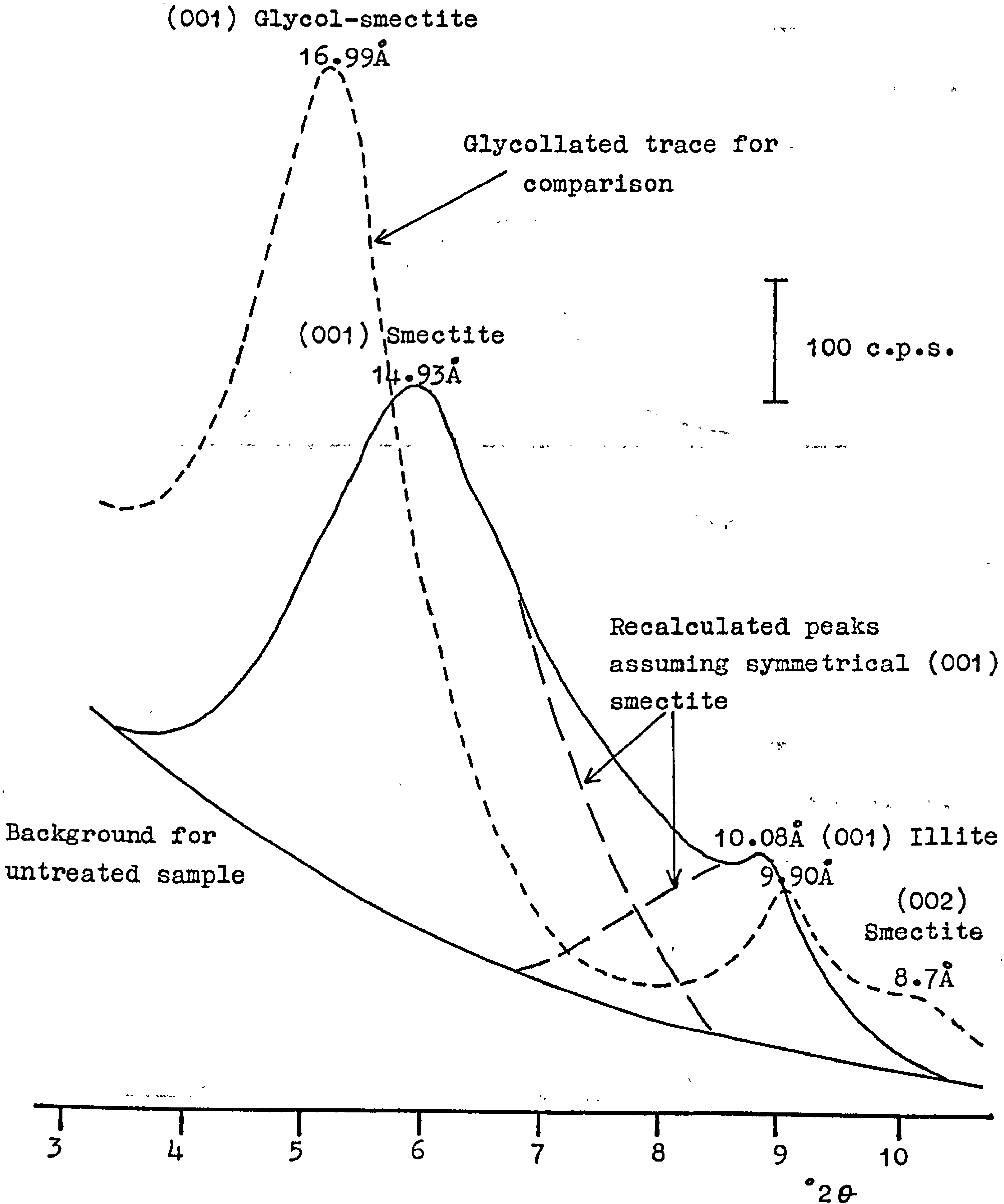
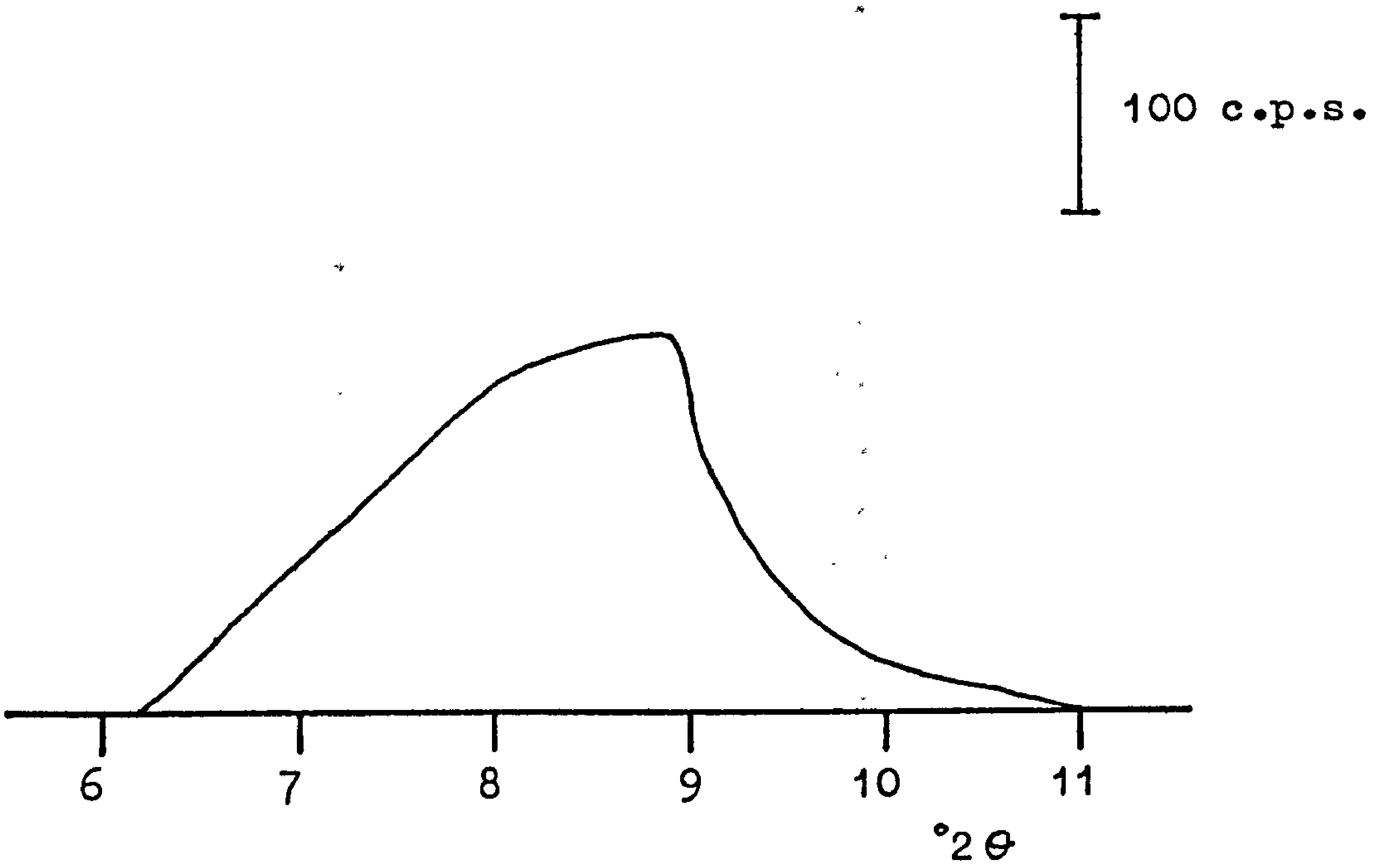


Figure 13

(001) Illite peaks produced by the recalculation procedure for samples 2 and 37

Sample 2



Sample 37

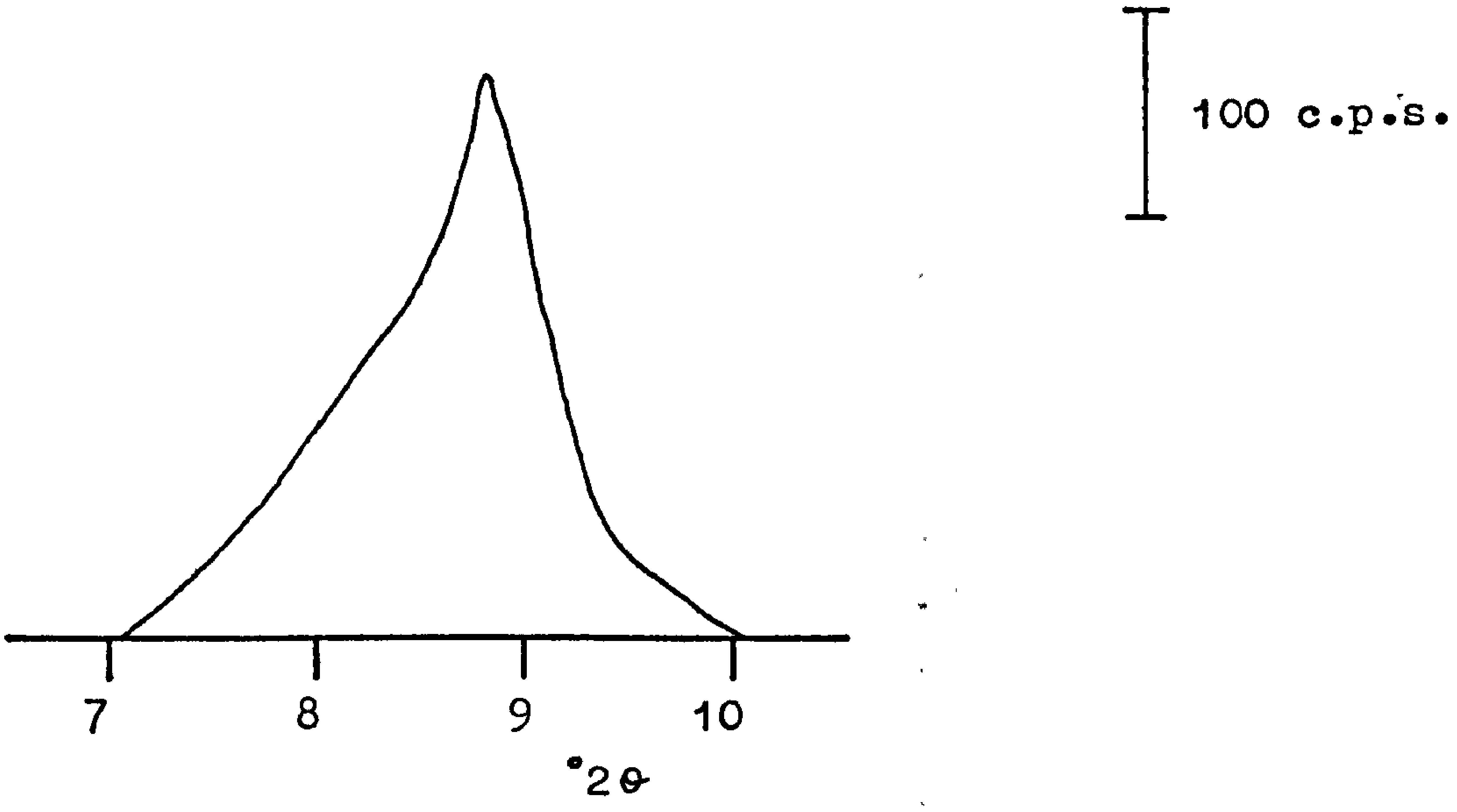


Table 27

Illite crystallinities

Sample no.	Recalculated $^{+}$ cm.	Glycollated cm.
2	4.8	3.3 *
7	5.0	1.2
10	2.5	1.7
27	4.7	1.1
28	1.9	0.9
29	2.0	1.1
31	2.7	1.1
32	2.5	0.8
33	2.3	1.2
36	3.2	1.4
37	5.0	1.2
39	4.3	1.3
45	4.7	1.1
47	2.1	0.8
49	2.3	0.8
51	4.3	0.9
52	1.5	0.9
54	3.1	1.7
55	?	1.4
64	?	1.2
65	3.1	1.0
66	3.4	1.0
67	2.6	1.2
74	1.6	0.9
77	3.8	0.9
95	1.9	0.7
102	3.2	1.0
111	3.7	1.8
112	4.4	1.2
116	2.8	1.8
119	4.7	1.8
121	4.6	1.9
122	5.1	1.5
123	3.1	1.3
124	5.6	1.6

Table 27 (contd.)

Sample no.	Recalculated + cm.	Glycollated cm.
126	2.6	1.7
129	2.9	1.7
134	1.8	1.1
136	2.1	1.1

N.B.

* Includes (002) glycol-smectite

? Illite peak not recalculated as illite-smectite present

\+ These values are thought to be slightly high (approximately 0.5 cm.) due to failure to allow for Lorentz and polarisation factors.

FOSCOLOS et al (1976), although a few samples contain more crystalline illite, suggesting the presence of different source rocks. As a final point, the (001) illite peaks shown in figure 13 are similar to those found by other workers in this Department in non-smectitic Carboniferous shales.

Since the smectite peak commonly occurs on a steeply sloping background, it is not possible to determine crystallinity by measuring the peak half-width. An alternative measure of crystallinity was defined by BISCAYE (1965) as valley depth divided by peak height, shown in figure 14. It was, however, mentioned that this value was partially dependent on smectite abundance in the sample. WEIR et al (1975) produced computer simulations of (001) smectite peaks with varying amounts of non-expandable layers. They found a positive relationship between the logarithm of peak height divided by valley height and the expandable layers percentage (shown in figure 15). Using these two methods crystallinity and percentage expandable layers were calculated for the smectites present in the Oligocene samples, these are listed in table 28. It can be seen that there is a general positive correlation between the two values, as may be expected. The sample with the highest crystallinity and percentage expandable layers is number 67.

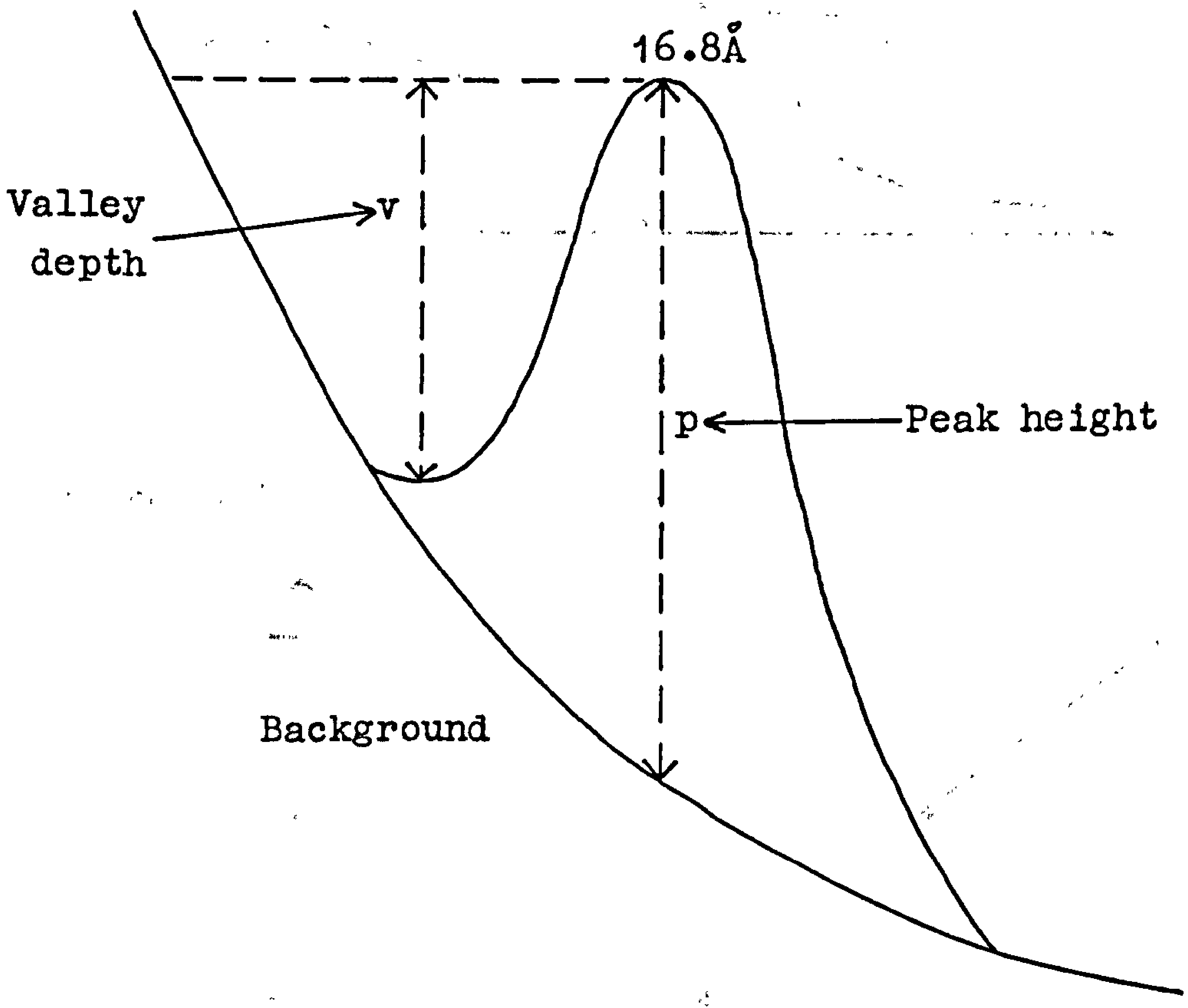
b) Mineral content

Since clay mineral analysis was carried out on a particular fraction of the sample, quantitative results need to be reexpressed to whole rock values in order to be comparable with the non-clay mineral and geochemical values. To achieve this the percentage of clay minerals in the sample needs to be known. This may be found by summing the quantity of non-clay minerals and subtracting this from one hundred percent to give the quantity of clay minerals. Quantification of certain non-clay minerals has been achieved by X.R.D. and for the remaining ones quantification was achieved by geochemical recalculation (see next section).

Two general methods exist for quantifying clay mineralogy from oriented samples. The first uses the peak areas from the glycollated specimen, while the second also uses peak areas from the sample after heating to 300°C. In the second method the kaolinite and illite peaks are measured on the trace obtained after heating the sample to 300°C and the illite peak is also measured for the glycollated sample. The smectite peak area is

Figure 14

Method of determining smectite crystallinity (from BISCAYE, 1965)



Crystallinity = v/p

Figure 15

Method of determining % expandable layers in smectite (from WEIR et al, 1975)

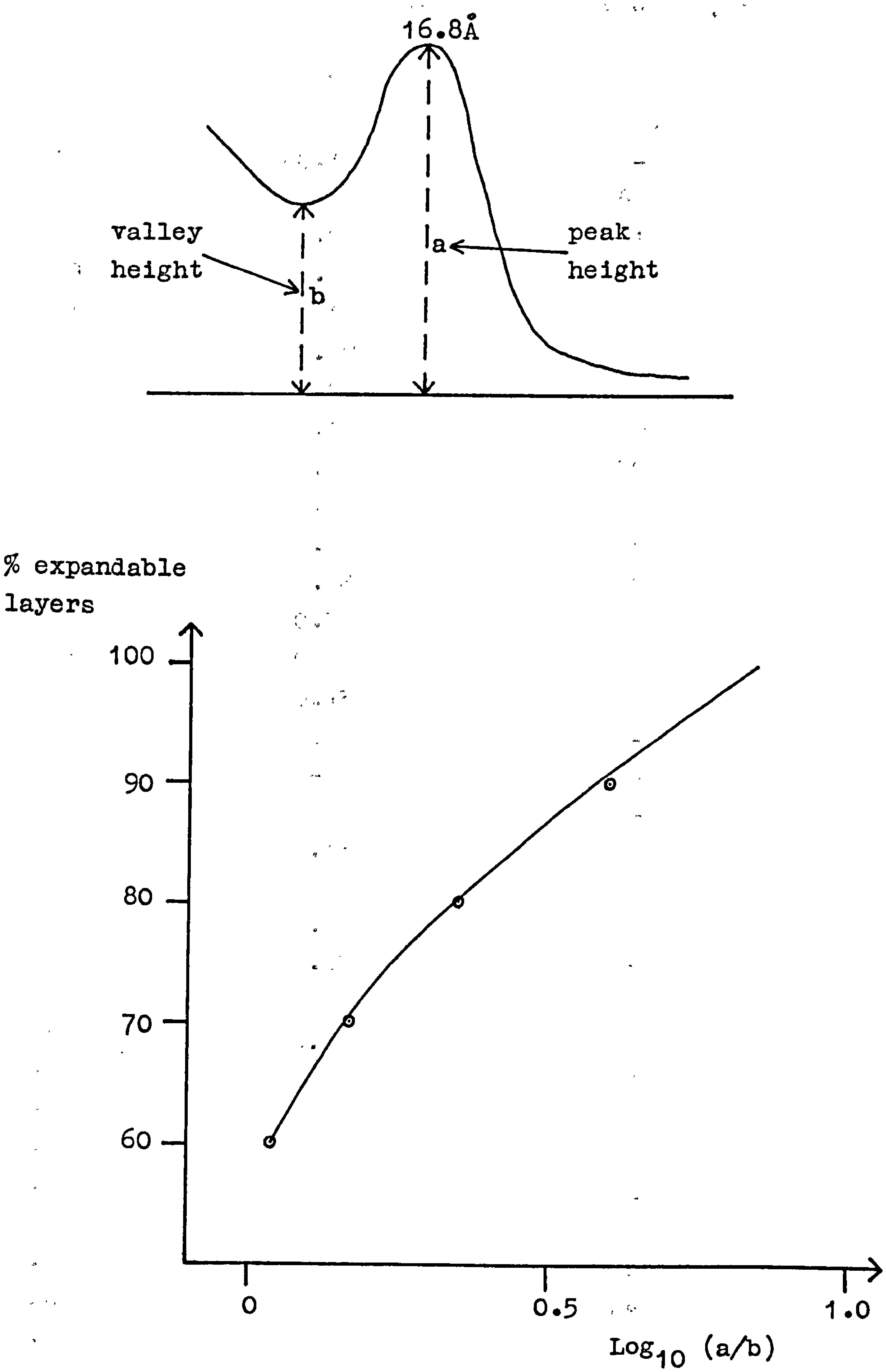


Table 28

Smectite crystallinities and % expandable layers

Sample no.	Crystallinity (BISCAYE, 1965)	% expandable layers (WEIR et al, 1975)
2	0.41	64
7	0.26	60.5
10	-0.36	-
27	0.36	65
28	0.29	61
29	0.15	60
31	0.10	59
32	0.19	59
33	0.24	60
36	0.16	60
37	0.11	59
39	0.18	60
45	0.22	61
47	0.28	62
49	0.36	65
51	0.19	61
52	0.43	67
54	-0.07	-
55	-	-
64	-	-
65	0.31	63
66	0.43	73
67	0.72	80
74	0.43	68
77	0.27	63
95	0.41	65
102	0.28	61
111	0.48	68
112	0.59	73
116	-0.43	-
119	0.27	62
121	-0.33	-
122	0.44	68
123	0.53	70
124	0.25	62

Table 28 (contd.)

Sample no.	Crystallinity (BISCAYE, 1965)	% expandable layers (WEIR et al, 1975)
126	0.11	59
129	-0.06	-
134	0.00	58
136	0.33	63

N.B. When crystallinity drops below 0.0, b>a. The graph of WEIR et al (1975) does not continue to negative values.

then measured as the difference between the two illite peak areas. AUSTIN and LEININGER (1976) examined the effect of heat treating illite-smectite mixed layers and found that great care was needed to obtain reproducible results. They found that slight variations in temperature and length of time in the furnace produced quite large changes in the (001) illite peak areas. It seems, therefore, that the former method, using only the glycollated trace is better for clay mineralogical quantification.

It is not possible to use the clay mineral peak areas directly as measures of mineral abundance, factors need to be applied to them in order to make them directly comparable, to allow for variations in X-ray response with changing diffraction angle and mineral crystallinity. The ratio of 4:1 for the area of (001) smectite and (001) illite peaks obtained from equal concentrations of the two minerals in one sample seems to be widely accepted (BISCAYE, 1965 and JOHNS et al, 1954). The smectite peak areas were, therefore divided by four. Both SCHULTZ (1964) and COLLINS (1976) considered that the ratio between (001) illite and (001) kaolinite peaks was dependent on kaolinite crystallinity. The latter author considered that with the kaolinite crystallinities shown by these samples, the kaolinite peak should be divided by 1.8 to render it comparable with the (001) illite peak.

Having decided on factors to render the (001) peaks of the three dominant clay minerals comparable, the effect of chlorite on the smectite and kaolinite peaks must be allowed for. SCHULTZ (1964) considered that the relationship between chlorite and kaolinite was $14\text{Å}_{550^\circ C}/1.5 : 7\text{Å}$, although COLLINS (1976) concluded that the chlorite peak should be multiplied by 1.5. The latter author also found that moderately iron rich chlorites gave double the intensity of the kaolinite peak. As the chlorite in these samples is thought to be moderately iron rich, from the small (001) peak after heating to 300°C (BROWN, 1955), the contribution of chlorite to the (001) smectite peak was taken to be $0.6 \times 14\text{Å}_{550^\circ C}$ and the contribution to the (001) kaolinite peak $1.5 \times 14\text{Å}_{550^\circ C}/3.6$.

Very little information regarding the diffracting capabilities of illite-smectite is available. From the (001) illite-smectite spacing of 12.6Å, the composition was calculated to be 33% illite and 67% smectite. As an estimated value, the illite-smectite peak was, therefore, divided by three.

The (001) peak areas measured from the X.R.D. trace of the glycollated sample were amended by the factors mentioned above and then normalised by expressing each peak area as a percentage of the total peak areas. The results thus obtained show each clay mineral as a percentage of the total clay minerals. The scheme of calculation of the normalised clay mineral contents is listed in table 29. The results obtained are listed in table 30.

In order that the clay mineral contents shown in table 30 may be considered representative of the whole rock clay mineralogy, it must be shown that the sample preparation procedure is not giving biased results and that the clay mineralogy of the size fraction examined is typical of the whole rock mineralogy. To check the former, two samples which gave low smectite contents were chosen for repeat analysis. It was thought possible that the low smectite contents could be due to the thinness of the clay layers (STOKKE and CARSON, 1973), especially for sample 116, where the clay layer was only 2.5μ thick. The repeat samples were deliberately made thicker, to observe any increase in the smectite values. The results obtained are shown in table 31.

Table 31 Effect of the thickness of the clay mineral layer on the determined clay mineral contents

Sample no.	Thicknessμ	Smectite %	Illite %	Kaolinite %
116	2.5	2	96	2
116	4	0	99	1
121	5	4	90	6
121	8	4	90	6

It can be seen that sample thickness has no effect on determined clay mineralogy, so it seems reasonable to conclude that for the sample thicknesses used (2.5 to 6μ), sample thickness is not affecting determined clay mineralogy. To confirm this, correlation analysis of sample thickness and clay mineral percentages showed only a probably significant negative relationship between thickness and smectite content.

To investigate the possibility that the size fraction examined did not contain a clay mineralogy representative of the whole rock mineralogy, the clay mineralogy of the <5μ fraction was determined for five samples. GRIM (1953) gave figures to show that although the common grain size ranges of smectite and illite were below two microns, kaolinite frequently occurred in grains up to four microns in size. Enrichment of kaolinite in the <5μ

Table 29

Factors used to determine normalised clay mineral contents

Illite = glycol 10Å

Smectite = glycol $17\text{Å} / 4 - 0.6 \times 14\text{Å}_{550^\circ\mathrm{C}}$

Kaolinite = glycol $7\text{Å} / 1.8 - 1.5 \times 14\text{Å}_{550^\circ\mathrm{C}}$

Illite-smectite = glycol $12\text{Å} / 3$

Chlorite = $14\text{Å}_{550^\circ\mathrm{C}} / 3.6 \times 1.5$

Then,

Illite = Illite / Illite + Smectite + Kaolinite + Chlorite + Illite-smectite

etc.

Table 30

Normalised clay mineral contents

Sample no.	Smectite %	Illite %	Kaolinite %	Chlorite %	Illite-smectite %
2	52	46	2		
7	32	53	14	1	
10	3	83	14		
27	48	35	16	1	
28	34	46	20		
29	32	48	20		
31	28	50	22		
32	25	50	25		
33	18	59	23		
36	42	36	22		
37	41	39	20		
39	36	39	25		
45	41	36	20	3	
47	49	30	20	1	
49	56	28	14	2	
51	52	34	14		
52	50	36	14		
54	7	79	14		
55		66	15		18
64		63	18		19
65	48	29	23		
66	44	33	23		
67	74	25	1		
74	60	23	15	2	
77	53	29	15	3	
95	44	33	22	1	
102	36	41	23		
111	47	49	4		
112	66	31	3		
116	2	96	2		
119	42	53	5		
121	4	90	6		
122	56	37	7		
123	54	38	8		
124	46	45	9		

Table 30 (contd.)

Sample no.	Smectite %	Illite %	Kaolinite %	Chlorite %	Illite-smectite %
126	35	52	13		
129	1	87	10	2	
134	33	49	16	2	
136	38	43	17	2	

fraction may, therefore, be expected, relative to the <2μ fraction.

The results obtained for the two size fractions are shown in table 32. It can be seen that overall agreement between the two is good. Samples 31, 39 and 129 show, within experimental limits, identical results. Sample 74 shows enrichment of illite in the <5μ fraction, which it is thought represents the presence of detrital micas, since the crystallinity of the illite in this sample (table 27) is appreciably higher than those of most other samples. Sample 111 shows the opposite results to sample 74, that is enrichment of smectite in the <5μ fraction. The difference between the two size fractions is, however, less marked and may represent experimental error. In general, it may be concluded that the clay mineral contents shown in table 30 are representative of the whole rock clay mineralogy.

c) Conclusions

In general the Oligocene samples may be described as having an illite/smectite/kaolinite assemblage, with minor amounts of chlorite. The mean clay mineralogy is 49% illite, 37% smectite, 14% kaolinite and 0.5% chlorite. The main exceptions to this are the samples containing illite-smectite with no discrete smectite and those containing very high amounts of illite - 10, 54, 116, 121 and 129. Sample 67 is again slightly exceptional due to its high smectite content. A more detailed interpretation of the clay mineralogy is given in chapter 7(B)(ii).

(C) Clay Mineral Examination by Electron Microscopy

Two samples were chosen for electron microscopic investigation, sample 67, to examine its higher than normal smectite content and sample 111, as more representative of the average clay mineralogy. The <2μ fraction of both samples was examined, the specimens being prepared by Mr. H.Brockley in the Department.

Plate 9(a) shows various grains from sample 67, which can be seen to range up to two microns in length. The general poor shape and presence of tails on some of the grains are similar to those described by BEUTELSPACHER and MAREL (1968) for montmorillonite from bentonites. These authors showed soil smectites to be of a more rounded form. This suggests an at least partial volcanic origin for sample 67. Plate 9(b) shows another

Table 32

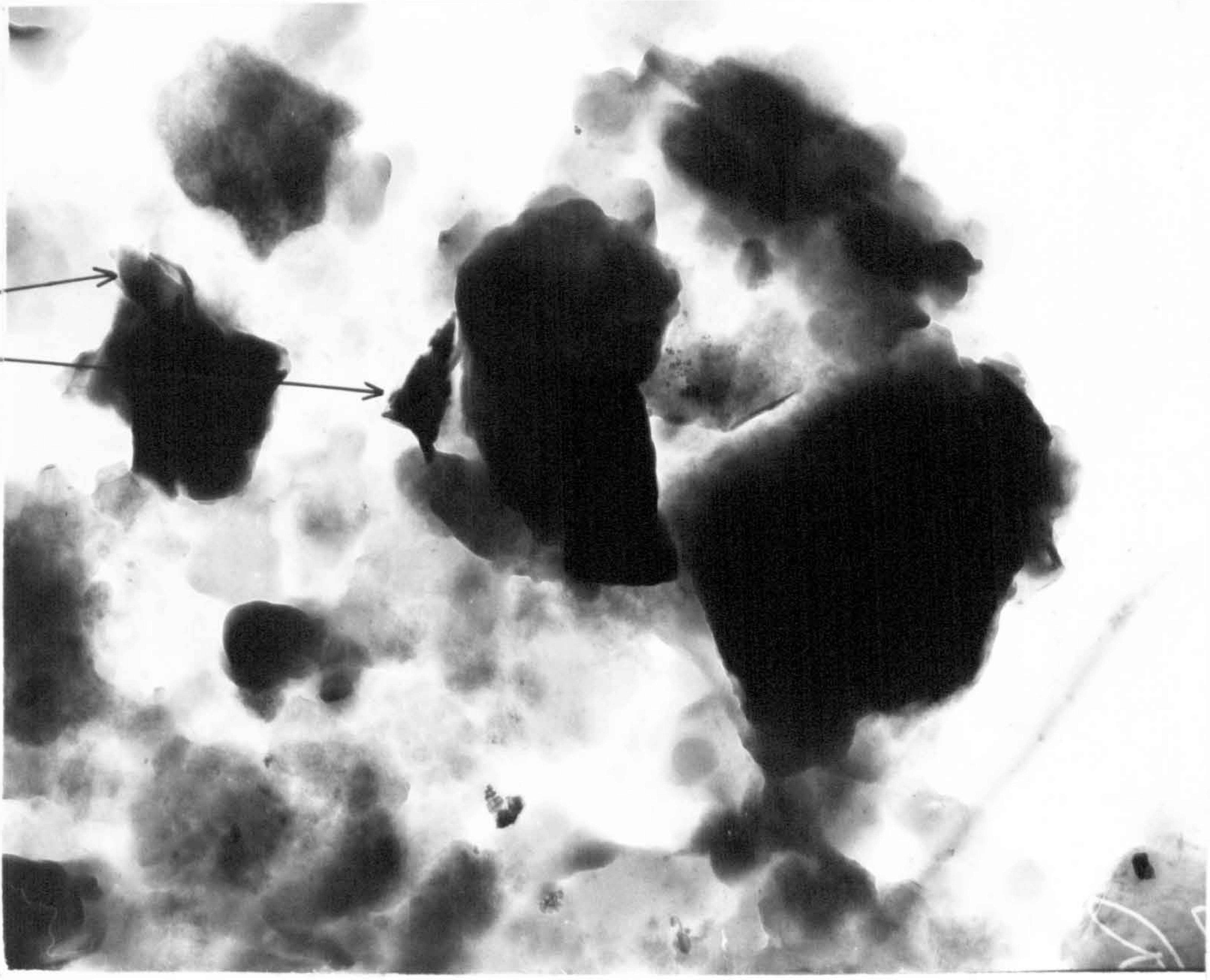
Comparison of <2μ and <5μ clay mineral contents for five samples

Sample no.	Size fraction	Smectite %	Illite %	Kaolinite %	Chlorite %
31	<2μ	28	50	22	
31	<5μ	28	50	21	1
39	<2μ	36	39	25	
39	<5μ	34	39	26	1
74	<2μ	60	23	15	2
74	<5μ	41	41	14	4
111	<2μ	47	49	4	
111	<5μ	53	41	6	
129	<2μ	1	87	10	2
129	<5μ		89	9	2

Plate 9(a)

Smectite grains showing 'tails' in sample 67

1μ

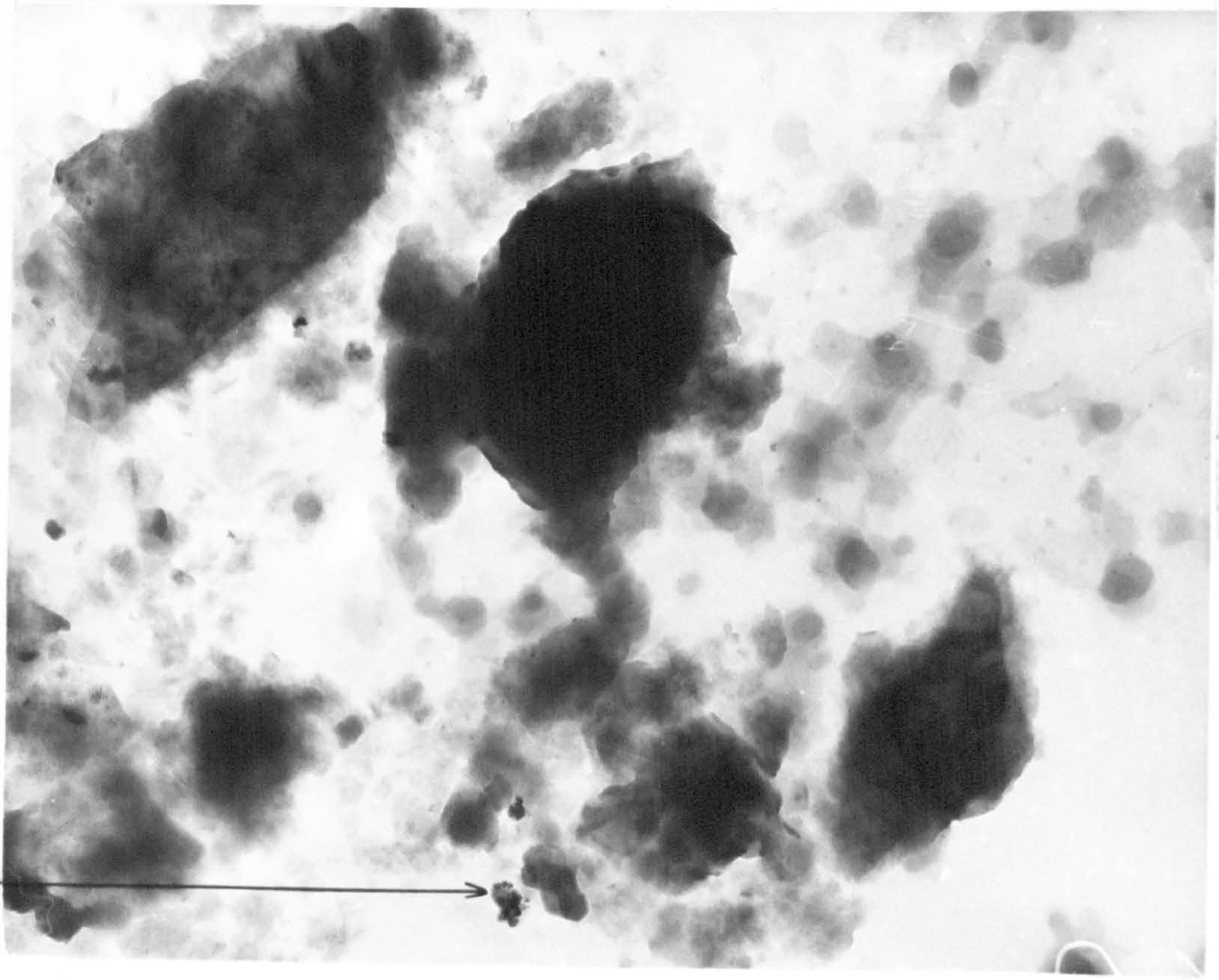


Smectite grains showing 'tails'

Plate 9(b)

Clay minerals in sample 67

1μ



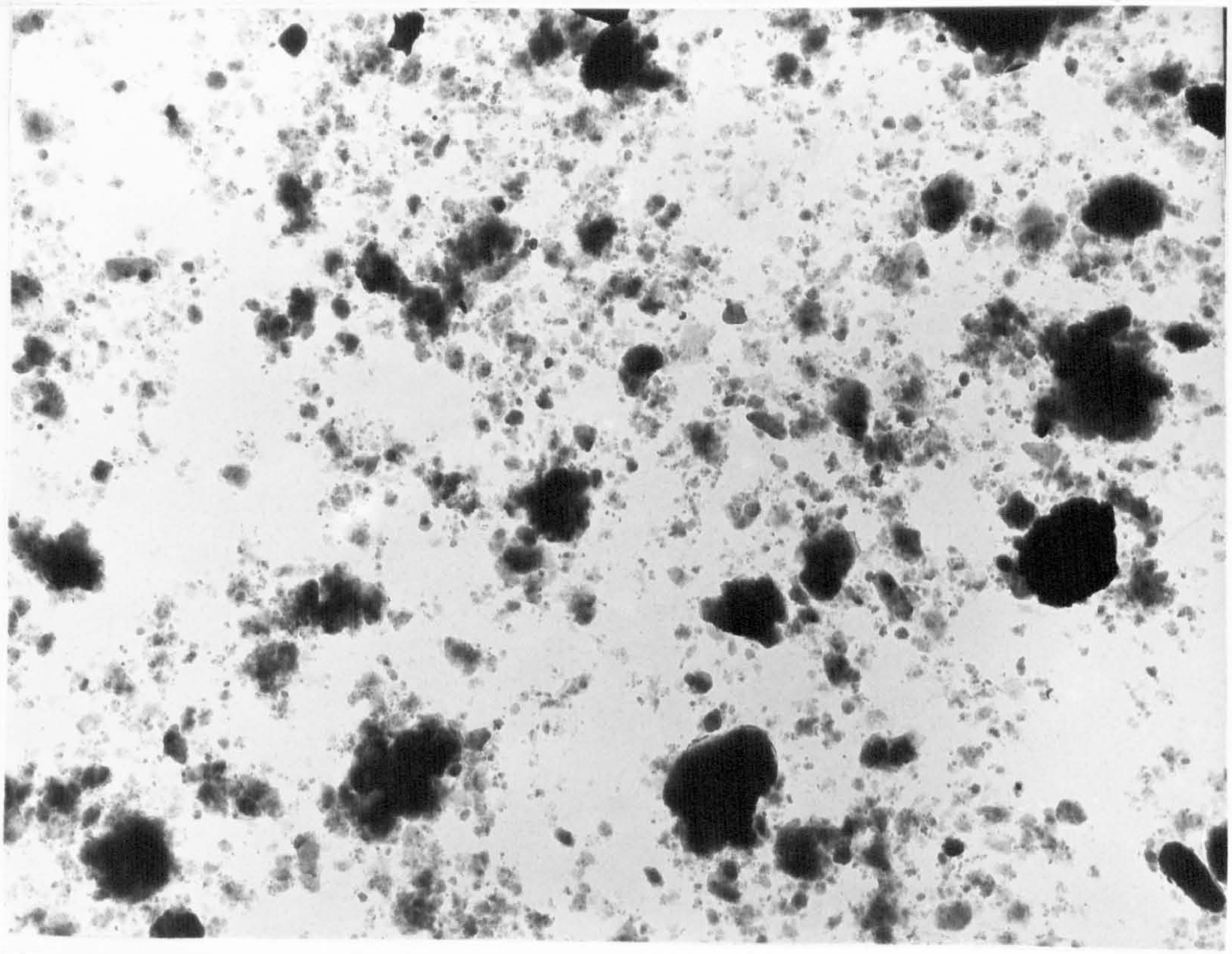
Small hexagonal grains

Plate 10(a)

Elongate grain in sample 67

Plate 10(b)

Clay minerals in sample 111



tailed grain together with small hexagonal grains, which are possibly illites. Again, the crystal shape denotes a non-detrital origin. Plate 10(a) shows an elongate grain from sample 67 which is similar to pictures of hectorite and saponite given by the above authors. It is possible, however, that this grain may be a rutile needle.

Plate 10(b) shows grains from sample 111 which exceed two microns in length. Some of the grains are reasonably angular and are thought to be kaolinite, the more rounded large grains being illite. The smectite is present as small, rounded grains, indicating a detrital origin. GILKES (1978) proposed neoformation of illite in calcareous lakes during the Oligocene. As this sample is from a marl bed within the Bembridge Limestone it may have been expected to contain neoformed illite, but there is no evidence for this.

(D) Mineralogical Quantification by Geochemical Recalculation

(i) Introduction

In order to express the normative clay mineral contents in terms of whole rock percentages, it is necessary to quantify the total clay mineral content of the samples. This is possible by quantification of the non-clay mineralogy. Calcite, aragonite and quartz contents have already been calculated, it remains only to quantify those minerals present in too small quantities to allow quantification by X.R.D.. This is possible by geochemical recalculation.

(ii) The calculation of non-clay minerals

The use of geochemical recalculation to supplement X.R.D. quantification in sediments has found widespread use, notably by SCHULTZ (1964). Amounts of the oxides corresponding to the X.R.D. mineral contents are subtracted from the geochemical analysis and the remaining oxides are recalculated into the other minerals known to exist in the sample.

SiO_2, CaO and MgO corresponding to the quartz and carbonate contents determined by X.R.D. were subtracted from the major element values in table 3. It was decided to assume that all of the TiO_2 was present in anatase or rutile, errors in failing to ascribe any TiO_2 to the clay minerals should be minimal. The only other minerals positively identified in the Oligocene samples were hemihydrate, pyrite, jarosite, goethite, hematite and the clay minerals. The three sulphur bearing minerals were calculated first. As the CaO remaining after removal of the carbonates was present in hemihydrate or exchange sites, hemihydrate was calculated in samples where CaO exceeded 0.5% and SO_3 exceeded 0.3%. Hemihydrate was calculated from CaO - 0.5%, the latter being an average CaO content present as exchangeable ions and in the minor quantities of apatite and feldspar. The amount of SO_3 in hemihydrate was calculated as 1.43 x (CaO - 0.5) and H_2O^- as 0.16 x (CaO - 0.5). In samples where this would have resulted in a negative SO_3 remaining, hemihydrate was calculated from SO_3 - 0.15%, the latter being an average SO_3 content for samples containing no sulphur bearing minerals. Summing these three oxides gave the hemihydrate content.

SO_3 remaining after the calculation of hemihydrate was expressed as either pyrite or jarosite, according to their presence in the whole rock diffratograms. Pyrite was calculated from SO_3 - 0.15%, the amount of Fe_2O_3 present in the pyrite being 0.5 x (SO_3 - 0.15). Pyrite content was then calculated as (Fe_2O_3 + SO_3)/2. In all samples there was sufficient Fe_2O_3 to form pyrite. Jarosite was identified in two samples, 51 and 52. In the former sample jarosite was the only sulphur bearing mineral identified, so that jarosite was calculated from SO_3 - 0.15%. In sample 52, hemihydrate was calculated first, the remaining SO_3 then being distributed between pyrite and jarosite. As the pyrite diffraction peak was very small, a pyrite content of 1% was assumed and removed from the chemical analysis, jarosite being calculated from the remaining SO_3 - 0.15%. The constituent oxides present in jarosite were calculated as follows and summed to give jarosite content -

$$K_2O = 0.3 \times (SO_3 - 0.15)$$
$$Fe_2O_3 = 1.5 \times (SO_3 - 0.15)$$
$$H_2O^- = 0.34 \times (SO_3 - 0.15)$$

The oxides calculated to be present in quartz, calcite, aragonite, hemihydrate, pyrite and jarosite were subtracted from the values in table 3 and the values remaining are listed in table 33. TiO_2 is not included in table 33 as it was assumed to be equal to the sum of anatase and rutile. MnO, Na_2O and P_2O_5 are not included in table 33 because they are present in low quantities in all samples.

Examination of table 33 may give an indication of the accuracy of the quantifications undertaken. The CaO values range

Table 33

Major elements remaining in clay minerals and iron oxides after the recalculation of non-clay minerals

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	SO_3	H_2O^+	H_2O^-
2*	31.14	13.19	9.82	0.32	1.98	-0.34	2.56	0.25	4.33	6.09
7	20.08	11.00	4.85	0.82	0.69	1.61	1.82	0.29	4.22	2.44
10	41.80	20.10	6.36	0.58	1.81	1.84	3.84	0.12	6.23	3.68
27	27.03	15.73	3.47	0.72	1.31	1.29	2.28	0.15	4.56	2.48
28	38.06	20.62	5.04	0.29	1.91	0.62	3.36	0.05	5.88	3.89
29*	28.68	17.55	4.05	0.17	1.73	0.63	2.88	0.15	6.38	3.95
31	31.02	17.45	3.68	0.53	1.74	0.51	2.94	0.15	6.09	3.70
32	30.48	18.15	5.07	0.67	1.94	0.50	2.94	0.15	6.39	2.79
33	30.75	17.50	4.69	0.72	2.02	0.50	3.04	0.15	6.50	3.25
36	27.90	17.29	4.35	0.53	1.36	0.50	2.60	0.15	5.09	2.42
37	37.35	17.68	4.50	0.61	1.52	0.50	2.70	0.16	5.51	3.08
39	26.42	18.04	3.86	0.59	1.64	0.50	2.76	0.15	6.01	3.22
45*	29.75	18.28	3.36	0.88	1.86	0.65	2.94	0.15	6.93	3.84
47	32.64	18.98	4.37	0.66	1.99	0.54	2.74	0.15	7.14	4.20
49	33.13	17.62	3.98	0.63	1.55	0.50	2.58	0.15	5.73	3.38
51	25.98	13.50	1.42	0.30	1.26	0.39	2.15	0.15	4.74	2.42
52	26.05	15.43	0.33	0.40	1.14	0.50	1.03	0.15	7.18	3.13
54	35.39	18.49	5.74	0.53	1.40	0.74	3.48	0.15	6.14	3.73
55	37.36	18.57	9.92	0.28	1.12	0.62	3.41	0.12	6.01	3.80
64	36.98	18.06	8.59	0.23	1.41	0.23	3.10	0.10	6.45	3.69
65	42.25	22.45	9.00	0.21	1.50	0.64	3.20	0.16	6.33	3.84
67	40.99	21.29	8.34	0.19	1.72	1.42	2.60	0.12	5.95	7.36
74*	28.54	17.26	3.43	0.68	1.23	0.58	2.66	0.16	5.06	2.68
77	38.73	19.34	8.51	0.70	1.46	0.60	2.77	0.14	6.30	2.44
95	38.39	20.08	5.63	0.52	1.82	0.78	2.91	0.15	6.96	4.35
102	22.41	13.82	3.99	0.19	0.93	0.52	2.38	0.23	5.77	2.39
111	40.74	16.58	5.22	0.28	2.06	1.55	2.73	0.19	4.22	3.42
112	19.82	7.90	2.83	0.29	1.17	1.19	1.25	0.23	2.98	2.86
116	40.29	15.46	6.85	0.43	2.52	0.40	4.06	0.14	4.67	4.40
119	22.63	11.31	4.89	0.40	1.55	-1.00	2.37	0.16	4.41	3.55
121	31.55	12.51	4.75	0.48	1.78	-0.12	3.05	0.27	3.62	1.73
122	16.53	3.61	1.10	0.09	0.32	0.18	0.91	0.05	1.45	0.76
123	22.61	13.33	3.69	0.41	1.64	1.06	2.37	0.15	4.76	3.53
124	31.68	15.95	4.99	0.47	1.99	1.18	2.79	0.15	6.11	4.69
126	32.03	15.10	4.92	0.47	1.71	0.50	2.57	0.15	5.99	4.08

Table 33 (contd.)

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	SO_3	H_2O^+	H_2O^-
129	24.83	13.87	4.96	0.44	1.65	0.09	2.98	0.20	5.13	2.84
134	10.43	5.46	1.21	0.63	0.25	0.85	1.13	0.12	1.77	0.66
136	37.62	20.91	5.28	0.70	1.55	0.80	3.29	0.19	6.42	3.82

N.B. * Determined free iron oxide contents subtracted from totals between -1.00 and 1.84%. While the former is obviously too low and the latter possibly too high to be accounted for by exchangeable calcium, apatite and feldspar, the range of values is only slightly in excess of 1% about an assumed mean of 0.5%. This indicates that the carbonate and hemihydrate contents are reasonably accurate. The Fe_2O_3 values remaining in pyritic and non-pyritic sediments are similar, suggesting that the pyrite values are accurate. In the two samples containing jarosite, however, the remaining Fe_2O_3 is very low, suggesting errors in the calculation of this mineral. It is possible that the mineral is, in fact, an intermediary between jarosite and alunite and that, therefore, some of the Fe_2O_3 should have been replaced by Al_2O_3.

An alternative method of checking the calculated mineral percentages (shown in table 34) is to compare them with the minerals identified by X.R.D. (shown in table 16). Several discrepancies exist between the calculated and observed sulphur bearing minerals. In two samples, 31 and 47, hemihydrate was identified by X.R.D., but insufficient CaO remained in the analyses to calculate hemihydrate. Conversely, in sample 39, hemihydrate was calculated to be present, but was not identified by X.R.D.. These slight differences may be due to sample inhomogeneity or to the apparently variable detection limits for pyrite and hemihydrate using X.R.D., reported by SCHULTZ (1964).

The oxides remaining in table 33 are those present in the clay minerals and iron oxides. It was not possible to quantify the iron oxides by X.R.D. due to their small peak size. JACKSON (1969) published a chemical method for determining the free iron oxide content of soils. This involves extraction of the sample with sodium citrate-bicarbonate-dithionite. The iron removed in solution is then determined colorimetrically as ferrous iron with orthophenanthroline. It was decided to analyse four samples by this method to delimit the free iron oxide content of the samples and to identify whether a correlation existed between total iron oxide content and free iron oxide content. The results obtained for the four samples are shown in table 35.

Table 34

Calculated mineral contents and estimated free iron oxide contents

Sample no.	Q	C	Ar	P	Hy	J	TiO_2	Fe_2O_3	Clays
2	9.2	13.9					0.3	5.1	71.5
7	10.8	40.8					0.5	1.0	46.9
10	10.7	1.8					0.8	2.0	84.7
27	20.2	19.1			0.8		0.8	0.5	58.6
28	19.2						1.0	1.5	78.3
29	26.3				4.8		0.9	1.8	66.2
31	24.0	3.8		1.5			0.9	0.5	69.3
32	23.1			2.2	1.4		0.9	1.5	70.9
33	23.7			2.1	1.8		0.9	1.0	70.5
36	31.4			0.7	3.2		1.0	1.0	62.7
37	21.7				3.7		1.0	1.0	72.6
39	30.8	1.4		0.7	2.2		0.9	0.5	63.5
45	27.9			0.6			0.9	0.7	69.9
47	17.2			3.8			0.9	1.0	77.1
49	21.3	5.4		0.4	1.3		1.0	0.5	70.1
51	42.4					4.4	1.3	0.5	51.4
52	26.9			0.5	1.3	12.9	0.9	0.5	57.0
54	13.2	8.4		0.4			0.7	1.5	75.8
55	17.1						0.9	3.5	78.5
64	11.8	8.5					0.8	3.0	75.9
65	9.0						0.8	3.0	88.2
67	9.0						0.8	3.0	88.2
74	35.9						1.4	0.2	62.5
77	17.6						1.1	3.0	78.3
95	16.0				0.9		0.9	1.5	80.7
102	45.7						1.1	0.5	52.7
111	12.3	9.7					0.6	1.5	75.9
112	3.3	55.4					0.3	0.5	40.5
116	7.9	12.3					0.5	2.0	77.3
119	17.6	30.8					0.5	1.0	50.1
121	12.7	0.9	26.5				0.4	1.0	58.5
122	63.8	3.4	7.4				0.2	0.5	24.7
123	32.0	10.8		1.2			0.6	0.5	54.9
124	16.8	9.1		1.7			0.7	1.0	70.3
126	8.7	12.7		4.5	1.0		0.6	1.0	71.5

Table 34 (contd.)

Sample no.	Q	C	Ar	P	Hy	J	TiO_2	Fe_2O_3	Clays
129	27.5	13.9					0.7	1.0	56.9
134	47.2	29.3					0.7	0.5	22.3
136	15.8	1.8					0.9	1.5	80.0

N.B. Q = quartz; C = calcite; Ar = aragonite; P = pyrite; Hy = hemihydrate; J = jarosite; TiO_2 = rutile and anatase; Fe_2O_3 = free iron oxides; Clays = total clay minerals.

Table 35 Free iron oxide contents

Sample no.	Fe_2O_3 content %	FeO content %	Free Fe_2O_3 content %
2	15.93	0.34	5.11
29	6.10	0.18	1.83
45	4.58	0.90	0.71
74	3.69	0.69	0.19

It is clear that a positive relationship exists between total iron oxide content and free iron oxide content, but that this relationship is not simple. The results also show that most of the Fe_2O_3 in the samples is present within the clay strutures. Since the quantities of free iron oxides in most samples would have been below two percent, it was decided to estimate free iron oxide contents rather than determine them by the method of JACKSON (1969). The values used in estimating the free iron oxide contents are listed in table 36.

Table 36 Estimated relationship between free iron oxide content and Fe_2O_3%

Fe_2O_3%	Estimated free iron oxide %
0 - 4	0.5
4 - 5	1.0
5 - 6	1.5
6 - 7	2.0
7 - 8	2.5
8 - 9	3.0
9 - 10	3.5

While the values in table 36 are very approximate, it may be expected that the free iron oxide content in all samples except number two does not exceed three percent and varies in relation to Fe_2O_3%. It is thought, therefore, that the estimated free iron oxide contents should be accurate to within 0.5%. Since the free iron oxide contents are needed solely to determine the total clay mineral contents, this variation should be unimportant. The estimated free iron oxide and total clay mineral contents are listed in table 34

(iii) The calculation of clay minerals

Whole rock clay mineral contents were calculated from the normalised clay mineral contents in table 30 using the total clay mineral contents in table 34. The values obtained are listed in table 37. To check the accuracy of these values it was decided to attempt a partial geochemical recalculation of the clay minerals. The main drawback to this is the very variable chemical composition of the clay minerals. With the exception of kaolinite, for which a reasonably stable formula can be assumed, the other clay minerals show large scale substitutions.

The most obvious mineral to calculate first is illite, as this is the only clay mineral with an appreciable K_2O content. In the smectites, potassium occurs as an exchangeable cation, but it was shown in chapter 4(D)(iv) that exchangeable potassium was unimportant in the Oligocene samples. Chemical analyses of illite show large variations. HOWER and MOWATT (1966) listed illite analyses showing a range of K_2O% from 6.94 to 9.07%, most of which they reported was due to interlayering of expandable material. Their samples with less than ten percent expandable layers contained between 8.04 and 9.07% K_2O. GRIM et al (1937) in their original paper on illite gave K_2O contents of 6.09 to 6.93%, while SCHULTZ (1964) used a K_2O content of 7.25% to calculate illite contents. Since the illite in the samples studied here gave an (001) spacing of less than 10.1Å, corresponding to five percent expandable layers, it was decided to use the K_2O content from HOWER and MOWATT (1966) corresponding to illite with less than ten percent expandable layers. An average content of 8.2% K_2O was obtained from their four samples. The illite formula given by the above authors was used -

$$K_{1.4}Mg_{0.6}Fe^{2+}{}_{0.1}Fe^{3+}{}_{0.5}Al_{3.6}Si_{6.9}O_{20}(OH)_{5.6}$$

The constituent oxides in illite were calculated from the K_2O% as follows, subtracted from the analyses in table 33 and summed to give the illite content.

$SiO_2 = 6.35 \times K_2O$

$Al_2O_3 = 2.84 \times K_2O$

$Fe_2O_3 = 0.60 \times K_2O$

$FeO = 0.15 \times K_2O$

$MgO = 0.37 \times K_2O$

$H_2O^+ = 0.76 \times K_2O$

$H_2O^- = 0.13 \times K_2O$

The only remaining clay mineral with an appreciable FeO content is chlorite, as smectites contain negligible amounts

(DEER et al, 1962). It was mentioned on page 57 that the chlorite in the Oligocene sediments was thought to be an iron rich variety, so the formula for chamosite given by DEER et al (1962) was used for the calculations. Chlorite was calculated for all samples in which over 0.2% FeO remained. The chlorite content was calculated from FeO - 0.1%, this latter figure being taken as an average FeO content for samples not containing chlorite. The constituent oxides were calculated as follows, subtracted from the totals in table 33 and summed to give chlorite content.

$$\begin{aligned} SiO_2 &= 1.02 \times (FeO - 0.1) \\ Al_2O_3 &= 0.70 \times (FeO - 0.1) \\ Fe_2O_3 &= 0.22 \times (FeO - 0.1) \\ MgO &= 0.44 \times (FeO - 0.1) \\ H_2O^+ &= 0.41 \times (FeO - 0.1) \end{aligned}$$

The illite and chlorite contents obtained by recalculation are listed in table 37.

The oxides remaining after the calculation of illite and chlorite are shown in table 38. These oxides are present in the smectite and kaolinite, but unfortunately there seems to be no way of calculating these minerals. The smectites show very large scale solid substitutions and there is no indication of the type of smectite present in these samples. While a montmorillonite formula may be appropriate for most samples, in sample 2 the high Fe_2O_3% remaining suggests the presence of nontronite. No attempt was, therefore, made to calculate smectite contents.

Inspection of the values remaining in table 38 shows several interesting points. There are many negative FeO and MgO values, suggesting that in the illite calculation too much FeO and MgO was assigned to the formula. The generally high Fe_2O_3% remaining suggest that some FeO and MgO should have been replaced by Fe_2O_3 in the formula. The two negative Fe_2O_3 values are due to the erroneous jarosite calculation, mentioned on page 62. In general it may be seen that geochemical recalculation of clay minerals is not a straightforward procedure, due to chemical variation of the minerals.

(iv) Comparison of the methods of quantifying clay mineralogy

In table 37 the calculated illite and chlorite contents are listed together with the X.R.D. clay mineral contents expressed as whole rock values. It can be seen that the chlorite contents show very close similarity. In only one sample was chlorite

Table 37

X.R.D. clay mineral contents and recalculated illite and chlorite contents

Sample			X.R.D. contents %			Recalc. contents	
no.	Smec.	Ill.	Ill-smec.	Kaol.	Chlor.	Ill.	Chlor.
2	37	33		1		31	
7	15	24		7	1	22	2
10	3	70		12		47	
27	28	21		9	1	28	1
28	27	36		16		41	
29	21	32		13		35	
31	19	35		15		36	
32	19	34		18		36	1
33	13	41		16		37	1
36	27	22		14		32	
37	29	29		15		33	
39	23	25		16		34	
45	28	26		14	2	36	1
47	37	23		16	1	33	1
49	39	20		10	1	32	1
51	27	18		7		26	
52	28	21		8		13	
54	5	59		11		42	
55		52	14	12		42	
64		48	14	14		38	
65	42	25		21		39	
67	64	23		1		32	
74	39	14		9	1	32	1
77	41	24		12	2	34	1
95	36	27		18		36	
102	19	22		12		29	
111	36	38		3		33	
112	27	13		1		15	
116	2	73		2		50	
119	21	27		3		29	
121	2	53		4		37	
122	14	9		2		11	
123	30	21		4		29	
124	33	32		6		34	

Table 37 (contd.)

Sample			X.R.D. contents %			Recalc. contents	
no.	Smec.	Ill.	Ill-smec.	Kaol.	Chlor.	Ill.	Chlor.
126	26	36		10		31	
129	1	49		6	1	36	
134	7	10		4	1	14	1
136	30	34		14	2	40	1

N.B. Smec.= smectite; Ill. = illite; Ill-smec. = illite-smectite; Kaol. = kaolinite; Chlor. = chlorite.

All contents expressed as % of whole sample.

Table 38

Major elements remaining after the calculation of illite and chlorite

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	H_2O^+	H_2O^-
2	14.87	5.92	8.29	-0.05	1.04	2.39	5.75
7	8.06	5.51	2.66	0.10	-0.18	2.66	2.20
10	17.40	9.21	2.07	0.02	0.41	3.33	3.16
27	12.24	9.05	1.55	0.10	0.35	2.72	2.17
28	16.71	11.07	1.55	-0.20	0.68	3.34	3.44
29	10.38	9.37	2.33	-0.25	0.68	4.20	3.56
31	12.34	9.10	1.42	0.10	0.66	3.87	3.31
32	11.66	9.70	1.78	0.10	0.80	4.11	2.40
33	11.25	8.73	1.84	0.10	0.83	4.13	2.84
36	11.38	9.90	1.80	0.15	0.41	3.12	2.07
37	20.09	9.93	1.87	-0.10	0.48	3.42	2.72
39	8.88	10.20	1.71	0.19	0.63	3.92	2.95
45	10.71	9.68	1.52	0.10	0.63	4.57	3.45
47	15.07	11.08	1.70	0.10	0.92	5.00	3.83
49	16.59	10.18	1.91	0.10	0.54	3.72	3.03
51	12.32	7.39	-0.36	-0.01	0.47	2.80	2.13
52	19.36	12.39	-0.82	0.10	0.69	5.43	2.99
54	13.28	8.60	2.16	0.02	0.13	3.51	3.26
55	15.69	8.88	4.38	-0.22	-0.13	3.43	3.34
64	17.28	9.25	3.74	-0.22	0.28	4.11	3.27
65	21.92	13.36	4.09	-0.26	0.33	3.91	3.41
67	24.47	13.90	3.79	-0.19	0.77	3.98	7.01
74	11.45	9.57	1.80	0.10	0.18	3.97	2.32
77	10.94	11.38	3.81	0.10	0.37	4.13	2.07
95	19.90	11.81	2.39	0.09	0.76	4.76	3.96
102	7.29	7.06	2.07	-0.16	0.06	3.97	2.07
111	23.39	8.82	2.09	-0.12	1.06	2.16	3.05
112	11.88	4.35	1.58	0.11	0.71	2.03	2.69
116	14.49	3.98	2.42	-0.16	1.03	1.60	3.86
119	7.57	4.58	2.47	0.05	0.68	2.64	3.23
121	12.17	3.84	1.93	0.03	0.66	1.31	1.32
122	10.75	1.02	0.06	-0.04	-0.01	0.76	0.64
123	7.55	6.60	1.77	0.06	0.77	2.97	3.21
124	13.95	8.02	2.32	0.06	0.97	4.00	4.32
126	15.70	7.80	2.38	0.09	0.77	4.05	3.74

Table 38 (contd.)

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	H_2O^+	H_2O^-
129	5.90	5.40	2.18	0.00	0.56	2.88	2.44
134	2.88	2.00	0.05	0.10	-0.32	0.77	0.51
136	16.60	11.48	1.78	0.10	0.30	3.88	3.38

identified by X.R.D. but not calculated, while in two samples sufficient FeO remained for chlorite to be calculated, but it was not identified by X.R.D.. The agreement between the two sets of illite values is not so good. They show a highly significant positive correlation, but regression analysis gave a slope of 1.94 with an intercept on the y axis (the X.R.D. values) of -32.05. This shows that at low values the X.R.D. values are generally lower than the calculated values, while at high values the X.R.D. values are higher. The mean illite values are similar for the two methods, 33% for the calculated values and 31% for the X.R.D. values.

There is no reason for preferring either set of illite values. If the X.R.D. values are correct, it indicates that in samples containing abundant illite, the illite is of a potassium depleted variety, while in samples containing less than average illite, the illite is potassium enriched. This explanation seems unlikely, rather it is thought that the X.R.D. method of quantification overestimates the major clay mineral. Since, however, it was not possible to calculate smectite and kaolinite contents and also since both sets of illite values show the same trends, it is thought that the X.R.D. contents are sufficiently accurate to be worthy of interpretation.

6 STATISTICAL ANALYSIS

(A) Introduction

With the large amount of data thus far accumulated, visual interpretation is not very effective. The use of statistical techniques allows the extraction of maximum information from large data sets and when these techniques are performed by computer, the workload on the geologist is minimised. Statistical analysis has found much use in geochemistry, but can also be applied to any set of results which can be expressed numerically.

The statistical results in this thesis were obtained by the use of three computer programs, with, however, only two main aims. The first aim, that of attempting to distinguish between samples representing different environments, was approached from two angles, using cluster analysis and discriminant analysis. The second aim, that of identifying inter-element and element-mineral relationships, used correlation analysis.

(B) Cluster Analysis

(i) Introduction

Cluster analysis is in essence a form of correlation analysis except that instead of calculating correlation coefficients of variables, a list of sample similarity coefficients is produced. By the construction of a dendrogram from these values (KRUMBEIN and GRAYBILL, 1965) an easily interpreted list of sample similarities is obtained. Cluster analysis was undertaken using the computer program of MATHER (1969). This program first calculates correlation coefficients for the variables and averages those variables which correlate above a specified level. The reduced volume of data is then transformed into values of standard deviation difference from the mean of each variable or pair of variables. The table of data obtained is then sorted and the most similar pair of samples are removed and replaced by their average. This process is carried on until all samples have been removed. The similarity coefficients between each pair of samples, or groups of samples, are calculated and listed. Finally a list of the samples is printed, from which the dendrogram may be manually constructed.

Cluster analysis was undertaken on the major and trace element values separately, in order to allow the inclusion of all samples analysed. Unfortunately the total number of variables involved in running both sets of data together would have exceeded the program capacity and necessitated extensive rewriting of the program.

(ii) Major elements

The dendrogram obtained for the sixty-seven samples analysed for twelve major elements is shown in figure 16 . Several points are worthy of note. Firstly, the very close similarities of the three sets of subsamples, which indicates the small contribution of subsampling variation to variation in major element values. Secondly, the marine and brackish samples are reasonably evenly distributed throughout the list, indicating that there is no major difference in whole rock geochemistry between marine and non-marine samples. In general terms the similarity table can be subdivided into quartzose, argillaceous and calcareous sample types. Finer subdivisions within these main divisions are also mainly related to variations in these three constituents, although the effect of abnormal values of single elements becomes more important.

This last point is worth considering. Since the oxide percentages are converted into standard deviation difference from the mean, equal weight is given to all of the elements, irrespective of their total values. Thus elements present in low quantities, such as MnO, P_2O_5 and Na_2O are considered to be equivalent to the major elements SiO_2 and Al_2O_3. It was, therefore, decided to repeat the cluster analysis using a reduced number of variables, MnO, P_2O_5 and Na_2O being removed. The dendrogram obtained is shown in figure 17. It can be seen that the similarities have been slightly increased, while leaving the broad groups unchanged. It may be concluded, therefore, that variations in whole rock major element geochemistry are of too coarse nature for use as anything more than broad environmental indicators.

(iii) Trace elements

The dendrogram obtained for the forty-seven samples analysed for thirteen trace elements is shown in figure 18. It can be seen that over half of the samples show very close

Figure 16

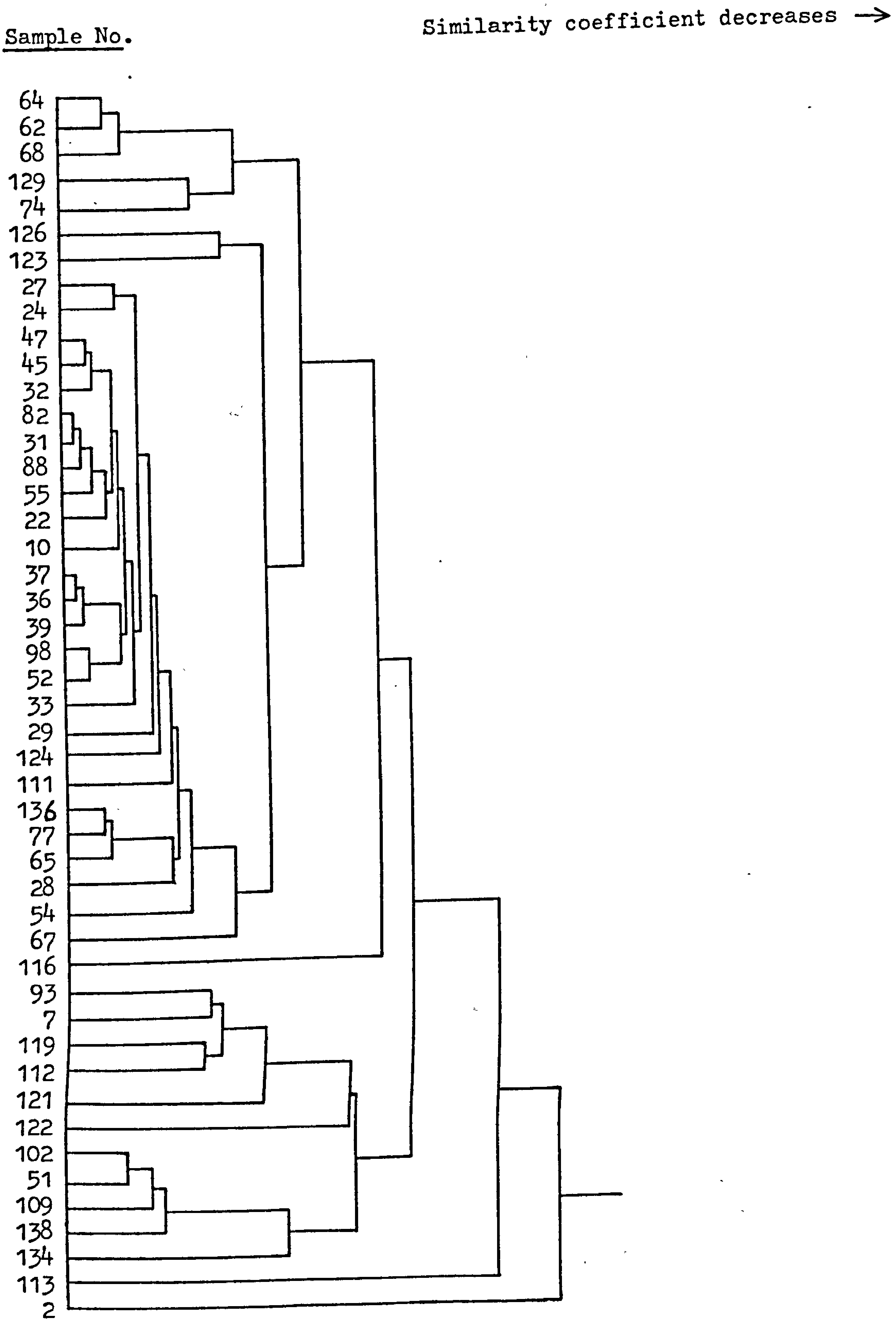
\+ Samples from brackish Bembridge Oyster Bed

* Samples from marine *Corbula* Bed

Figure 17


Sample No.
Similarity coefficient decreases →
8
7
112
114
113
33
32
47
52
42
126
2
58
29
62
64
55
82
28
88
67
65
91
121
119
24
22
27
111
86
98
5
129
133
19
50
123
93
116 II
116
68
124 II
124
124EX
124In
39
37
31
36
49
74 II
74
76
95
10
54
136
77
45
122
105
109
106
102
51
138
134

Figure 18


Sample No.
Similarity coefficient decreases →
64
62
68
129
74
126
123
27
24
47
45
32
82
31
88
55
22
10
37
36
39
98
52
33
29
124
111
136
77
65
28
54
67
116
93
7
119
112
121
122
102
51
109
138
134
113
2

similarities and that this cluster contains marine and non-marine samples, indicating that the trace element contents are not useful palaeosalinity indicators. It is thought to be worthwhile elucidating the reasons for the clusters shown in figure 18.

The first cluster contains three samples which are marls with high manganese contents, taken to be present in the calcite structure. The second cluster contains two samples with higher than average barium contents. In sample 74, the illite has a higher crystallinity than the average and it is thought, therefore, that the barium could be present in a detrital mica. Sample 129 is very illitic and this may be contributing to the high barium value, although the possibility of small amounts of barytes being present is not precluded. The third cluster contains two marl samples with higher than average lead contents. No explanation for this is apparent.

The first three clusters have reasonably close similarity coefficients with the main group of samples (cluster four), which are clays containing little or no calcite. Of the twenty-six samples in this cluster, two are worthy of note. Sample 54 is, to some extent, different, due to its high cobalt and nickel contents. Sample 67 is even more dissimilar from the rest of cluster four, due to its slightly high zinc and chromium contents and low rubidium, vanadium and copper. It has been mentioned that this sample contains more smectite than any other and is thought to be of partial volcanic origin. The trace element contents support the conclusion that this sample is different from the other clays. The samples considered thus far may be taken to form one large cluster.

Cluster five contains only one sample, number 116, which is distinguished by its very high rubidium content. As this sample contains over seventy percent illite it is to be expected that the rubidium is substituting for potassium in the illite structure.

Cluster six contains five samples containing little clay, due to high quartz and calcite contents. This results in dilution of the trace element contents, with the exception of manganese and strontium. Sample 121 is dissimilar to the other samples in the cluster as it has a very high strontium content present in aragonite.

Cluster seven is another single sample cluster, number 122. This sample has a very high quartz content and as a result contains lower than average quantities of all the trace elements with the exception of strontium and zirconium.

The next group of samples consists of argillaceous sandstones, typified by low contents of all trace elements except zirconium and to a lesser extent barium and yttrium. This suggests that the latter two elements are largely present in detrital minerals and it was mentioned above that barium was thought to be concentrated in detrital micas.

The final two clusters consist of single samples, numbers 113 and 2. The former is from the Bembridge Limestone and gives an indication of the trace element content of the freshwater calcite. Low contents for almost all trace elements are shown, the main exception being strontium. To a lesser extent the lead, manganese, cobalt and nickel contents are not too far below average, suggesting that these elements are present in the calcite.

Sample 2 is even more dissimilar from the other samples than is the Bembridge Limestone. This sample contains very high copper, lead, nickel, cobalt and vanadium contents. Three possible explanations exist for these high contents. The sample contains more organic matter than average and organic matter has been shown by RASHID (1974) to be an effective concentrator of trace metals. The sample also contains a higher content of free iron oxides than average and these are similarly known to be concentrators of trace metals. Finally, one of the clay minerals in the sample is very rich in iron, it is thought that either glauconite or nontronite is present and the enriched elements may be substituting for iron in the clay structure.

In conclusion it may be said that cluster analysis can provide useful geological information, although in the Oligocene samples the main differences have been shown to be due to variations in the contents of quartz, calcite and total clay minerals.

(C) <u>Discriminant Analysis</u>

(i) Introduction

In cluster analysis a null hypothesis that all samples are identical is erected and tested, deviations from this null hypothesis being listed. A reverse approach is the method of discriminant analysis, where a null hypothesis that certain samples are different is set up and tested. In this study discriminant analysis was used solely to test the hypothesis that marine and non-marine samples were different. MILLER and KAHN (1962) described discriminant analysis with respect to its use in palaeontological investigations. In simple terms, the procedure is to select a group of samples typical of the chosen group. Each sample is then plotted in n (the number of variables) dimensional space and the mean vectors of each group are calculated. The distance between the means of any two groups is the Mahalanobis D^2 distance and the significance of this difference is tested by Snedecor's F ratio of the two groups' variances. The significance of the F ratio obtained may be read off probability tables.

Discriminant analysis was undertaken using the computer program of WOLLEBEN et al (1968) to calculate the significance of differences between groups, the discriminant function coefficient and the discriminant index. These latter two values may be used, once a significant difference has been proved between two groups, to assign unknown samples to either group.

(ii) Results obtained

Four groups were set up, marine, non-calcareous samples (from the Corbula Bed); non-marine, non-calcareous samples (from the Lower Hamstead Beds); brackish, calcareous samples (from the Bembridge Oyster Bed); and non-marine, non-calcareous samples (from the Bembridge Marls). As it had been shown by cluster analysis that the trace element contents of the marine and non-marine samples were very similar, it was decided only to use major element values for discriminant analysis. It was not expected that much difference would be found between the marine and non-marine samples, as cluster analysis had shown that their major element contents were also very similar.

The first problem encountered was that insufficient samples were present for the brackish, calcareous group, which rendered the statistics meaningless. Consequently this group had to be discarded. For the remaining three groups the only significant difference was found between the non-marine, non-calcareous group and the non-marine, calcareous group. The difference between the marine and non-marine groups was not significant at the 95% probability level. This result supports the conclusion arrived at above, by cluster analysis, that the geochemistry of the marine and non-marine samples is similar. There are, however, slight differences between the mean vectors of the marine and non-marine groups, the marine group containing more Al_2O_3, MgO, K_2O and SO_3, suggesting the presence of more clay minerals and sulphur bearing minerals. The spread of values about the mean is, however, too large to allow any of these elements to be used as palaeosalinity indicators.

(D) Correlation Analysis

(i) Introduction

The measure of correlation used in this work is Pearson's product moment correlation coefficient - r, which may be calculated by dividing the covariance of any two variables by the product of the standard deviations of the variables. The value obtained will range between one and minus one, the former indicating perfect positive correlation, while the latter shows a perfect antipathetic relationship. The significance of the value of r may be tested by the Student's t test.

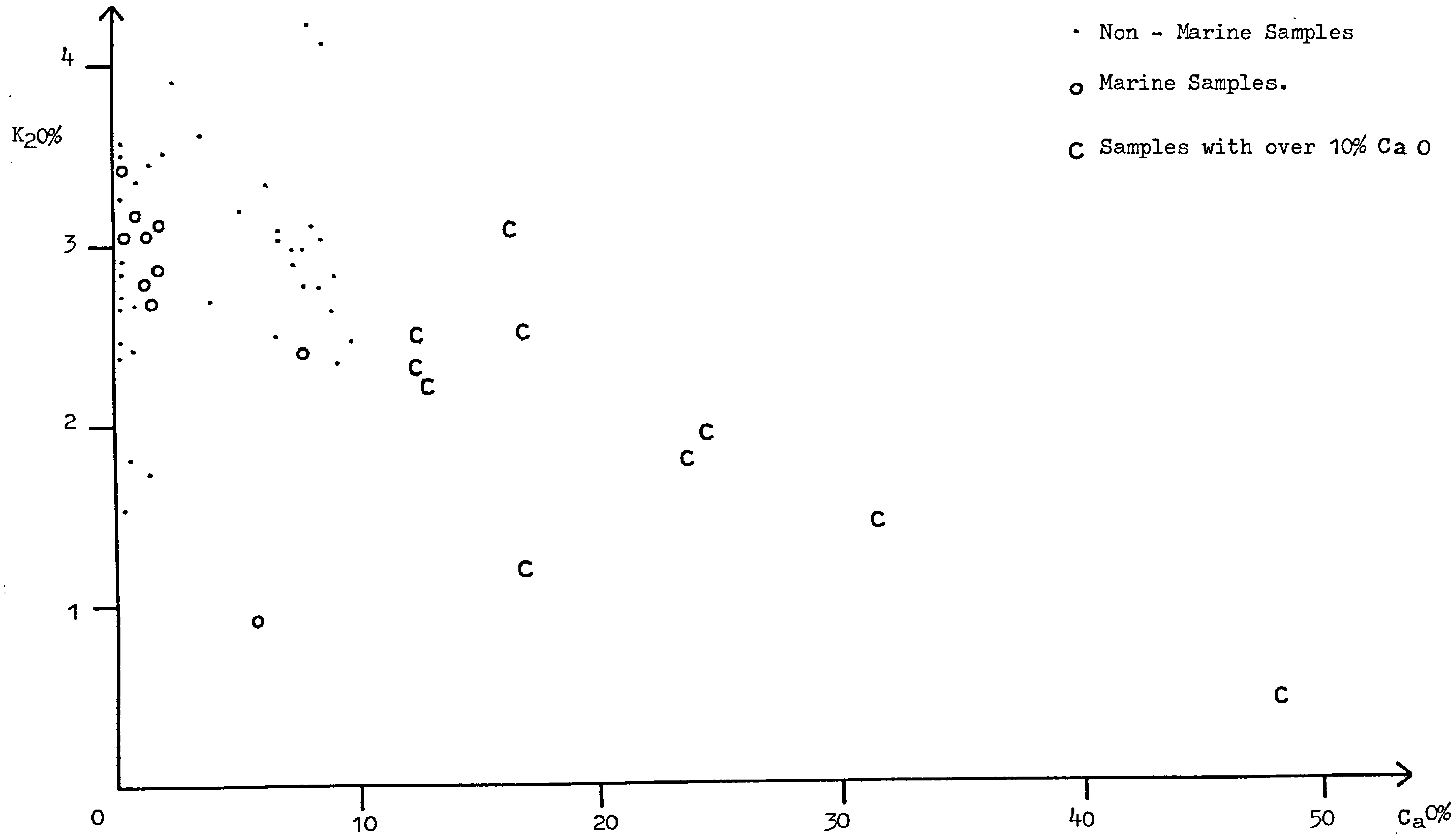
Correlation coefficients were at first calculated using the computer program of TILL (1969). This program calculates r and plots graphs of variables which correlate above a specified level. An example of the output is given in figure 19, the different symbols indicating different types of samples. This graphical output allows an estimate to be made of the normality of the variable distributions. The calculation of correlation coefficients may be greatly affected by non-normal variable distribution. Thus the observed correlation in figure 19 is largely due to the six samples C plotting in the bottom right hand corner of the graph. Removal of these samples would result in a lower correlation coefficient being calculated.

To enable the normality of variable distribution to be calculated, a computer program was written to calculate r and to express the variable distributions in terms of standard deviations difference from the mean. This allows easy comparison of each variable's distribution with a normal distribution.

There are two further points of note concerning correlation analysis. Firstly, geochemical data is not ideal for correlation analysis, because it is expressed as parts of a constant sum (100%). MIESCH (1969) described the problem of this constant sum effect. Since geochemical results add up to a constant value, there is of necessity an interrelationship between all variables, it is impossible for the value of one variable to change while those of all the others remain constant. This means that correlation coefficients obtained from geochemical data do not fit

Figure 19

Example of the output of the correlation analysis program of TILL (1969)



the assumptions of the Student's t test. The second factor concerning correlation analysis was well expressed by MORONEY (1969), 'at no point are statistical methods more of a sausage machine than in correlation analysis'. The effects of non-normal variable distribution and the constant sum effect on the values of r have been mentioned, but even in data affected by neither of these problems, a significant correlation between two variables does not prove a causal relationship between the two. Care must, therefore, be taken in interpreting correlation matrices.

(ii) Results obtained

The correlation coefficients for twelve major elements determined for sixty-seven samples are shown in table 39. It was mentioned on page 70 that the three main mineralogical constituents of the Oligocene samples are quartz, calcite and the clay minerals, representing the resistate, precipitate and hydrolysate phases. From the correlations shown in table 39 it should be possible to distribute the major elements between these three phases. The dominant oxide in the precipitates is CaO and this shows only one significant positive correlation in table 39, indicating that MnO is the only oxide concentrated in the precipitates. Significant negative correlations exist between CaO and SiO_2, Al_2O_3, TiO_2, Fe_2O_3 and K_2O, suggesting that these oxides do not occur in the precipitates. The lack of significant correlations with the remaining oxides may be taken to indicate that they are partially associated with the precipitate phase.

The typical mineral in the resistates is quartz, but SiO_2 also occurs in the hydrolysates (the clay minerals). SiO_2 shows a highly significant positive correlation with TiO_2, indicating that this oxide is present mainly in detrital minerals (anatase and rutile were identified by X.R.D.). Significant negative correlations exist between SiO_2 and the two precipitate oxides, CaO and MnO.

In the hydrolysates, Al_2O_3 may be taken as the representative oxide, being common in most clay minerals. Al_2O_3 shows significant positive correlations with TiO_2, Fe_2O_3, K_2O and MgO. The latter three oxides also show positive correlations with each other, but not with TiO_2. This suggests that they are present either in the clay mineral structures or as oxide coatings on the clay particles. The correlation between TiO_2 and Al_2O_3 is thought to be mainly due to calcite dilution.

Table 39 Correlation matrix for major element contents

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	SO_3
SiO_2												
Al_2O_3	0											
TiO_2	*	*										
Fe_2O_3		*										
FeO												
MgO	-+	*	-0	*								
CaO	-*	-*	-*	-+								
Na_2O					-+							
K_2O	0	*	0	*		*	-*					
MnO	-+						+					
P_2O_5	-0		-0									
SO_3					0	0		-0				

* Highly significant positive correlation
-* Highly significant negative correlation
+ Significant positive correlation
-+ Significant negative correlation
0 Probably significant positive correlation
-0 Probably significant negative correlation

Correlation coefficients for the major and trace element data were calculated using the author's program, described earlier. Values for the variable distribution among the forty-seven samples are shown in table 40. It can be seen that all of the variables are non-normally distributed. It will obviously be fortuitous for any variable to show a perfectly normal distribution, what is required is a reasonably symmetrical distribution. Many of the variables show such a distribution, the main exceptions being CaO, Na_2O, SO_3, Mn and Sr. The significance of correlations involving these elements is, therefore, questionable. The correlation coefficients obtained are shown in table 41.

In order to determine the effect of non-normal distribution on the correlation coefficients obtained, quartz and carbonate rich samples were removed. The resulting variable distribution, shown in table 42, shows that Na_2O, SO_3, Mn and Y have markedly non-normal distributions. The correlation matrix obtained is shown in table 43. In an attempt to further normalise the variable distributions, samples containing more than 3.5% CaO and 61% SiO_2 were removed, thus leaving samples with very low quartz and calcite contents. Table 44 shows that the effect on variable distribution was small, SO_3, Mn and Y still showing poor distributions, as does Al_2O_3. The correlation coefficients obtained for this data are shown in table 45.

Studying the three tables of correlation coefficients systematically should allow an evaluation of the inter-element relationships. For the resistate phase, Zr may be taken as the representative element, as it is to be expected that Zr will be present only in the detrital mineral zircon (PEARSON, 1972). Zr shows significant positive correlations with SiO_2 and TiO_2 in all three correlation matrices, indicating that these two elements are concentrated in detrital minerals, as was concluded above. Significant positive correlations exist between Zr and Y in tables 41 and 43 and between Zr and Ba in table 41. These suggest that both Y and Ba are partially present in detrital minerals. On page 69 it was mentioned that Ba was thought to be concentrated in detrital micas, while Y may be expected to be present in detrital phosphates such as xenotime, which was found in Tertiary sediments of the Hampshire Basin by BLONDEAU and POMEROL (1968).

The precipitate phase may again be taken to be represented by CaO. This shows many significant negative correlations, but only one significant positive correlation, with Sr in tables 41 and 43. This indicates that the most important location for Sr is

Table 40

Distribution of major and trace elements

% between limits given by standard deviation difference from mean

Variable	+2S.D.	+1S.D.	Mean	-1S.D.	-2S.D.	
Normal distribution	2.3	13.6	34.1	34.1	13.6	2.3
SiO_2	2.1	10.6	44.7	36.2	2.1	4.3
Al_2O_3	0.0	10.6	51.1	25.5	6.4	6.4
TiO_2	4.3	8.5	42.6	27.7	12.8	4.3
Fe_2O_3	2.1	12.8	29.8	44.7	8.5	2.1
FeO	2.1	21.3	21.3	38.3	17.0	0.0
MgO	2.1	12.8	38.3	31.9	8.5	6.4
CaO	4.3	6.4	27.7	61.7	0.0	0.0
Na_2O	8.5	0.0	31.9	48.9	10.6	0.0
K_2O	0.0	10.6	48.9	27.7	6.4	6.4
P_2O_5	2.1	14.9	25.5	46.8	10.6	0.0
SO_3	6.4	8.5	12.8	72.3	0.0	0.0
H_2O^+	0.0	6.4	53.2	27.7	6.4	6.4
H_2O^-	4.3	6.4	48.9	29.8	4.3	6.4
Zn	0.0	21.3	36.2	23.4	14.9	4.3
Cu	4.3	2.1	34.0	48.9	10.6	0.0
Pb	4.3	4.3	34.0	48.9	8.5	0.0
Ba	2.1	8.5	53.2	14.9	17.0	4.3
Ni	2.1	6.4	38.3	42.6	10.6	0.0
Co	4.3	6.4	27.7	55.3	6.4	0.0
Mn	6.4	6.4	14.9	72.3	0.0	0.0
V	2.1	2.1	61.7	21.3	8.5	4.3
Cr	0.0	6.4	55.3	25.5	6.4	6.4
Rb	2.1	4.3	53.2	27.7	6.4	6.4
Sr	4.3	0.0	25.5	70.2	0.0	0.0
Y	4.3	4.3	42.6	38.3	6.4	4.3
Zr	4.3	10.6	27.7	48.9	6.4	2.1

Table 41

Correlation matrix for major and trace element contents

	Si	Al	Ti	Fe^{3+}	Fe^{2+}	Mg	Ca	Na	K	P	S	H_2O^+	H_2O^-	Zn	Cu	Pb	Ba	Ni	Co	Mn	V	Cr	Rb	Sr	Y	Zr
Si																										
Al																										
Ti	*	*																								
Fe^{3+}		*																								
Fe^{2+}																										
Mg	-0	*		*																						
Ca	-*	-*	-*	-+																						
Na					-+																					
K		*	+	*		*	-*																			
P																										
S								-0																		
H_2O^+		*	*	*		*	-*		*		0															
H_2O^-		*		*		*	-+		*			*														
Zn		*	+	*		+	-*		*			*	*													
Cu				*		0							+													
Pb				*				-+			+	+	+		*											
Ba	+	*	*				-*		*			*		*												
Ni		*		*		+	-+		*			*	*	*	*	*										
Co		0		*		0			+				*	+	*	*		*								
Mn	-0																									
V		*		*		+	-*		*			*	*	*	*	*	+	*	*							
Cr	+	*	*	*		+	-*		*			*	*	*	+		*	*	+		*					
Rb		*		*		*	-*		*			*	*	*	+			*	+		*	*				
Sr	-*	-*	-*				*	*	-*	0		-*	-+	-*			-*				-+	-*	-+			
Y	*	+	*				-*		0			+		+			*					*		-*		
Zr	*		*			-+	-*										+							-*	*	

Key as for table 39

Table 44

Distribution of major and trace element contents in samples containing <3.5% CaO and <61% SiO_2

% between limits given by standard deviation difference from the mean

Variable	+2S.D.	+1S.D.	Mean	-1S.D.	-2S.D.	
Normal distribution	2.3	13.6	34.1	34.1	13.6	2.3
SiO_2	0.0	15.8	42.1	26.3	15.8	0.0
Al_2O_3	5.3	15.8	21.1	52.6	0.0	5.3
TiO_2	5.3	5.3	31.6	47.4	5.3	5.3
Fe_2O_3	5.3	15.8	26.3	36.8	15.8	0.0
FeO	0.0	10.5	47.4	15.8	26.3	0.0
MgO	0.0	15.8	31.6	36.8	15.8	0.0
CaO	0.0	21.1	26.3	21.1	31.6	0.0
Na_2O	5.3	5.3	31.6	52.6	5.3	0.0
K_2O	5.3	10.5	26.3	42.1	10.5	5.3
P_2O_5	5.3	10.5	26.3	47.4	10.5	0.0
SO_3	5.3	15.8	26.3	52.6	0.0	0.0
H_2O^+	0.0	15.8	36.8	36.8	5.3	5.3
H_2O^-	5.3	0.0	42.1	42.1	10.5	0.0
Zn	0.0	15.8	31.6	26.3	26.3	0.0
Cu	0.0	21.1	26.3	36.8	10.5	5.3
Pb	5.3	10.5	36.8	31.6	15.8	0.0
Ba	5.3	10.5	26.3	36.8	21.1	0.0
Ni	5.3	15.8	15.8	47.4	15.8	0.0
Co	5.3	10.5	21.1	52.6	10.5	0.0
Mn	5.3	5.3	26.3	63.2	0.0	0.0
V	5.3	15.8	31.6	36.8	10.5	0.0
Cr	0.0	15.8	36.8	36.8	5.3	5.3
Rb	0.0	15.8	31.6	42.1	5.3	5.3
Sr	5.3	5.3	42.1	26.3	21.1	0.0
Y	10.5	0.0	26.3	57.9	5.3	0.0
Zr	0.0	21.1	42.1	21.1	10.5	5.3

Table 45

Correlation matrix for samples containing $< 3.5\%$ CaO and $< 61\%$ SiO_2

	Si	Al	Ti	Fe^{3+}	Fe^{2+}	Mg	Ca	Na	K	P	S	H_2O^+	H_2O^-	Zn	Cu	Pb	Ba	Ni	Co	Mn	V	Cr	Rb	Sr	Y	Zr
Si																										
Al	-0																									
Ti	0																									
Fe^{3+}	-+																									
Fe^{2+}																										
Mg																										
Ca																										
Na	-+	*	-0	0	-0																					
K																										
P	-0	0																								
S		-+						-+	-+																	
H_2O^+	-0																									
H_2O^-	-0		-+		-0			+																		
Zn							-+																			
Cu					0				0				-0													
Pb		-0			0			-+	-0		*															
Ba		0							0		-+															
Ni		0					-0							0			+									
Co																	0	0								
Mn																										
V		0															+	+	0							
Cr		*									-0						0	+	+		+					
Rb									*				-+				+	0			*					
Sr														-0						-0						
Y			+														+	0								
Zr	*	-*	+	-+						-0			-+			0										

Key as for table 39

in the carbonate minerals. The lack of a significant correlation between CaO and Sr in table 45 indicates that in non-calcareous samples the two occur in different minerals.

In table 41 there are a large number of elements showing highly significant positive correlations with Al_2O_3, suggesting their presence in the hydrolysate fraction. Apart from the major elements mentioned already, these are H_2O^+, H_2O^-, Zn, Ba, Ni, V, Cr and Rb. Of these elements, the only one to retain a highly significant positive correlation with Al_2O_3 in the succeeding correlation matrices is Cr. This suggests that Cr is almost entirely present substituting for Al in the clay minerals. H_2O^+, Zn and V all show significant positive correlations with Al_2O_3 in table 43, but these are not retained in table 45. This indicates that these three elements are closely related to the clay minerals. Of the three, V shows the highest correlation and it is to be expected, therefore, that V is occurring as a substitute for Al in the clay minerals. As Zn shows no significant positive correlations in table 45, it is felt that this element must be occurring in a variety of locations.

Two significant correlations that exist in all three correlation matrices are those between K_2O and Rb and Pb and SO_3. The former is easily explained as due to Rb substituting for K in illite. The explanation of the latter is not so obvious. HIRST and KAY (1971) reported a similar correlation between Pb and S, but did not attempt an explanation. As FLEISCHER (1955) reported that the Pb content of pyrite was negligible, it is thought that the correlation between Pb and SO_3 is not a causal relationship, i.e. Pb is not present mainly in sulphur bearing minerals. Rather, samples in which pyrite and gypsum are concentrated also have higher than average Pb contents, the Pb possibly being present associated with organic matter, or the clay minerals.

Of the three trace elements which have not been considered so far (Cu, Co and Ni), two of them, Co and Ni, show significant positive correlations with each other in tables 41 and 43. The other correlations shown by these two elements are not, unfortunately, indicative of the locations of the elements in the samples. It seems that they must be distributed between various minerals, as was suggested for Zn. A similar variety of locations must be proposed for Cu. This element is notable in that it shows no significant correlations in tables 43 and 45, indicating that it must be distributed between resistate, hydrolysate and precipitate minerals.

7 GEOLOGICAL INTERPRETATION

(A) Geochemical Interpretation

(i) Conclusions on the locations of the trace elements

In chapters 4 and 6, two methods have been used to assist in defining the locations of the trace elements determined. Studying the effect of a dilute acid attack on a sample's trace element geochemistry may appear to be a direct method of determining trace element locations, but it does not in fact produce unambiguous results. On the other hand, correlation analysis is obviously an indirect method of obtaining trace element locations, since it involves the assumption that inter-element relationships are, at least partially, causal. The conclusions obtained by these two methods have been mentioned in the chapters concerned. It is now intended to combine these results with additional information obtainable from the tables of major and trace element contents (tables 3 and 8) to produce conclusions on the locations of the trace elements in the samples studied.

In both of the samples studied for the effect of acid attack on the trace elements, approximately 40ppm Ba was removed in the first hour, after which no further removal occurred. This indicates that Ba is partially present in exchangeable positions. The analysis of the Bembridge Limestone sample (113) shows that the Ba content of the calcite is low, approximately 80ppm. This compares well with the average Ba content for limestones given by TUREKIAN and WEDEPOHL (1961). Since Ba shows positive correlations with K_2O, Rb and Zr, the majority of Ba would seem to be associated with the detrital micas and illite, substituting for K.

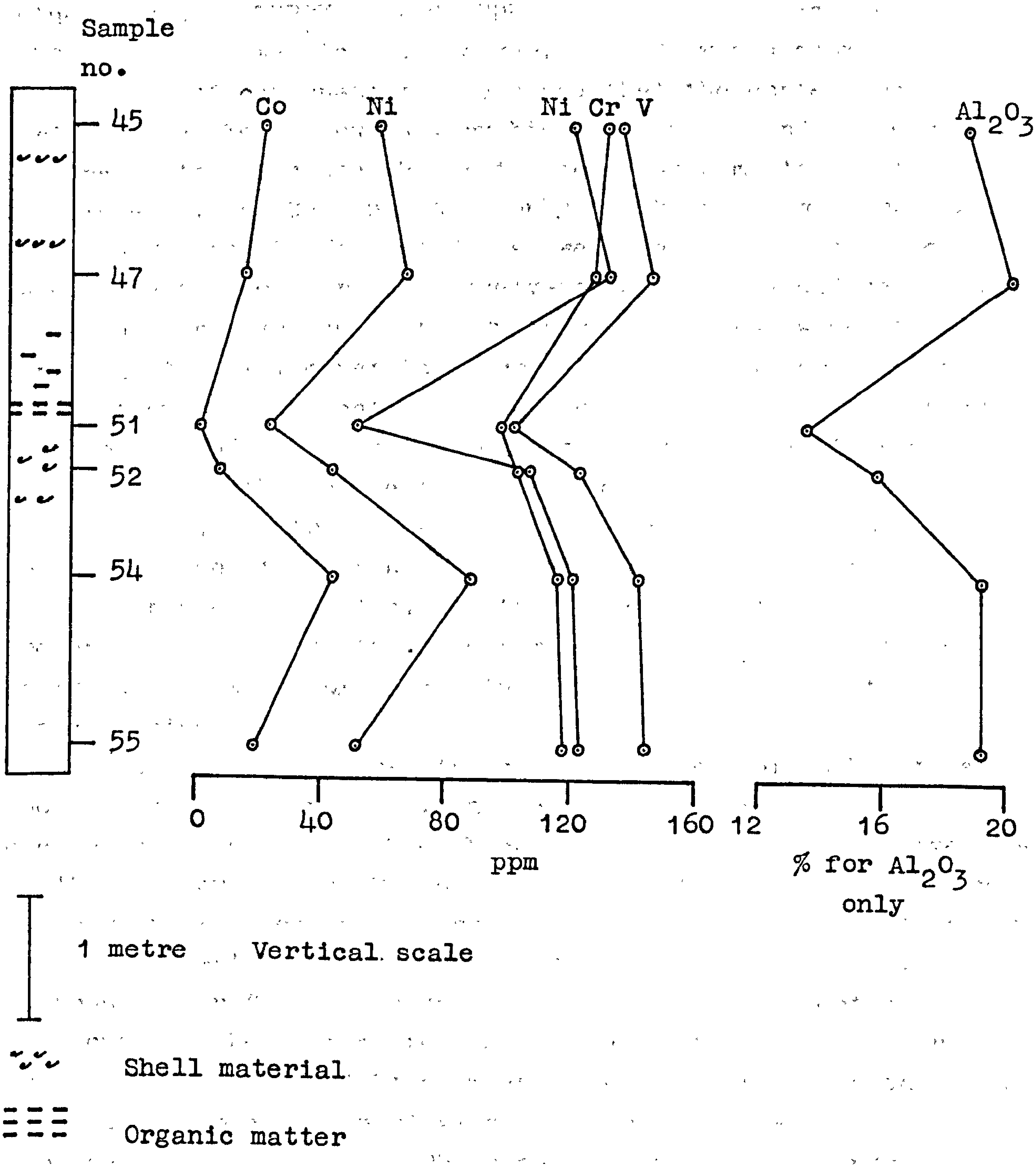
Co and Ni are two elements which show a consistently strong positive correlation, indicating that the two elements may be considered together. In the acid treatment experiment, no Co was removed from either sample, while 10ppm Ni was removed from the calcareous sample (31). WEDEPOHL (1971) stated that Ni was a common substituent in carbonate minerals and TUREKIAN and WEDEPOHL (1961) gave an average Ni content for limestones of 20ppm. Analysis of the Bembridge Limestone, however, gave a Ni content of only 4ppm. It seems, therefore, that while some Ni is present in the carbonate minerals, some must also be present in the exchangeable locations. These two locations account for only a small part of the total Ni content. Correlation analysis showed that Co and Ni were associated with the hydrolysate fraction, but failed to produce further information on this association.

Examination of the Co and Ni contents for samples 2, 28 and 51 gives more information as to the locations of these two elements. Samples 2 and 28 show significantly higher than average Co and Ni contents. The former sample is a palaeosol containing much organic matter, a high (4%) content of free iron oxides and an iron rich clay mineral (either nontronite or glauconite). Sample 28 is a marine clay which has suffered appreciable (periglacial ?) weathering and contains no organic matter or sulphides. It does, however, contain free iron oxides formed from decomposing pyrite. Conversely, sample 51 shows an almost zero Co content and a significantly lower than average Ni content. This sample shows field evidence for being an underclay to a carbonaceous bed and contains no sulphides or free iron oxides. The sample also shows evidence for the loss of clay minerals due to leaching by humic acids. The Co value in sample 51 shows that Co is not present in the clay structures, whereas 30 to 50% of the Ni is present as structural substitution (presumably for Mg or Fe). Co and the remaining Ni are, therefore, present associated with the sulphides and free iron oxides. By comparison of sample 51 with the two samples from above the carbonaceous bed (45 and 47) it can be seen that approximately twice as much Ni has been lost as Co. This is in agreement with the results of FLEISCHER (1955), who found that in sedimentary pyrite Ni content always exceeded Co content. From examination of figure 20 it can be seen that the Ni and Co leached from sample 51 were redeposited in the upper layers of an impervious clay, possibly onto pre-existing free iron oxides. The weathering suffered by sample 28 was obviously far less intense than the leaching of sample 51, resulting only in the loss of sulphide sulphur as soluble sulphate ions. The metalliferous elements present in the original pyrite were redeposited with the iron oxides released on oxidation of the pyrite. The above average contents of Co and Ni in sample 28 show that the original pyrite content must have been high.

In the acid dissolution study, no Cr was removed from either sample. The correlation matrices show a constantly high positive correlation with Al_2O_3, indicating that Cr exists substituting for Al in the clay minerals. Further evidence for this conclusion can be seen in figure 20, where the Cr removal pattern, associated with leaching under the carbonaceous bed, parallels the Al_2O_3 distribution.

Figure 20

Distribution of certain elements above and below a carbonaceous bed in the Hamstead Beds



The acid dissolution data for Cu shows a loss of 5 to 10ppm from both samples in the first hour of acid treatment, followed by a lesser, more gradual decrease. This suggests that Cu is present in exchange sites and possibly also associated with organic complexes. The Cu content of the Bembridge Limestone is similar to the average Cu content of all samples and higher than the values given by TUREKIAN and WEDEPOHL (1961) for limestones. WEDEPOHL (1971) mentioned, however, that Cu was a common constituent of carbonate minerals and that the content was very variable. Sample 2 shows a very high Cu content and it seems reasonable to associate this with the organic matter in the sample. In sample 51, the Cu content is only slightly below average and since RASHID and LEONARD (1973) showed that migrating humic acids were efficient removers of loosely-bound Cu, it would seem that an appreciable percentage of the Cu in most samples is substituting for Mg in the clay minerals. Correlation analysis provided no information on the location of Cu, due it is thought to the even distribution of this element between the main mineral types.

Mn is another element which shows few significant correlations, due to the many possible locations for this element. The acid dissolution data shows that a small amount of Mn is present in exchange sites, but that an appreciable amount is present in the carbonates. The remaining Mn would seem to be distributed between oxide coatings and structural substitution in the clay minerals.

15ppm Pb was removed in the first hour from both samples in the acid dissolution study, indicating that this is present in exchangeable locations. The Pb content of the Bembridge Limestone is 10ppm, showing that Pb is also present to a small degree in the carbonate minerals. Pb shows few significant correlations, the most consistent one being a positive correlation with SO_3. Sample 2 shows a significantly higher than average Pb content and this is thought to be related to the organic content and free iron oxides. Samples 28 and 51 show average Pb contents. In the former sample, for which an originally high pyrite content has been proposed, this shows that Pb is not occurring in the pyrite structure. The analyses of FLEISCHER (1955) similarly showed low Pb contents in pyrite. HIRST and KAYE (1971) in a study of Carboniferous sediments found a strong positive correlation between Pb and S, but did not propose an explanation. It seems most likely that an indirect relationship exists between Pb and SO_3 contents. The original SO_3 bearing mineral in these sediments is pyrite, which is formed in quiescent reducing conditions. Such conditions would favour the concentration of organic matter and smectites, both of which have been shown above to contain Pb. In addition, due to the similar ionic radii of Pb and K, there is likely to be some Pb occurring in the illite structure.

Rb showed no loss from either sample following treatment with acid, indicating that it does not occur as an exchangeable cation. A constantly significant positive correlation is shown between Rb and K_2O in the correlation matrices, indicating that Rb exists as a substitute for K in the illite structure.

Sr showed a marked removal after one hour's contact with acid in both samples, more so in the calcareous sample. This indicates that Sr is present to a large extent as exchangeable ions or substituting in the carbonate mineral (especially in aragonite). After acid treatment both samples contained 70 to 80 ppm Sr. The only significant positive correlation shown by Sr is with CaO, negative correlations existing with the resistate and hydrolysate elements. It seems likely that some of the Sr not accounted for by the carbonate phase and exchangeable ions is present substituting for K in illite, while there is likely to be Sr substituting in the small amounts of apatite present.

Approximately 10ppm V was removed from both samples by acid treatment, although it is unlikely that V is occurring in exchangeable positions, due to the relatively high charge density of its ions. Rather it seems more probable that this amount of V is associated with the organic content of the samples. V shows consistent positive correlations with the hydrolysate group of elements, indicating that its main mode of occurrence is structural substitution within the clay minerals. This conclusion is further supported by examination of figure 20, where the behaviour of V can be seen to parallel that of Cr and Al_2O_3. Since more V than Cr was removed from sample 51, it seems likely that V is also associated with the free iron oxides. Sample 2 shows a significantly higher than average V content and this is thought to be related to the high iron oxide and organic contents of the sample. Also, since the ionic radius of V is closer to that of Fe than to Al, more V would be expected substituting in Fe-rich clay minerals.

The acid dissolution data shows a loss of 15ppm Y from both samples, which again, due to the high charge density of the Y ion, is unlikely to be present in exchangeable locations. The amount of Y removed corresponds to 25 to 50% of the total Y content of the samples. Y shows consistent positive correlations with TiO_2 and Ba and lesser positive correlations with SiO_2 and Zr. These indicate that Y is largely associated with the resistate phase. BLONDEAU and POMEROL (1968) and WALDER (1964) both identified monazite in Tertiary sediments from the Hampshire Basin and this would be a likely location for Y. As monazite is insoluble in dilute HCl, Y must also be present in an additional location. WEDEPOHL (1974) lists analyses of organic matter, showing that Y is a common constituent. It is, therefore, possible that some of the acid soluble Y is associated with the organic content of the samples, but it is not thought that this would be sufficient to account for the total Y removed by HCl. It seems, therefore, that some Y must be present as exchangeable ions.

Following acid treatment, one sample showed a loss of 20ppm Zn, while the other showed no loss, indicating that Zn is present in some samples as an exchangeable ion. On page 32, it was suggested that Zn was present in exchangeable positions mainly in marine sediments. The correlation matrices show significant positive correlations between Zn and the hydrolysate elements. In figure 20, it can be seen that whereas sample 51 has 75% of the average Al_2O_3 content, it contains only 50% of the average Zn. This indicates that Zn occurs in association with the iron oxides or sulphides, as well as substituting in the clay structures. Since sample 2 shows an average Zn content, it is evident that Zn is associated with the sulphides rather than the iron oxides.

Zr showed no removal after acid treatment and shows significant positive correlations with SiO_2 and TiO_2. These indicate that Zr is associated with the resistate fraction and since there is a large difference in ionic radii between Zr and Si, it is likely that all of the Zr is occurring in detrital zircon.

In conclusion, the major and trace elements may be divided between three main mineral types - detrital minerals, carbonates and clays. The former consists dominantly of the following elements - Si, Ti and Zr, with lesser amounts of Y and Ba present in detrital phosphates and micas repectively. The carbonate fraction is composed of two minerals - calcite and aragonite and contains the following elements - Ca, Mg, Mn and Sr, with lesser amounts of Ba, Zn and Cu. The majority of the trace elements are associated with the clay fraction, but it must be mentioned that this contains not only the clay minerals, but also sulphides, iron oxides and organic matter. The elements associated with the clay minerals may be subdivided into two groups, those occupying structural positions - Al, K, Mg, Cr, Rb and V and those filling exchangeable sites - Ca, Mg, Ba, Sr, Cu and Pb. The only sulphide mineral identified was pyrite and this contains Co, Ni and Zn. Field evidence shows that the free iron oxides are, to a large extent, formed from the oxidation of pyrite and, therefore, contain a similar trace element suite. The organic fraction has been shown to contain significant quantities of Cu and Pb, together with minor amounts of V and Y.

(ii) Comparison of the mean element contents with the results of other workers

In table 46, the means and standard deviations for the major and trace elements determined in this work for forty-seven samples are listed, together with the mean values for average shales cited by TUREKIAN and WEDEPOHL (1961). From the major element values it can be seen that the Oligocene samples are relatively enriched in Ca and SO_3, but depleted in SiO_2, MgO and Na_2O. The trace element values show enrichment of Pb in the Oligocene samples and depletion of Ba, Cu, Mn, Ni and Sr.

Several anomalies are evident in this pattern of enrichment and depletion. While the high CaO content in the Oligocene samples can be partially explained by the presence of gypsum, it must be mainly due to a higher calcite content. Three of the elements commonly associated with calcite, however, show lower contents than in the average shale, suggesting that the calcite has lower than average contents of these substituent elements - Mg, Mn and Sr. In the case of Mg, this can be easily verified by comparison of the Bembridge Limestone MgO content of 1.2% with that of average limestones, 7.9% (TUREKIAN and WEDEPOHL, 1961). WEDEPOHL (1971) mentions that the MgO content of limestones tends to increase with age, due to reaction with Mg-bearing solutions, thus partially explaining the low MgO contents in the Oligocene carbonates.

As regards the lower than average Mn value, an explanation is not so obvious. While the Bembridge Limestone has a Mn content considerably lower than the average limestone, other calcareous samples (e.g. 7, 62 and 68) show high Mn values, which it seems reasonable to conclude are present in the calcite. The Mn content of calcite varies through the section, possibly due to loss of Mn from certain samples during recrystallisation of the calcite. Calculation of the average Mn content, excluding quartz and calcite rich samples, gives a value of 487ppm, with a standard deviation

Table 46

Comparison of mean major and trace element contents with those of TUREKIAN and WEDEPOHL (1961)

	Oligocene samples		
	Mean	Standard deviation	Average shale of TUREKIAN and WEDEPOHL (1961)
SiO_2	52.9	12.6	58.4
Al_2O_3	16.1	4.7	15.1
TiO_2	0.8	0.3	0.8
Fe_2O_3	6.1	2.6	6.7
MgO	1.6	0.4	2.5
CaO	7.0	9.3	3.1
Na_2O	0.3	0.1	1.3
K_2O	2.7	0.8	3.2
P_2O_5	0.1	0.1	0.1
SO_3	1.2	1.7	0.6
Cu	25	16	45
Zn	90	29	95
Pb	47	27	20
Ba	347	99	580
Ni	46	24	68
Co	16	13	19
Mn	517	469	850
V	122	41	130
Cr	110	24	90
Rb	147	47	140
Sr	200	164	300
Y	31	14	26
Zr	172	71	160

N.B. Major element contents in percentages, trace elements in ppm.

of 428ppm. Again this mean is well below the average shale, although the high standard deviation shows the large range in Mn contents found in these samples. It is felt that the generally low Mn content is due partially to low Mn contents in the calcite and also to a below average content of oxide coatings on the clay minerals.

The Sr content for the Bembridge Limestone is higher than that for the average limestone given by TUREKIAN and WEDEPOHL (1961), but within the range for calcite given by DEER et al (1962). The latter authors stated that high Sr contents were only found in limestones which had undergone little recrystallisation. Sr is usually concentrated more in aragonite than in calcite and this is shown by samples 121 and 122. Since many aquatic organisms deposit shells containing aragonite, many other samples must have originally contained aragonite.This has since been converted into calcite, with consequent loss of Sr. The Sr content of the samples, excluding those rich in quartz and carbonates, averages 154ppm, with a standard deviation of 40ppm. This is even further below the average shale value given in table 46 and that given by KRAUSKOPF (1967) of 450ppm. It is thought that the low Sr content is due to the virtual absence of feldspars in the Oligocene samples. Detrital feldspars are common accessory minerals in many shales and would contain Sr substituting for Ca and K.

The slightly below average SiO_2 content in the Oligocene samples may be explained as an antipathetic relationship with CaO, the increase in calcite being balanced by a decrease in quartz content.

Na_2O in the Oligocene samples shows an average content well below that quoted by TUREKIAN and WEDEPOHL (1961). WEDEPOHL(1970) gave an average Na_2O content for argillaceous sediments of 0.8%, with a standard deviation of 1.1% and a range of 0.1 to 9.2%. The Oligocene sediments are well below this average, but an obvious explanation is available. The main minerals containing Na in clastic sediments are feldspars, only minor amounts usually being present in micas and clay minerals. By reference to table 16, it can be seen that feldspars were only positively identified in two samples and then only in very low quantities. The virtual absence of feldspars from the Oligocene sediments may be taken to be the reason for the below average Na_2O contents. It is thought that the low Ba value is also related to the paucity of detrital feldspars, since Ba would be expected to substitute for K in these minerals.

The two other elements which show depletion in the Oligocene sediments, relative to average shales, are Cu and Ni. As regards Cu, while TUREKIAN and WEDEPOHL (1961) cite an average of 45ppm and KRAUSKOPF (1967) gives 57ppm as the average, WEDEPOHL (1970) gives a grand average of 39ppm, which he considers to be an overestimation, due to the large amount of results from a limited number of geological formations. He quotes a preferred average of 35ppm, with a range of other workers' averages of 20 to 65ppm. The Oligocene samples fall within this range, but towards its lower end. It is not thought, therefore, that too much significance can be attached to the below average Cu contents. KRAUSKOPF (1967) gives an average Ni content of 95ppm for shales, which is far in excess of the Oligocene average. It is thought that the low Ni average for the Oligocene samples may be due to lower than average pyrite contents. The Oligocene sediments are of dominantly freshwater origin and pyrite is, in general, less common in freshwater sediments than in brackish-marine sediments.

The only trace element which shows enrichment in the Oligocene samples, compared to the average shales, is Pb. The difference between the Pb contents of the Oligocene and the average shale appears to be one of the more significant, especially when the results of WEDEPOHL (1974) are considered. He gives an average Pb content for argillaceous sediments of 23ppm, with a range of 18 to 27ppm. Compared to these, the Oligocene mean of 47ppm is significantly higher. In the acid dissolution investigation, 15ppm Pb was removed from both samples in the first hour of treatment. This is almost equal to the quoted average Pb content for shales and must, to a large extent, account for the higher Pb values in the Oligocene samples. It is possible that the high content of adsorbed Pb in the Oligocene samples is due to their being of dominantly freshwater origin, since the Pb content of freshwater is approximately ten times that of sea water (WEDEPOHL, 1974). In the acid dissolution results, however, the adsorbed Pb content for the marine sample is similar to that for the non-marine sample. It is thought that the high adsorbed Pb contents may only partially explain the high total Pb contents in the Oligocene samples. WEDEPOHL (1974) mentions that soils formed over the Cornubian granites contain up to seven times the Pb concentration of the underlying granite. Since the Cornubian massif is likely to have been one of the major ultimate source areas of the Oligocene clays, it seems likely that high Pb contents were fixed in clay minerals during soil formation over the

Cornubian granites. These high Pb contents have then been retained by the clay minerals during several periods of erosion and deposition.

(iii) Use of geochemistry as an indicator of palaeoenvironment

Many workers have shown relationships between sediment geochemistry and the conditions prevailing during and after sedimentation. These relationships have then been used in the reverse procedure, i.e. determining palaeoenvironments from sample geochemistry. One of the most frequently determined environmental parameters is depositional salinity, as was mentioned on page 12. In chapter 4(D) an attempt was made to confirm the relationship between exchangeable cations and palaeosalinity demonstrated by SPEARS (1973). For the two marine beds sampled such a relationship was not observed. In the case of the Corbula Bed, it was shown that any pre-existing relationship between palaeosalinity and exchangeable cations had been destroyed during a period of pyrite oxidation and gypsum formation. In the Bembridge Oyster Bed, it was shown that in calcareous samples the value of exchangeable Mg/Ca tends to equilibrate with the Mg:Ca of the carbonate. The latter conclusion was also reached by KELLEY and LIEBIG (1934), who concluded that in outcrop samples the value of exchangeable Mg/Ca would be dependent on groundwater movement rather than on conditions at the time of sample deposition. It is, however, possible that in more strongly lithified (i.e. less permeable) samples the effect of groundwater movement may be negligible.

Many workers have shown relationships between whole rock geochemistry and palaeosalinity. MILLOT (1970) suggested that Rb and Ni should be concentrated in marine sediments relative to Cr, while SPEARS (1973) showed that K was enriched in Carboniferous marine sediments. This latter finding corroborates the laboratory findings of WEAVER (1958) who showed that 'expanded' micas fixed K from sea water. In the present work no such variations in whole rock geochemistry have been observed between marine and non-marine samples. It is thought that geochemical differences proposed between marine and non-marine sediments are largely reflections of mineralogical variations. In the case of K-fixation, the lack of K enrichment in the Oligocene samples may be taken to indicate that the smectites present are not of an 'expanded' mica variety (WEAVER, 1958) but are the result of non-micaceous transformation or neoformation.

It is possible to obtain certain information about the source area for the Oligocene sediments from the geochemical results. The low contents of Na and to a lesser extent Ba and Sr, have been taken to indicate that the samples contain little feldspar, which was proved by X.R.D.. This indicates that the hinterland was largely pre-existing sediments. The high average Pb content has been taken to indicate ultimate derivation for the clay minerals from soils formed over the Cornubian granites. Such soils would also have been expected to contain feldspars from the granites. That these feldspars are not present in the Oligocene sediments indicates that the Pb-enriched clay minerals and feldspars underwent several periods of erosion and deposition, during which the feldspars were altered, presumably to clay minerals, before deposition in the Oligocene.

From the strong positive correlation existing between Zr and SiO_2, it appears that Zr content may be used as an indicator of the rate of deposition, as was mentioned by PEARSON (1972). In certain samples, however, the relationship between Zr and SiO_2 does not exist. This is notably so in the Bembridge Oyster Bed sands, where sorting has separated the zircon from quartz and left a zircon depleted quartz sand.

Information about pH and Eh conditions during and after sedimentation may be obtained from minerals formed during that period. Minerals such as carbonates and phosphates are, to a large extent, dependent for their formation upon the pH of depositional and pore waters, while sulphides, organic matter and iron oxides are more dependent on the prevailing Eh. Unfortunately, in outcrop samples, evidence of the depositional Eh is frequently destroyed by oxidation during the period of exposure.

Commencing at the base of the sequence studied, the Bembridge Limestone is evidence of alkaline conditions (pH exceeding 7.8 according to KRUMBEIN and GARRELS, 1952). The lack of organic matter in the limestone suggests that oxidising conditions prevailed. During deposition of the limestone, there is evidence that a change in conditions occurred. In the Whitecliff Bay section, the Bembridge Limestone contains one and a half metres of marl, the bottom half of which contains organic matter. This indicates that sediment influx increased, concomitant with which would be expected an increase in the supply of freshwater. This would lead to a decrease in pH, which is shown by the lower calcite content of the sediment. Coupled to this was also a decrease in Eh, producing slightly reducing conditions. The reason for this increase in sediment supply is not apparent, but may be related to tectonic or climatic events. The marl becomes lighter coloured and more calcareous upwards, passing eventually into a second bed of limestone. This shows that the sediment supply dwindled and that pH and Eh both increased. In the Hamstead Cliff section there is also evidence for a decrease in Eh and pH during deposition of the Bembridge Limestone, although there is no evidence that these two periods were synchronous. The limestone in Hamstead Cliff contains a thin parting with rootlets (shown in plate 4(b)). The lack of abundant calcite and the presence of organic matter indicate a decrease in pH and Eh, so that reducing conditions existed within the sediment. The sample (2) collected from this parting analysed 15.9% Fe_2O_3, of which only 4.6% was present as free iron oxide. As pyrite does not occur in the sample, an iron rich clay mineral must be present. Two alternative minerals exist, nontronite and glauconite. Since the FeO content of the sample is low and the K_2O content is below average, it is evident that glauconite is not present (DEER et al, 1962). The iron bearing clay mineral must, therefore, be nontronite. No evidence exists that nontronite is present in other samples, so it is reasonable to conclude that the nontronite in sample 2 was neoformed. HARDER (1976) showed that nontronite could be neoformed at low temperatures, if reducing conditions prevailed so that ferrous iron was present in solution. In oxidising conditions he found that neoformation of nontronite was only possible at raised temperatures. The conditions prevailing during the deposition of sample 2 have been shown to have been those which would permit the neoformation of nontronite. Obviously the rate of detritus supply must have been very slow, otherwise the neoformed nontronite would have constituted only a small proportion of the total clay minerals.

The sediments succeeding the Bembridge Limestone are marls which occasionally contain organic matter, indicating that a decrease in pH to between 7.0 and 7.8 had occurred and that conditions varied between oxidising and reducing. Although such conditions would have been suitable for the formation of phosphate minerals, no evidence exists to show that this occurred. Instead it is thought that the low P_2O_5 contents represent the contribution of detrital apatite. While palaeontological evidence shows that brackish-marine conditions were established for a short while during deposition of these marls, there is no geochemical variation related to the salinity change. In the beds immediately succeeding the Bembridge Oyster Bed transgression and regression, pyrite occurs regularly through a sediment thickness of one metre. This shows that more strongly reducing conditions prevailed during or post-sedimentation. The remainder of the Bembridge Marls are calcareous, although calcite content rarely exceeds 50%. Occasional samples contain organic matter and one sample was found to contain a small amount of pyrite. This indicates that conditions were mainly oxidising. In two parts of the Bembridge Marls concretions were found, indicating that post-depositional solution and reprecipitation of minerals had occurred. In the Whitecliff Bay section the concretions are ironstones, showing that mobilisation of iron, possibly associated with organic matter (BERNER, 1971) had occurred. The iron was deposited on encountering oxidising conditions as ferric oxides/hydroxides. In the Hamstead Cliff sequence the concretions are calcareous, showing dissolution of calcite in acid waters and reprecipitation in an alkaline environment.

The Lower Hamstead Beds are, in general, less calcareous than the Bembridge Marls and, with a few exceptions, do not contain organic matter. This indicates that deposition occurred in dominantly oxidising conditions, with pH varying between slight acidity and slight alkalinity. Towards the base of the Hamstead Beds is a pyritiferous, black clay and thin plant beds also occur, indicating conditions of negative Eh. Due to surface weathering, much of the original pyrite has been oxidised to gypsum and iron oxides, but the presence of these two minerals in association is good evidence for original pyrite. The association of pyrite and leaf beds suggests that organic matter may have been the source of sulphur for the pyrite. Towards the top of the Lower Hamstead Beds a thin red bed occurs, containing hematite. While the majority of the Oligocene sediments show evidence for having been deposited in conditions suitable for the formation of hematite (i.e. slightly alkaline and oxidising, KRUMBEIN and GARRELS, 1952), hematite was only identified in the sample from this thin bed, goethite occurring in all other samples. The presence of mottled red-green marls in the Bembridge Marls and Lower Hamstead Beds suggests the presence of hematite, but this could not be proven by X.R.D.. BERNER (1971) produced theoretical evidence to show that goethite had no geochemical stability field and would be dehydrated to hematite in ancient sediments. He did, however, also quote previous workers who had found that goethite was the stable iron oxide at most diagenetic temperatures. This discrepancy is explained as being due to the very slow rates of reaction at low temperatures. Goethite is the common iron oxide formed during weathering and it is reasonable to conclude that detrital goethite was supplied during the Oligocene sedimentation. This goethite has then been retained during diagenesis without any alteration to hematite. The hematite found in sample 67 is not likely to have been formed from goethite, especially as it occurs in a thin bed with goethite present in the sediments above and below. Rather it is proposed that the hematite in sample 67 was formed from the alteration of an iron bearing mineral whose only occurrence in the Oligocene was in the thin bed. In the field, the bed occurs within a forty centimetre thick grey clay and shows well defined upper and lower contacts. This field evidence, together with the high smectite content (approximately 50%) and the morphology of the smectite grains (see page 59)is thought to indicate that the bed is, at least partially, an altered volcanic ash. If this is so, iron oxides and silicates in the ash fall would have been available for alteration to hematite, under the prevailing oxidising conditions. The presence of hematite in sample 67 indicates that the origin of the thin bed was different from the rest of the Oligocene sediments, but the evidence for derivation from volcanic ash is, unfortunately, not conclusive.

The sediments forming the top of the Lower Hamstead Beds and the Upper Hamstead Beds (the Cerithium and Corbula Beds) show evidence for prevailing reducing conditions. These beds represent an upwards increase in salinity from hyposaline to normal marine conditions (MURRAY and WRIGHT, 1974). The clays are all carbonaceous and pyrite occurs regularly, indicating that a negative Eh existed in the sediment. That reducing conditions may have existed at the sediment-water interface is suggested by the sparse, stunted fauna, although this may have been due to the muddy nature of the substrate. The Cerithium Beds contain a carbonaceous clay, the beds beneath which show evidence for leaching by organic acids (see page 77).

It has been shown that the physicochemical conditions prevailing during sedimentation in the Oligocene were very variable. The Bembridge Limestone is evidence of a high depositional pH, but the succeeding sediments show that the pH decreased, as is to be expected in freshwater conditions (WEDEPOHL, 1971). Oxidising conditions are usually shown by both fresh and se water, although bottom and interstitial waters frequently show a lower Eh. The freshwater Bembridge Marls and Lower Hamstead Beds show evidence that oxidising conditions were prevalent, although the presence of organic matter in some beds indicates that reducing conditions existed locally, either in the water or in the sediment, in the latter case possibly associated with waterlogging of the sediment. Noteworthy is the association of pyrite with the marine sediments. The main pyritiferous beds are the marine *Corbula* Beds and the underlying hyposaline *Cerithium* Beds, together with the beds above the Bembridge Oyster Bed. Thus pyrite is not confined to the marine beds, but does occur in association with them. Of the two marine incursions in the Oligocene, one was characterised by and the other associated with, reducing conditions. Since sea water is concentrated in $SO_4^=$ relative to river water by a factor exceeding 100 (WEDEPOHL, 1971), it is to be expected that reducing marine conditions will produce pyrite.

(B) Mineralogical Interpretation

(i) Non-clay mineralogy

The most common non-clay mineral is quartz, a representative of the resistate fraction. It was suggested on page 47 that secondary quartz could be present in the majority of samples, due to the low $(1\bar{1}00)/(1\bar{1}01)$ diffraction peak ratios obtained (ESLINGER et al, 1973). If such secondary quartz does exist it is not a major component of the sediments, as there is no evidence for quartz cementation in the samples. Quartz content is, of course, a useful sedimentary parameter, indicating depositional energy. Inspection of the quartz contents in table 23 shows that the marine *Corbula* Beds have on average a slightly higher quartz content than the underlying clays, indicating that the marine transgression was associated with an increase in depositional energy. Some of the non-marine samples show markedly higher quartz contents than the marine samples, showing that fast flowing water prevailed at times. It is thought that these samples represent periods when the overbank lakes were incorporated into the river system during periods of flooding or channel migration (DALEY, 1973). One quartz rich sample which does not fit into this general state of affairs is 51, which has been shown (page 77) to be comparable to a Coal Measures ganister. As the distribution of Zr through the sequence closely mirrors the quartz distribution, it is reasonable to conclude that zircon exists in the samples and may be used as an alternative indicator of depositional energy.

Zircon has been identified in the Oligocene sediments of the Hampshire Basin by BLONDEAU and POMEROL (1968).

Two TiO_2 minerals occur in the Oligocene sediments and it would seem reasonable to conclude that they are of detrital origin. WALDER (1964), however, demonstrated that overgrowths occurred on both rutile and anatase grains in the Eocene of the Isle of Wight, indicating a partial authigenic origin.

The carbonate fraction of the Oligocene sediments is represented by two minerals - calcite and aragonite. The calcite is a low-Mg variety, with an average $MgCO_3$ content of 3 mole% and a range of 0.5 to 5.1 mole%. In most samples the carbonate can be seen to be present as pelecypod and gastropod shell debris. BLATT et al (1972) listed analyses showing that such shells are usually composed of a mixture of low-Mg calcite and aragonite. Their data, which was from a limited number of analyses, gave an average $MgCO_3$ content of 0.5 mole% and a range of 0.0 to 2.8 mole%. Due to the small number of their analyses it is not thought that much significance can be attached to the higher $MgCO_3$ contents found in the Oligocene samples. It is, however, significant that aragonite was only identified in samples from the Bembridge Oyster Bed. Evidently aragonite was originally present in many more samples, but has been altered to calcite. Such alteration commonly occurs, due to the instability of aragonite, with respect to calcite, under surface conditions (DEER et al, 1962). The problem, therefore, is not the absence of aragonite through most of the section, but its retention in one small part. This is thought to be due to two factors. Firstly, the presence of aragonite in the robust shells of <u>Ostrea</u> would be more resistant to dissolution and alteration than the thinner shells. Secondly, the presence of large amounts of substituting Sr would not be acceptable into the calcite structure. A possible alternative for the retention of aragonite is that the Bembridge Oyster Bed remained in contact with formational waters rich in Mg. MILLIMAN (1974) showed that the alteration of aragonite to calcite was halted by the presence of Mg rich solutions (e.g. sea water). It seems, however, unlikely that the waters contained by the Bembridge Oyster Bed should have varied so much from the waters contained in the overlying and underlying beds.

The only sulphide mineral identified in these samples was pyrite. Reflected light microscopy showed the pyrite to have surface tarnishing and low reflectivities, due to surface weathering. It has been mentioned that the occurrence of pyrite is related to the prevalence of marine conditions. In both pyritiferous parts of the sequence oxidation of much of the pyrite has occurred, with the associated formation of gypsum, or more rarely jarosite. The original pyrite is usually replaced by goethite, the gypsum occurring on joint planes and fractures in the underlying beds. In the Corbula Beds, the gypsum has a different mode of occurrence, gypsum rosettes occurring at one level in the beds. CODY (1976) studied experimentally the growth of gypsum crystals in bentonite mud and found that rosettes were deposited at the interface of the calcium and sulphate bearing solutions. He found that crystal size was inversely related to the temperature of formation. The crystals found in the Corbula Beds range up to ten centimetres in length and are frequently twinned. This corresponds to crystallisation at low (c. 20°C) temperatures. CODY (1976) also found that the gypsum crystals formed were corroded and that the extent and type of corrosion could be related to temperature, NaCl content of the solutions and the organic content of the clay. The Oligocene crystals show corrosion, although it was not possible to determine whether this was related to genetic history or solution on exposure of the samples. In conclusion, the gypsum in the Corbula Beds is thought to have formed during a period of deep weathering, when the water table stood at the present gypsiferous level. Associated with the gypsum crystals are calcareous concretions whose origin may also be related to water table level. The gypsum found along joint and fracture planes occurs as much smaller crystals and it is thought that these were formed following Recent exposure and oxidation of pyrite.

Two iron oxide minerals occur in these sediments, goethite and hematite. While some of the goethite has been shown above to have formed during the oxidation of pyrite, most of the samples containing goethite did not contain pyrite. In these samples the goethite is thought to be mainly of detrital origin, possibly as oxide coatings on the clay minerals. There is also the possibility of crystallisation of goethite from iron bearing chelates and it seems likely that the goethite in the samples could have either origin. Hematite was only identified in sample 67 and it was proposed on page 88 that the hematite in this sample was a product of the alteration of volcanic material. The field and mineralogical evidence for this sample suggest that its origin differs from other samples, but, even accepting a possible volcanic origin, no reason can be suggested for the formation of hematite rather than goethite, as the stability fields for the two minerals are essentially similar under surface conditions (BERNER, 1971).

(ii) Clay mineralogy

The clay mineralogy of any sedimentary sequence is a product of the interaction of three factors - inheritance, neoformation and transformation. The latter two processes may occur before, during or after deposition of the sediment. Determination of the origin of a clay mineral in any sample is not always possible, but in considering a sequence of sediments, more evidence is usually available, facilitating interpretation of the general origin of the clay minerals.

On page 56 it was mentioned that the recalculated illite peak shapes were similar to illite peaks found by other workers from Sheffield for Carboniferous shales. The observed broadening of the illite peak is due to substitutions in the tetrahedral and octahedral layers and corresponding charge deficiency and hydration of the interlayers. This similarity in peak shape suggests either that the illite in the Oligocene samples is detrital Palaeozoic illite, or that the Oligocene samples have undergone similar formational histories to the Carboniferous samples. Evidence for the former comes from the work of COWPERTHWAITE et al (1972) who obtained $^{40}Ar/^{39}Ar$ age data for the London Clay (Eocene) of 350 m.y.. This indicates that the London Clay is dominantly composed of reworked Palaeozoic phyllosilicates. This does not, however, necessarily indicate that the hinterland was composed of Palaeozoic sediments. It seems more likely that the illite has been through several periods of erosion and deposition without appreciable change. GILKES (1978) considered that the Oligocene depositional basin was, at least partially, surrounded by Lower Eocene sediments, which acted as a source for clay minerals. He also considered that some illite was neoformed, although the electron microscopic evidence (page 60) does not support this. The only suggestion for a non-detrital origin for illite is given by those samples which contain a low quantity of smectite (numbers 10, 54, 116, 121 and 129). It seems possible that in these samples illite has either been neoformed or transformed from pre-existing smectite.

Smectites are the clay minerals for which a neoformed origin has most frequently been postulated, due to their instability in leaching conditions. HALLAM and SELLWOOD (1970) concluded that smectite rich beds in English Mesozoic and Tertiary sediments were almost certainly of volcanic origin, even if no direct evidence of vulcanicity was present. This conclusion is, to some extent, opposed by the results of PERRIN (1971), who showed that smectites were an almost ubiquitous constituent in British Mesozoic and Tertiary sediments, usually being of secondary importance to illite in the <5μ fraction. Although he gave no evidence for the smectite being of a detrital or neoformed origin, its widespread occurrence suggests that the former is more important. Since the work of PERRIN (1971) shows that the sediments surrounding the Oligocene depositional basin contained smectite, there is no reason to postulate a neoformed origin for the smectite in most of the Oligocene samples. That the smectite is not a product of the transformation of illite into an expanded mineral is shown by the presence of smectite in the marine *Corbula* Bed samples. WEAVER (1958) showed that K-depleted illites, which showed all of the properties of true smectites, reverted to illites on exposure to sea water for short periods of time. The smectite in the Oligocene samples is, therefore, of an ultimate neoformed origin, although, in conjunction with the illite, it has probably been through several periods of erosion and deposition since its formation.

In contrast to the general detrital origin for the smectite, there are two samples (2 and 67) which show evidence for an, at least partial, neoformed origin. While geochemical evidence suggests that the former contains neoformed nontronite, field and mineralogical evidence suggests that the latter contains smectite formed from the alteration of volcanic material.

Two samples (numbers 55 and 64) contain an interlayered illite-smectite mineral and no discrete smectite. The origin of the interlayered mineral is questionable. PERRIN (1971) found illite-smectite in the Wealden sediments of Southern England and the author, in a clay mineralogical study of sediments from Lulworth Cove, found illite-smectite in the Purbeckian. A detrital origin for the illite-smectite in the Oligocene is, therefore, possible, but highly improbable, due to the very limited distribution of the mineral in the section studied. BURST (1959) found that illite-smectite was produced from original smectite by burial to depths exceeding one thousand metres, but again such an origin is not possible for the Oligocene sediments as discrete smectite occurs in underlying beds. The absence of discrete smectite in the two samples suggests, however, that the illite-smectite is the result of illitisation of original smectite. Similarly, it was mentioned above that five samples contained very high illite contents, with only traces of discrete smectite. Since these five samples contain average kaolinite contents it seems reasonable to conclude that the smectite contents have been decreased by transformation into illite. While the evidence indicates that transformation of smectite into illite-smectite and illite has occurred, there is no obvious method for such transformations. Most of the samples concerned are of freshwater origin, indicating the availability of little potassium in solution and the sporadic distribution of the samples through the sequence shows that the transformations must have occurred close to the time of deposition. A possible explanation is that these samples represent periods of more intensive weathering in the hinterland, such that smectites in the exposed Mesozoic and Tertiary sediments were stripped of cations. These cation depleted minerals took on potassium during transportation and deposition to form interlayered illite-smectite or illite.

Kaolinite is a ubiquitous constituent of the Oligocene sediments, although in a few samples the kaolinite content is very low. The co-existence of kaolinite and smectite in most samples suggests a dominantly detrital origin for both minerals, as their stability fields are so disparate. PERRIN (1971) reported that kaolinite was a common constituent of most Mesozoic and Tertiary sediments, indicating a ready source for the mineral in the Oligocene.

Chlorite was identified in only eleven samples and then in quantities of less than five percent. It is possible that chlorite exists in all samples, but in quantities so small as to make identification imprecise. MILLOT (1970) reported that in calcareous lake environments in the French Triassic, neoformed chlorite occurred. While calcareous lakes existed during deposition of the Oligocene samples, there is no evidence for the neoformation of chlorite, this mineral being absent from samples typical of such environments. The chlorite occurs in coarser-grained samples and in more average clays, indicating that it is of a detrital origin. PERRIN (1971) reported that chlorite was a major constituent of Triassic and older sediments, but previous work by the author has shown chlorite to be present in Cretaceous sediments.

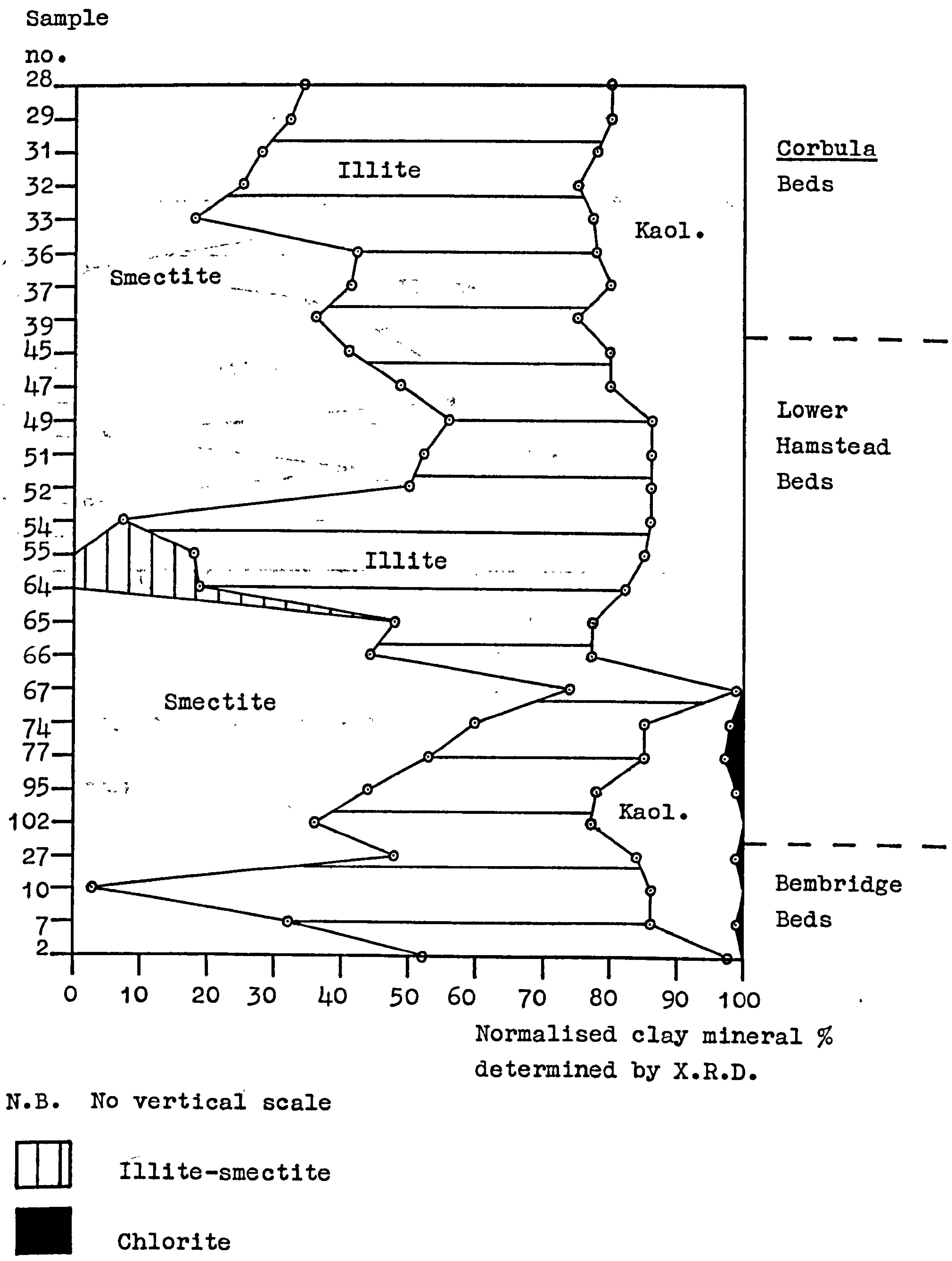
In general it has been shown that the major factor determining the clay mineralogy of the Oligocene was inheritance. Evidence exists for the neoformation of smectite in two samples while in seven samples there is evidence for the transformation of smectite into interlayered illite-smectite and illite.

In figure 21 the vertical distribution of clay minerals through the Hamstead and Bouldnor cliff sections is shown. One of the most notable features is that, with the exception of two samples, the kaolinite content varies only between 14 and 25%. This indicates that in the period of time represented by these samples, potential discriminatory factors (such as flocculation and sorting) were of minor importance in determining the clay mineralogy. An antipathetic relationship exists between illite and smectite contents and the ratio of these two clay minerals' contents shows marked variations. Evidence has been shown for the transformation of smectite into illite and this could account for these variations. The two samples which do not comply with this general statement are the two which have been shown to contain neoformed smectite. The low kaolinite contents in both these samples indicates that detrital supply was unimportant in determining their clay mineralogy.

Figure 22 shows the distribution of clay minerals through the Whitecliff Bay section. The main points of note are that the kaolinite contents are generally lower than those in figure 21 and that kaolinite content shows an upwards increase through the section. It should be mentioned that the bottom nine samples in figure 22 correspond to a stratigraphic thickness represented by only the bottom two samples in figure 21. The disparity between the two distributions is, therefore, partially a factor of different sampling densities. GILKES (1978) showed that the Lower Eocene sediments of the Hampshire Basin could be divided into a western illite/kaolinite province and an eastern smectite/illite/kaolinite province, although he found that this division did not persist into the Oligocene. The results presented here for samples from the Upper Bembridge Beds (7, 10 and 27 from Hamstead Cliff; 126, 129, 134 and 136 from Whitecliff Bay) support the latter conclusion. There is, however, an appreciable difference in the kaolinite contents of samples from the Bembridge Limestone, the Bembridge Oyster Bed and the interbedded marls in Whitecliff Bay and those from higher in the Bembridge Marls sequence. It is thought that this is due to a variation in the source area. GILKES (1978) considered that the Oligocene sediments were mainly derived from exposed Eocene sediments. Bearing in mind his mineralogical provinces mentioned above, derivation from an easterly direction would result in a clay mineralogy poorer in

Figure 21

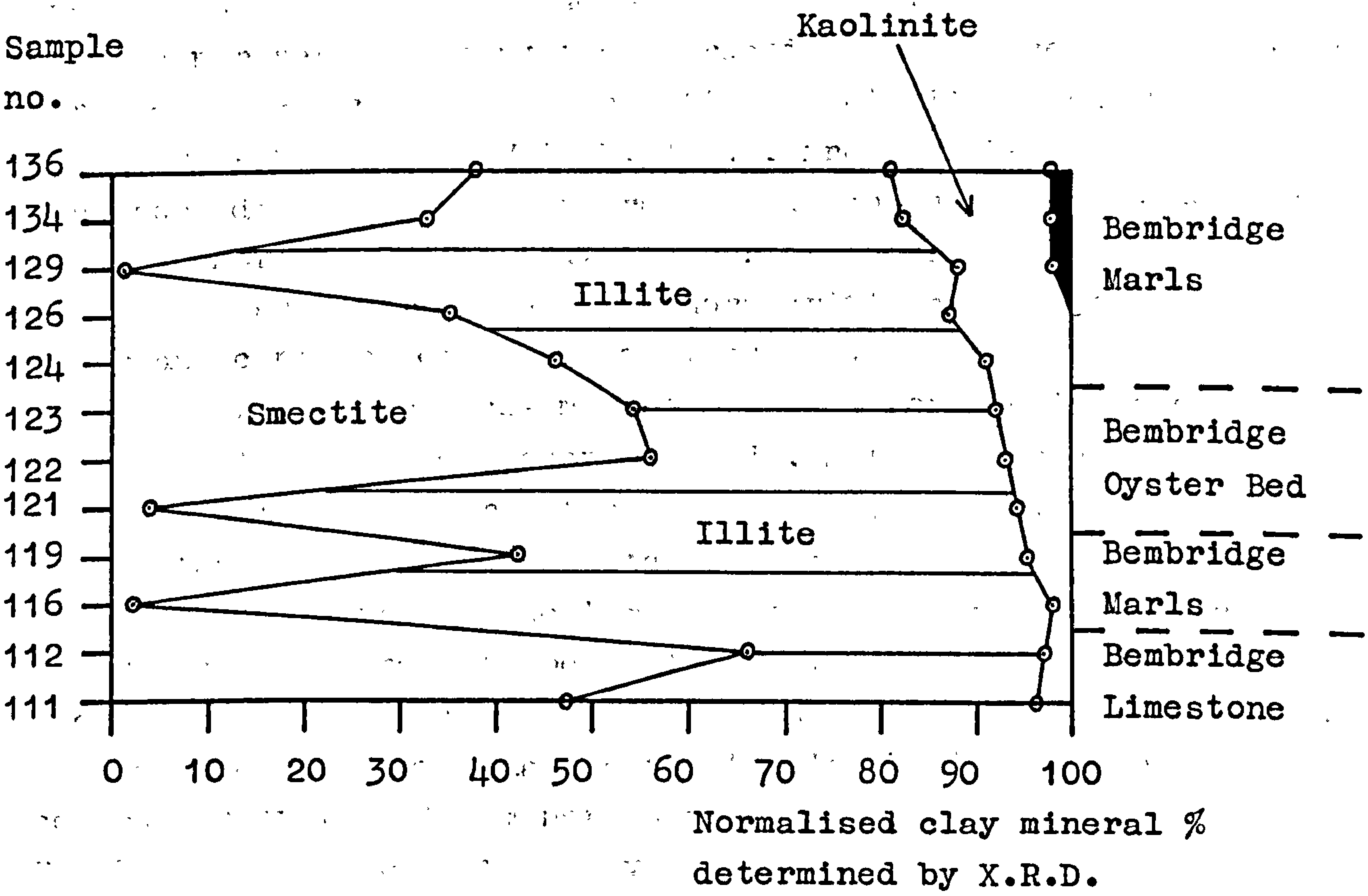
Distribution of clay minerals in the Hamstead and Bouldnor cliff sections



N.B. No vertical scale

Figure 22

Distribution of clay minerals in the Whitecliff Bay section



N.B. No vertical scale

■ Chlorite

kaolinite than derivation from a more westerly source. DALEY (1968) showed that in the Upper Bembridge Beds derivation was from a north-westerly direction, although there is no evidence that the source area for the preceding sediments had been the same. It seems more likely that during deposition of the Lower Bembridge Beds (up to and including the Bembridge Oyster Bed) a north-easterly sediment source had been important. This could either have been rivers draining that direction, or, since the sediments were deposited in brackish conditions (salinities ranging between 10 and 25‰ MURRAY and WRIGHT, 1974), from north-easterly longshore drift. With the regression which succeeded deposition of the Bembridge Oyster Bed, the north-easterly source became less important, suggesting that longshore drift may have been the more important contributor to sediment supply.

Alternative reasons may be proposed for the low contents of kaolinite in the Lower Bembridge Beds, although none of them explain fully the distribution shown in figure 22. MILLOT (1970) showed that kaolinite was unstable in alkaline conditions, but while this may explain the low contents in samples from the Bembridge Limestone, it does not explain the low contents in the succeeding marls, which frequently contain low calcite contents. A second possible explanation for the low kaolinite contents is separation of the clay minerals prior to deposition. BROOKS and FERRELL (1970) showed that rivers entering brackish lakes in the Mississippi delta area deposited their kaolinite preferentially to smectite and illite. They considered that this was due to flocculation, although an alternative explanation, since kaolinite usually occurs in larger grains than the other two clay minerals (GRIM, 1953), is a decrease in energy of the depositional environment. There is, however, no evidence that the beds succeeding the Bembridge Limestone were deposited in exceptionally quiescent conditions, indeed the Bembridge Oyster Bed contains a twenty-five centimetre thick sand bed (sample 122). The micropalaeontological evidence (LIENGJARERN, 1973) suggests that the beds were deposited in freshwater - brackish conditions, indicating that flocculation would not have been an important factor. The only suitable explanation for the low kaolinite contents in the Lower Bembridge Beds in Whitecliff Bay is that derivation from a north-easterly, kaolinite poor sediment source was important.

Further to the minimal effect of flocculation on determining clay mineralogy, in figure 21 it can be seen that no decrease in kaolinite content occurs between the freshwater Lower Hamstead Beds and the marine Corbula Beds. Considering the grain size differences between kaolinite and the other two major clay minerals, mentioned above, this may also be taken to indicate that the depositional energy of the marine sediments was not lower than that of the non-marine sediments, as was suggested on page 89 from the quartz contents of the respective samples.

(C) Conclusions

DALEY (1972) showed that the climatic conditions prevailing during deposition of the Bembridge Marls were comparable with present day Eastern Margin Warm Temperate climates. An area experiencing such a climate at the present is south-eastern U.S.A., so it is to be expected that studies on Recent sediments from that area should have general conclusions comparable to those presented here. GRIFFIN (1962), in a clay mineral study of surface sediments from a large area of the Gulf of Mexico, showed that inheritance was the major factor in determining clay mineralogy. He found that changes in clay mineralogy during transportation from a freshwater to a marine environment were of minimal extent. He did, however, show that clay mineralogy was related to the degree of weathering in the hinterland, that eastwards kaolinite became more important due to more intensive weathering. BROOKS and FERRELL (1970) found a smectite/illite/kaolinite assemblage in part of the Mississippi delta, but reported that salinity (or possibly depositional energy) partially determined the clay mineral distributions. They did, however, agree with GRIFFIN (1962) that the clay minerals were mainly of a detrital origin, with little evidence being shown for transformations during deposition. Further westwards, MORTON (1972) found that the clay mineralogy of Holocene and Pleistocene sediments from the Guadeloupe delta was essentially identical to that of sediments being eroded in the hinterland. No variation in the clay mineral assemblage was observed between the different depositional environments (freshwater to brackish conditions). In general in the Gulf of Mexico area, sediments derived from a sedimentary hinterland have a similar clay mineralogy to the original sediments.

In the light of the above findings, it can be seen that the conclusion of GILKES (1978), that the clay minerals in the Oligocene sediments are of detrital origin, is valid. There is, however, no indication that the source rocks during the Oligocene were of Lower Eocene age. Consideration of the results of PERRIN (1971) shows that most Mesozoic rocks in Southern England could have supplied the clay mineralogy found in the Oligocene sediments. Evidence has been shown in this thesis that transformation of smectite into illite occurred sporadically through the Oligocene. GILKES (1978) considered that the high illite contents he found in certain samples were due to neoformation in calcareous lakes, but as the illite rich samples found here contain an average kaolinite content, this conclusion is not thought to be justified. Rather, transformation of smectite into illite is preferred, the presence of illite-smectite in two samples supporting this conclusion.

Suggestions for the neoformation of clay minerals were only found in two samples and in both the clay mineral thought to be neoformed is a smectite. One sample shows evidence for the neoformation of nontronite during a period of very low sediment deposition, while the second shows evidence for the formation of smectite from volcanic material. In both instances further investigation would be needed to verify these conclusions.

The clay mineralogy remains fairly constant through the section studied, with the main exception being the Lower Bembridge Beds in Whitecliff Bay, where the samples show significantly lower than average kaolinite contents. These are thought to represent derivation from a more easterly source than usual. No difference in clay mineralogy was found between the non-marine Lower Hamstead Beds and the marine Corbula Beds, indicating that the clay mineralogy is independent of depositional salinity.

With regards to geochemistry, the Oligocene sediments have higher Pb contents than average shales. It is proposed that this is due to a higher than usual Pb content in the clay structures, due to their ultimate derivation from alteration of the Cornubian granites. No relationship was found between geochemistry and depositional salinity, due largely to the effects of Pleistocene and Recent weathering, especially of the Corbula Beds. The distribution of pyrite through the section can, however, be broadly correlated with palaeosalinity, indicating that the main source of sulphur was from solution, rather than from organic matter. From the information obtained on the location of the trace elements, it is possible to conclude that certain trace elements were added to the sediments during or after deposition. Co, Ni and Zn have been added to the sediments in association with the sulphide phase, while Ba, Cu, Mn, Pb and Sr have all been added to the clay minerals, in the form of exchangeable cations. Cu and Pb are also associated with the organic phase, together possibly with Y, while Mn and Sr are mainly associated with the carbonate minerals.

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