Geochemistry and mineralogy of British carboniferous seatearths from Northern coalfields

M. J. Reeves

How to cite:

Reeves, M. J. (1971) Geochemistry and mineralogy of British carboniferous seatearths from Northern coalfields. Doctoral thesis, Durham University.

GEOCHEMISTRY AND MINERALOGY OF BRITISH CARBONIFEROUS SEATEARTHS FROM NORTHERN COALFIELDS.

by : M. J. Reeves B.Sc.
Department of Geology
Science Laboratories
South Road
Durham

Submitted for the degree of Ph.D. at the University
of Durham, June 1971

LIST OF CONTENTS

PAGE

CHAPTER ONE INTRODUCTION

CHAPTER TWO MINERALOGY

PAGE

CHAPTER THREE CHEMICAL AND MINERALOGICAL VARIATION WITHIN SEATEARTHS

PAGE

Figure 3.1 Mineral frequency distribution histograms for 42 Upper Carboniferous seatearths.

3.2 Major element frequency distribution histograms for 42 Upper Carboniferous seatearths.

3.3 Trace element frequency distribution histograms for 42 Upper Carboniferous seatearths.

<u>CHAPTER FOUR</u> <u>VARIATIONS WITHIN ROOF ROCKS</u>

CHAPTER FIVE THE SIGNIFICANCE OF CHEMICAL AND MINERALOGICAL DIFFERENCES BETWEEN SEATEARTHS AND ROOF ROCKS

CHAPTER SIX SUMMARY AND CONCLUSIONS

APPENDIX I ANALYTICAL PROCEDURES

APPENDIX II STATISTICAL METHODS

PAGE

APPENDIX III COMPUTER PROGRAMMING

ABSTRACT

The palaeogeographic, tectonic, and biologic conditions of seatearth deposition are briefly reviewed.

Detailed mineralogical examination reveals that seatearths are essentially quartz-illite-kaolinite assemblages with minor chlorite, siderite, and organic matter. The illites show wide variation from well ordered sedimentary muscovites to disordered and/or interlayered 'illitic' minerals. The kaolinites are found to be relatively well crystalline and the chlorites are Mg rich. Siderite is commonly associated with minor kaolinite and pyrite in nodules. The organic matter consists of terrestial plant debris.

The distribution functions of elements and minerals in seatearths are discussed. A normal model is reasonably satisfactory for SiO_2, Al_2O_3, CaO, P_2O_5, Ni, Y, and Zr; a lognormal model for TiO_2, Fe_2O_3, MgO, Na_2O, K_2O, S, C, H_2O^+, H_2O^-, CO_2, Ba, Cr, Cu, La, Mn, Nb, Rb, Sc, Sr, and Zn.

Stepwise multiple linear regression is used to assess the relationships between chemistry and mineralogy. It is found that the major components are controlled by the mineralogy to a large extent and that the trace elements and similarly controlled but to a lesser degree.

The present data, when compared with previous data, is shown to be comparable.

R-mode factor analysis is used to derive factors which control the distributions of trace elements and minerals in seatearths. Eight factors are extracted and they relate to the depositional environment and stratigraphic controls.

Roof rocks are examined and the pattern they produce after R-mode factor analysis is shown to be similar to that for a set of clastic cyclothemic sediments.

The significance of differences between seatearths and roof rocks are discussed. It is concluded that seatearths are leached relative to their corresponding roof measures.

The data is summarised and a detailed theory for the origin and genesis of seatearths, based on that of MOORE (1968), is developed.

ACKNOWLEDGEMENTS

Prof. G. M. Brown and Prof. M. H. P. Bott acknowledged for the use of the facilities afforded by the Geology Department of the University of Durham.

All the staff and research students of the Geology Department are thanked for advice and discussion during the 28 months in which the work was completed.

Dr. D. M. Hirst and Mr. R. K. Taylor are gratefully acknowledged for the instigation and supervision of the work and many hours of discussion, advice and encouragement.

Dr. J. G. Holland is acknowledged for his advice on the X-Ray Fluorescence method.

The staff of the University of Durham Computer Unit are thanked for their help in the use of the Northumbrian Universities Multiple Access Computer. Special thanks are extended to Mr. R. N. Oddy for his advice on programming problems.

The staff of the National Coal Board Opencast Executive in Yorkshire, Durham, Northumberland, and Fife are acknowledged for their aid in the collection of samples.

Grateful thanks are extended to Miss G. Thorpe who typed the manuscript.

Miss M. Brawn is gratefully thanked for drawing all the illustrations and diagrams, and, as Mrs. M. Reeves for her endless patience, encouragement and help in the final preparation.

Finally, N.E.R.C. are acknowledged for the research grant which made the work possible.

CHAPTER ONE

INTRODUCTION

1.1 AIMS OF THE WORK

The aims of the study may be summarised as follows :-

(a) To deduce the factors affecting the element and mineral distribution in seatearths.

(b) To determine the relative importances of the factors deduced.

(c) To compare seatearths with associated sediments and interpret the chemical implications of cyclic sedimentation.

(d) To use seatearths to elucidate changes in the pattern of sedimentation in the Upper Carboniferous.

(e) To investigate methods for the presentation, processing, and interpretation of geochemical and mineralogical data.

1.2 TECTONIC AND PALAEOGEOGRAPHIC CONDITIONS

Seatearths have two outstandingly obvious features as sedimentary units :-

(a) Their association with coal seams.

(b) Their occurrence as a member of a cyclic unit.
Cyclic sedimentary units are found in the Carboniferous of Great Britain from Viséan to Westphalian times. Fig. 1.1 illustrates the main features of Carboniferous cyclothems after BENNISON and WRIGHT (1969). The ideal cyclothem, from shallow water limestone to coal, is found in the Yordale facies of the Viséan originally described by HUDSON (1924) and similar cyclothems are found to extend into the early Namurian. Later Namurian and Westphalian cyclothems do not have a limestone unit (apart

from the Mansfield Marine Band, TAYLOR and SPEARS (1967)) and occasional periods of marine incursions are represented by rare marine bands. Sedimentation of the ideal cyclothem follows the general pattern :-

(a) Deposition of shallow water marine limestone.

(b) Detrital sediment begins to appear and calcareous shales are deposited.

(c) Precipitation of calcite is reduced to a minimal rate and black shale is deposited. Marine fossils are usually present in this unit.

(d) Marine fossils disappear and a non-marine shale is deposited.

(e) The non-marine shale grades up into siltstone, sandy siltstone and finally sandstone as the deltaic area becomes silted up.

(f) Seatearth accumulation is accompanied and followed by the development of vegetations which may subsequently be preserved as coal.

Stages (a), (b), and (c) are progressively less commonly developed as the Carboniferous period passes. Fig. 1.2 illustrates the progressive decrease in "cyclothemic amplitude" during the Carboniferous period. Stages (a) to (e) may be summarised as a progressive fall in precipitative sedimentation and a progressive increase in detrital rate of accumulation as a shallow shelf sea was invaded by estuarine/deltaic deposits and finally became a coastal swamp. An abrupt change in conditions occurs between stages (e) and (f) and the seatearth and coal accumulate. The nature of this break, or indeed, the very presence or absence of such a break must be explained by any theory of seatearth accumulation.

Fig. 1.3 shows the approximate palaeogeography of Northern Britain through the Namurian, as envisaged by GREENSMITH (1965). The different facies developed are :-

(a) In Scotland the Limestone Coal Group were deposited consisting of cyclothemic units from which limestones were essentially absent. The high density of coals developed, especially in the North East,indicates that this area was often a coastal swamp.

(b) In the North of England Yordale cyclothemic units with limestones continued to be deposited in the regions of the stable Alston-Askrigg blocks.

(c) In the Lancashire - Yorkshire region Millstone Grit facies began their development with the onset of the Grassington Grit delta.

(d) In the more Southerly parts of the area the Edale and Bowland shaley facies were developed. As the Namurian progressed the development of productive coals spread in a South Westerly direction indicating an extension of coastal swamps from the North East. Fig. 1.4 illustrates that by the beginning of Westphalian times a very extensive delata/swamp environment had developed and productive coal accumulated over wide areas. Fig. 1.5 shows the distribution of coalfields preserved to the present day in Northern Britain. Consideration of the palaeogeographic evidence raises two important points :-

(a) Coastal delta/swamps were first established in the North East and spread to the South and West.

(b) Areas close to the stable continental blocks were submerged less often than those towards the centre of the paralic basin.

MOORE (1968) remarked on "the fireclay propensity in regions bordering St. George's Land and flanking the Southern Uplands in the Midland Valley of Scotland". This fact is a direct result of (b). When rapid submergence of peat does not occur bacterial decay and atmospheric oxidation tend to destroy peat accumulations. Hence, in coastal areas seatearths are often present without the accompanying coal. Rivers flowing through low lying peaty swamps may often be traced by washout structures in which coarse cross bedded sandstones are preserved. Simultaneous with coal and seatearth accumulation in swamps, on the edge of the delta the deltaic sands were being deposited. Finer material was probably carried even further into the basin where shales and mudstones accumulated. Thus constant facies changes complicate correlations within the sedimentary units of the Upper Carboniferous. Fig. 1.6 illustrates facies changes, seam splitting, and washout structures.

1.3 BIOLOGICAL CONDITIONS

The development of coal in an area implies a flourishing flora and a rate of accumulation of plant debris greater than the rate of destruction by bacterial decay and/or atmospheric oxidation. The evidence of both present day analogues and the palaeobotanical studies of coal indicate that during the Carboniferous period a sub-tropical climate was prevelent in Britain. The palaeomagnetic evidence of polar positions substantiates this conclusion. The macrofossils of seatearths are usually restricted to Stigmaria rootlets, and fossil wood and microspores tend to be most useful parameters in accessing palaeoclimate and environment. PEPPERS (1964) examined the distribution of spores in Pennsylvanian cyclothems but failed to reveal a consistent pattern of relative abundances between the various cyclic units. However, a close relationship between the spore assemblages of seatearth and associated coal was apparent. MARSHALL and SMITH (1965) found an increase in spore species present in Yorkshire seatearths with increasing distance from the coal. MOORE (1968) concluded that the combined biological evidence for seatearths indicated that successive vegetations which were not preserved as coal are represented by the spore content.

1.4 MINERALOGICAL EVIDENCE OF PREVIOUS WORKERS

The mineralogy and petrology of seatearths has been the subject of fairly extensive research. GRIM and ALLEN (1938), SCHULTZ (1958), and HUDDLE and PATTERSON (1961) have examined Pennsylvanian seatearths in the U.S.A. and WILSON (1965) has discussed seatearths in the South Wales Coalfield. Such studies are confined to mineralogy and petrology. KELLER (1956) made some preliminary chemical observations on the conditions favourable to the accumulation and formation of various clay minerals but presented no specific chemical data. MOORE (1968) presented a few analyses, whilst ENNOS and SCOTT (1924) presented a large number of partial and complete analyses of fireclays. Most authors who have worked on seatearths agree that subdivision into at least three units may be made on the basis of field evidence.

They are :-

(a) An upper carbonaceous unit, containing coaly partings and plant debris. The unit may be bedded or unbedded, with or without rootlets or convolute structures.

(b) A middle, usually unbedded, clay unit, often with rootlets, slickenslides, and convolute structures. The unit often grades into coarser material at its base where ironstone carbonate nodules become increasingly common.

(c) A lower transition unit, grading into a normal sandstone, siltstone, mudstone, or shale.

Any one or two of the above mentioned units may be absent in particular cases but unit (b) is usually developed and is commonly the most extensive unit. The mineralogical evidence, in general, points to two conflicting theories for the origin of seatearths.

(a) That they are the result of "gleying" of peats, that is, severe in situ weathering.

(b) That they are the result of fairly severe chemical weathering essentially at source prior to the detritus entering the basin of deposition.

1.5 SAMPLING PROCEDURES

The foregoing information was used to design a sampling procedure and the following points were taken into account during sampling :-

(a) The seatearth samples were selected in order to give adequate coverage of a wide stratigraphic range. In practice, this was possible from the base of the Namurian to the Similis - Pulchra Zone of the Westphalian, as illustrated by the sections in Fig. 1.7.

(b) In some cases roof rocks were sampled since it can be argued that no significant change in source material occurs between floor and roof and hence rapidly deposited sandy roof may reflect the source rocks fairly accurately.

(c) All three Brockwell coals and three Hutton coals were sampled for seatearth; in the case of the Brockwells, roof rocks were also sampled. Close sampling of consecutive coals in this manner was carried out in order to examine minor, as well as major, stratigraphic variation.

(d) Several sections from some 100 cm. above the seam to 100 cm. below the seam were sampled in extreme detail to assess small vertical variations.

(e) All material was taken from boreholes sunk by the National Coal Board, from depths greater than 10 metres. The minimum depth was taken as the limit of the worst effects of surface weathering.

(f) In a number of cases material for the same horizon in different boreholes was sampled. However, the lateral separation of such samples rarely exceeded 100 metres and such material was only available for a few of the more shallow cores. These samples were taken to check on local lateral variations in composition.

(g) Several miscellaneous samples of special interest, for example, ironstone bands, tonsteins, etc. were also taken.

(h) It was found that adequate cover of vertical variations in seatearth and roof rocks could be obtained by taking two samples from each unit at distances of 15 and 50 cm. from the seam. This was decided after preliminary results from detailed sections had been examined. About 500 gms of material was taken for each sample.

The samples gathered may be classified as follows :-

(a)	Seatearths for statigraphic coverage.	42
(b)	Roof rocks for source rock investigation.	24
(c)	Detailed sections.	17
(d)	Seatearths for areal variation.	4
(e)	Miscellaneous	4
		91

A restricted number of samples were taken in order that a large number of variables could be measured with a high degree of precision and accuracy. The coverage of local areal variation is small but variation over local areas was found to be trivial, essentially consisting of quartz content variation. Samples were not available for the investigation of broad areal variation which is known to be quite significant (MOORE, 1968). Seatearth samples were taken in such a way as to maintain as far as possible the same postion on the palaeogeographical delta front. Overlapping of sections between coal fields was not possible in many cases but comparisons with the work of other authors (NICHOLLS and LORING, 1962; WILSON, 1965) suggests that the conclusions drawn on a stratigraphical basis can be extended in a general sense between basins. Table 1.1 gives details of all the samples analysed.

TABLE 1.1

IDENTIFICATION OF SAMPLES

SAMPLE	SEAM	TYPE	LOCALITY	DEPTH m.
DY5	Shafton	Seatearth	Sprotsborough Lane, Doncaster	167
DY6	"	"	" " "	167
DY3	Edmondia Band	"	" " "	197
DY4	" "	"	" " "	197
DY1	Sharlston Top	"	" " "	219
DY2	" "	"	" " "	219
FB1	Brass Thill	"	Embleton Hall, Fishburn	160
FB2	" "	"	" " "	160
FB3	U. Top Hutton	"	" " "	188
FB4	" " "	"	" " "	188
FB5	L. Top Hutton	"	" " "	191
FB6	" " "	"	" " "	191
FB7	Bottom Hutton	"	" " "	200
FB8	" "	"	" " "	200
FB9	Harvey Marine Band	"	" " "	226
FB10	" " "	"	" " "	227
FB11	Bottom Harvey	"	" " "	243
FB12	" "	"	" " "	243
TB1	Top Busty	Sandstone	Whittonstall, Nr. Consett	11
TB2	" "	Siltstone	" " "	11
TB3	" "	Sandstone	" " "	12
TB4	" "	Seatearth	" " "	12
TB5	" "	"	" " "	13
TB6	" "	"	" " "	13
TB7	" "	"	" " "	13
BS2	U. Brockwell	Siltstone	West Hedley Hope	10
BS4	" "	"	" " "	10
BS6	" "	Seatearth	" " "	11
BS8	" "	"	" " "	11
BS12	M. Brockwell	Mudstone	" " "	14
BS14	" "	"	" " "	14
BS16	" "	Seatearth	" " "	15
BS18	" "	"	" " "	15
BS20	L. Brockwell	Siltstone	" " "	18
BS22	" "	"	" " "	18
BS25	" "	Seatearth	" " "	19
BS27	" "	"	" " "	19
ST1	Hirst	Siltstone	Standalane, Nr. Dunfermline	30
ST2	"	"	" " "	30
ST4	"	Seatearth	" " "	31
ST6	"	"	" " "	31
KB2	Rough	"	Keirsbeath, Nr. Dunfermline	10
KB3	"	"	" " "	10
KB5	"	"	" " "	11
KB8	"	"	" " "	11

(continued overleaf)......

TABLE 1.1 (CONTINUED)

IDENTIFICATION OF SAMPLES

SAMPLE	SEAM	TYPE	LOCALITY	DEPTH m.
KB13	Kelty Main	Mudstone	Keirsbeath, Nr. Dunfermline	25
KB15	" "	"	" " "	25
KB18	" "	Seatearth	" " "	26
KB20	" "	"	" " "	26
KB21	U. Jersey	Mudstone	" " "	32
KB23	" "	"	" " "	32
KB25	" "	Seatearth	" " "	33
KB27	" "	"	" " "	33
KB37	Lochgelly Splint	"	" " "	48
KB39	" "	"	" " "	48
KB43	" "	"	" " "	49
KB45	" "	"	" " "	49
LL1	U. Little Limestone	Sandstone	Blagill, Nr. Alston	15
LL2	" " "	"	" " "	15
LL3	" " "	"	" " "	15
LL4	" " "	"	" " "	15
LL5	" " "	"	" " "	15
LL6	" " "	Seatearth	" " "	16
LL7	" " "	"	" " "	16
LL8	" " "	"	" " "	16
LL9	" " "	"	" " "	16
LL10	" " "	"	" " "	16
LL13	L. Little Limestone	Siltstone	" " "	18
LL16	" " "	"	" " "	18
LL18	" " "	Seatearth	" " "	19
LL20	" " "	"	" " "	19
NP1	Dunfermline Splint	Mudstone	North Pitdinnie, Nr. Dunfermline	21
NP3	" "	"	" " " "	21
NP4	" "	Seatearth	" " " "	22
NP6	" "	"	" " " "	22

MISCELLANEOUS SAMPLES

SAMPLE	
ISN	Ironstone nodule from sample FB2.
ISB	Ironstone band from immediately above Hirst Coal.
PYT	Pyrite from slickenslided surfaces in sample FB8.
MIC	Coarse micaceous flakes from sample LL6.
TBA	
TBB	Areal samples of Top Busty seatearth, Whittonstall.
TBC	
TBD	

FIG.1·1 MAIN FEATURES OF CARBONIFEROUS CYCLOTHEMS, AFTER BENNISON AND WRIGHT (1969)

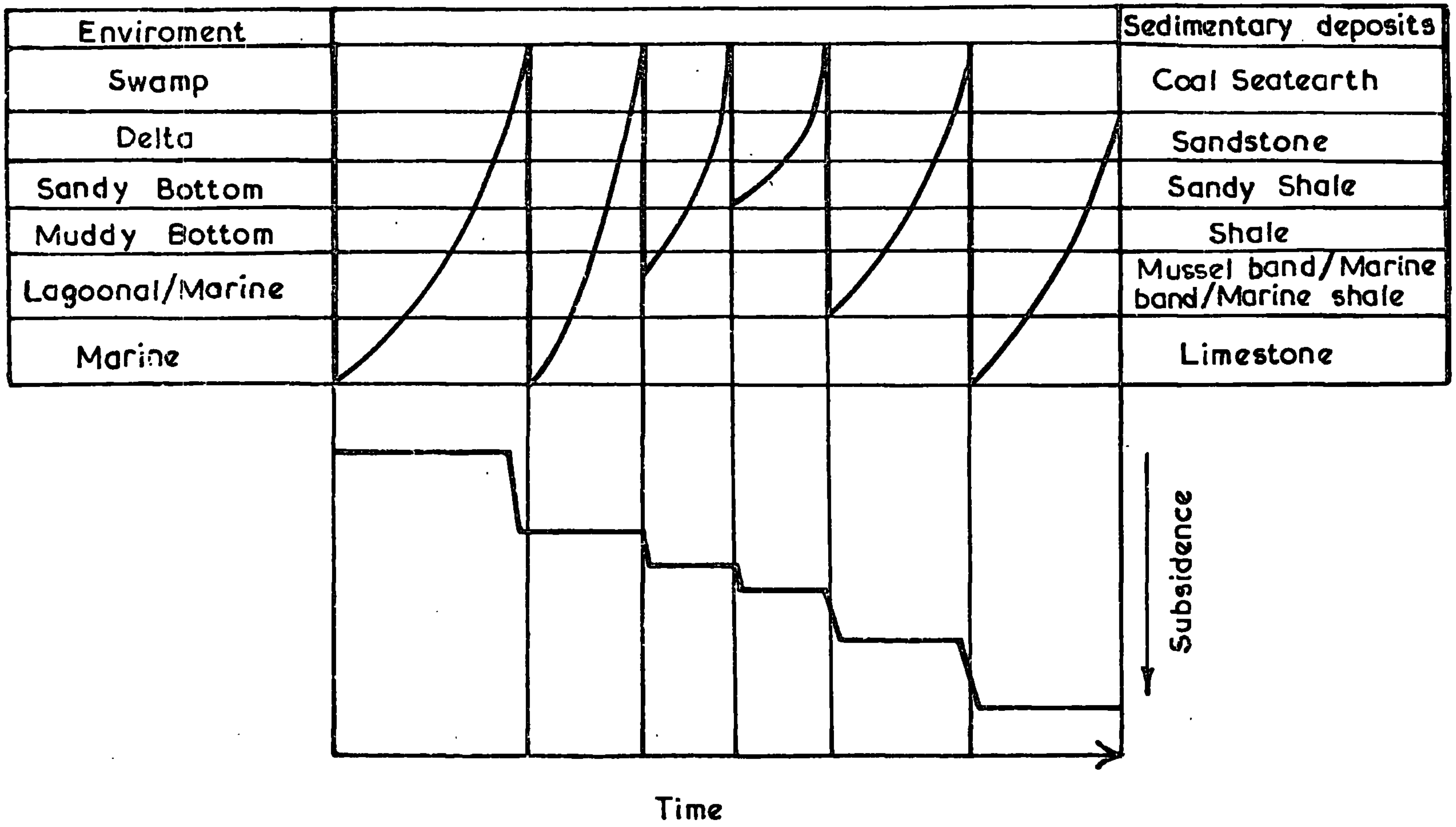


FIG.1·2 DIAGRAMATIC ILLUSTRATION OF DECREASE 'CYCLOTHEMIC AMPLITUDE' THROUGH THE CARBONIFEROUS

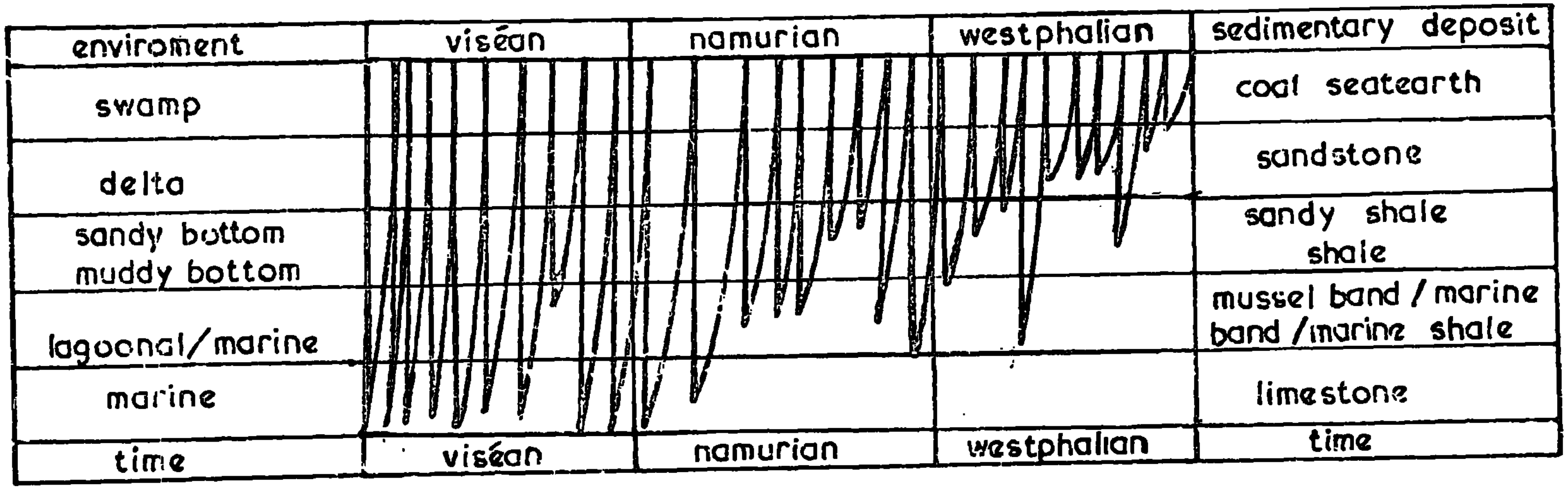
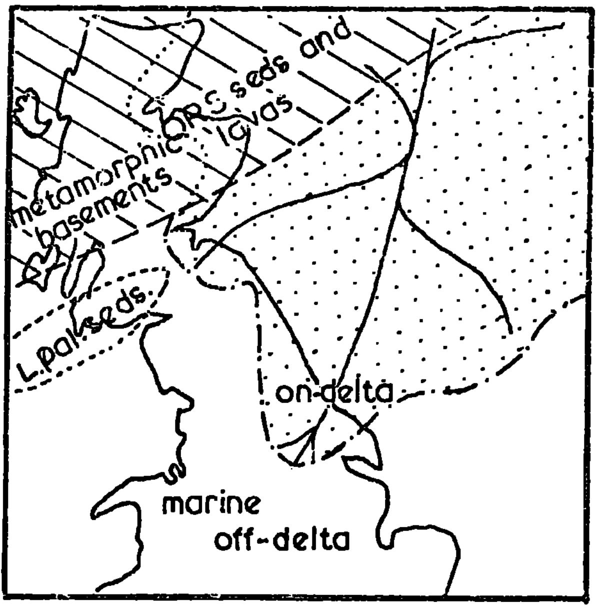
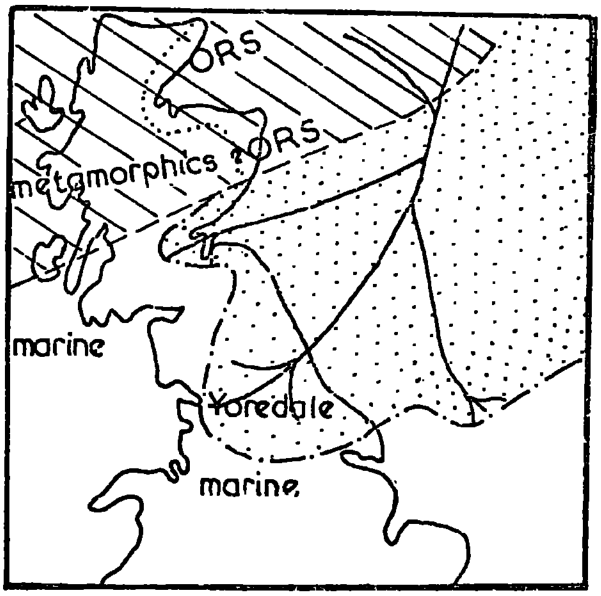


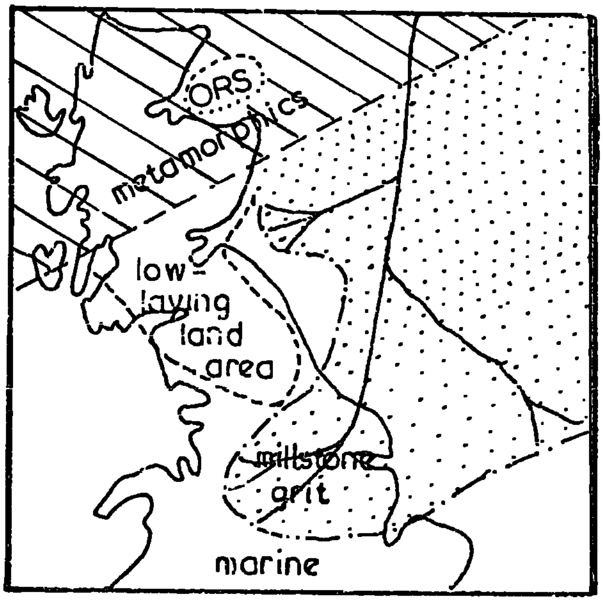
FIG.1·3a PALAEOGEOGRAPHIC DEVELOPMENTS DURING THE NAMURIAN



Late Viséan (D)

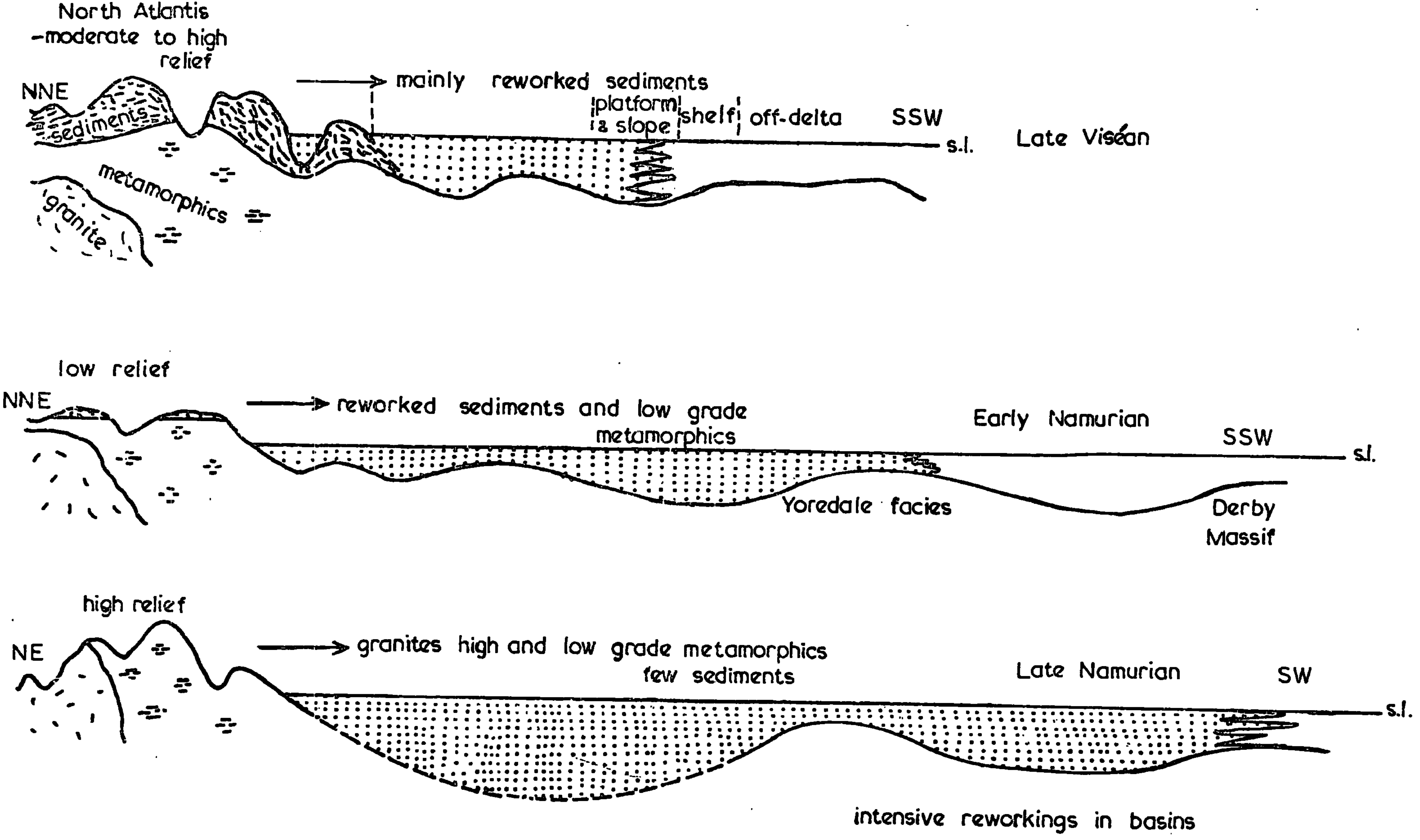


Early Namurian (E)



Late Namurian (R)

FIG. 1·3b SECTIONS SHOWING THE DEVELOPMENT OF THE NAMURIAN DELTAS



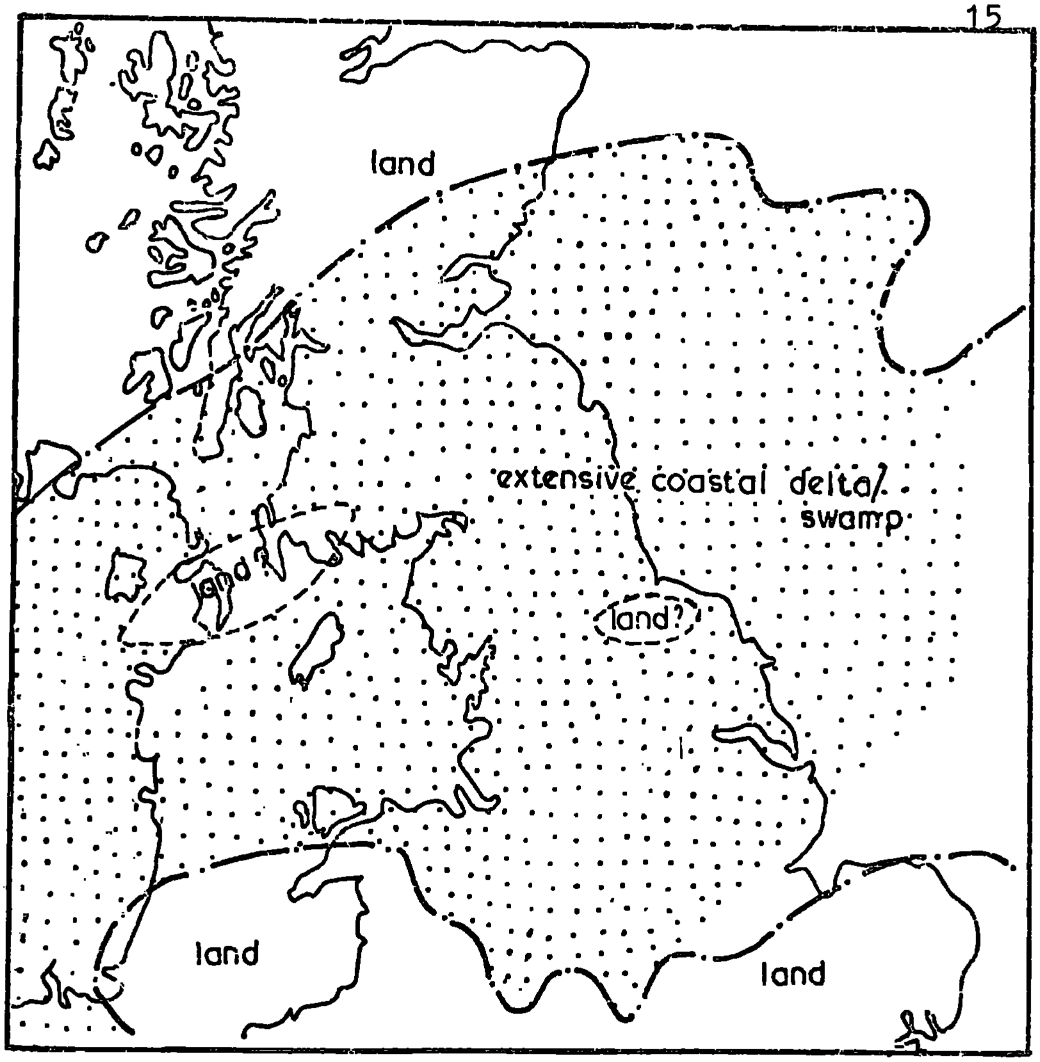


FIG. 1·4 LOWER WESTPHALIAN PALÆOGEOGRAPHY

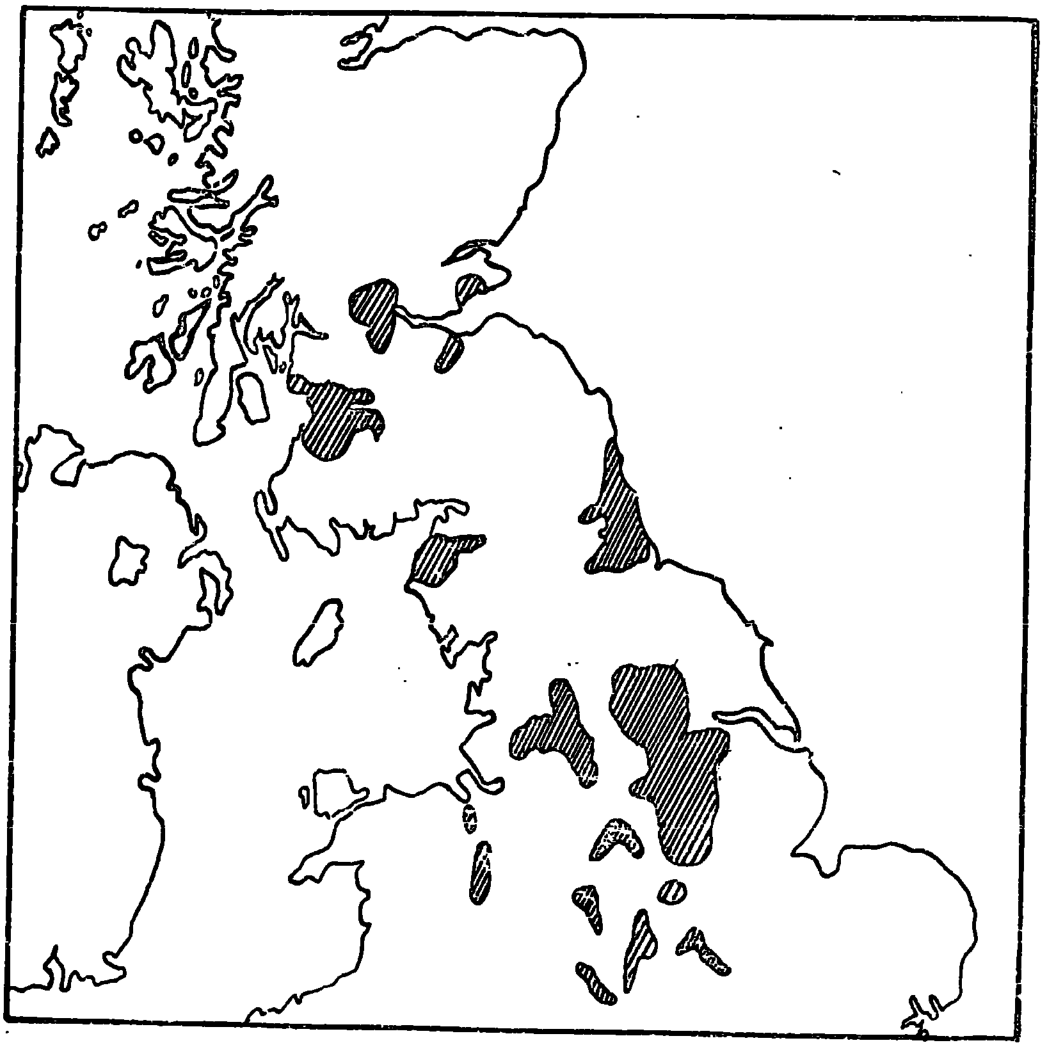
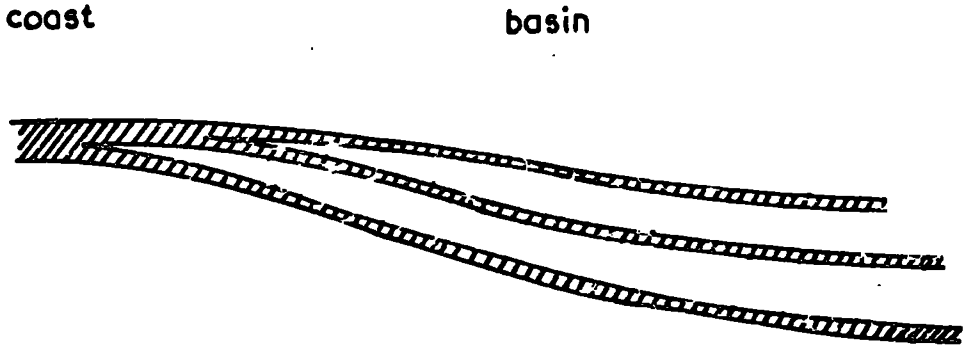


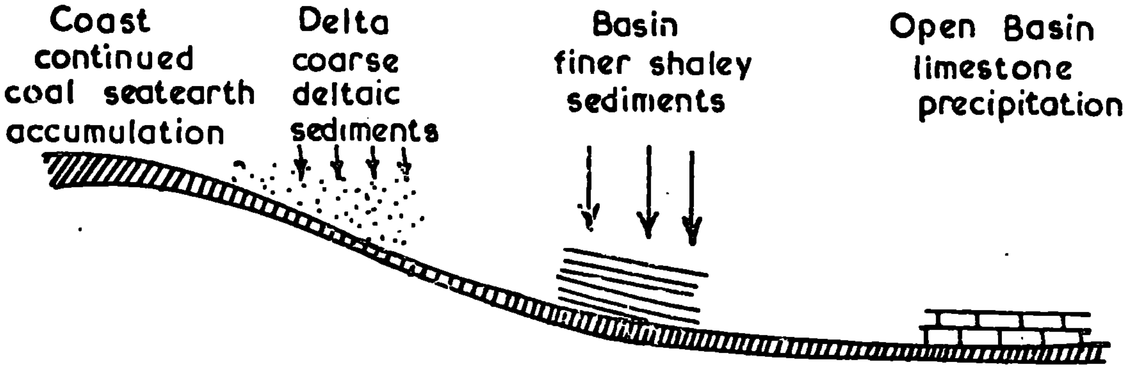
FIG. 1·5 DISTRIBUTION OF NORTHERN COALFIELDS

FIG.1·6 ILLUSTRATION OF FACTORS COMPLICATING CORRELATIO
IN CARBONIFEROUS SEDIMENTS

(a) Seam Splitting



(b) Facies Changes



(c) Washout Structure

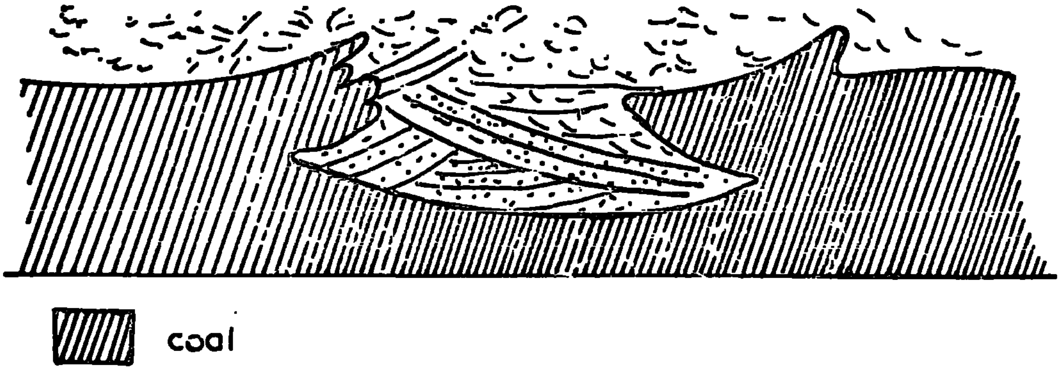


FIG. 1·7 STRATIGRAPHIC SECTIONS

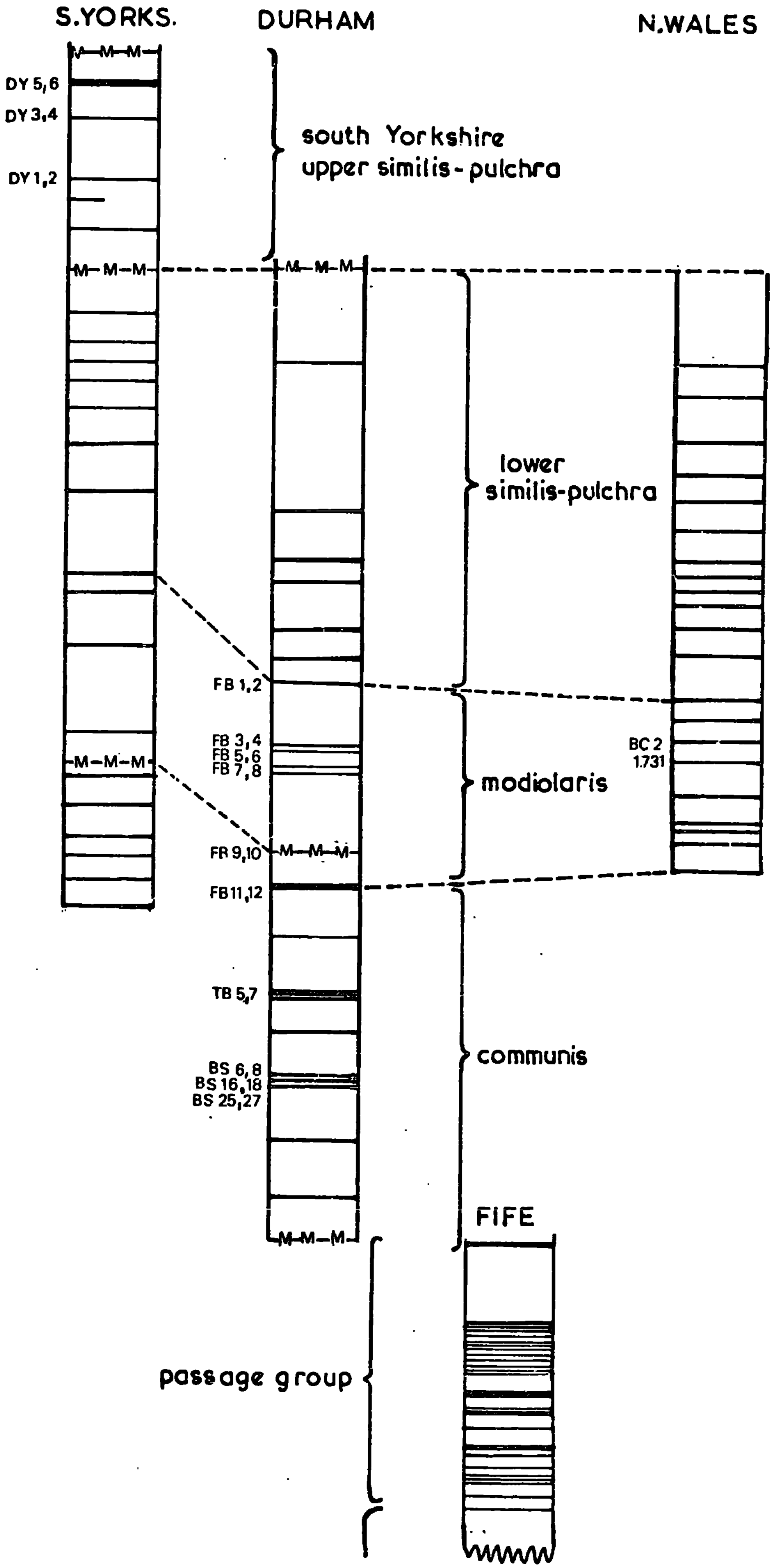
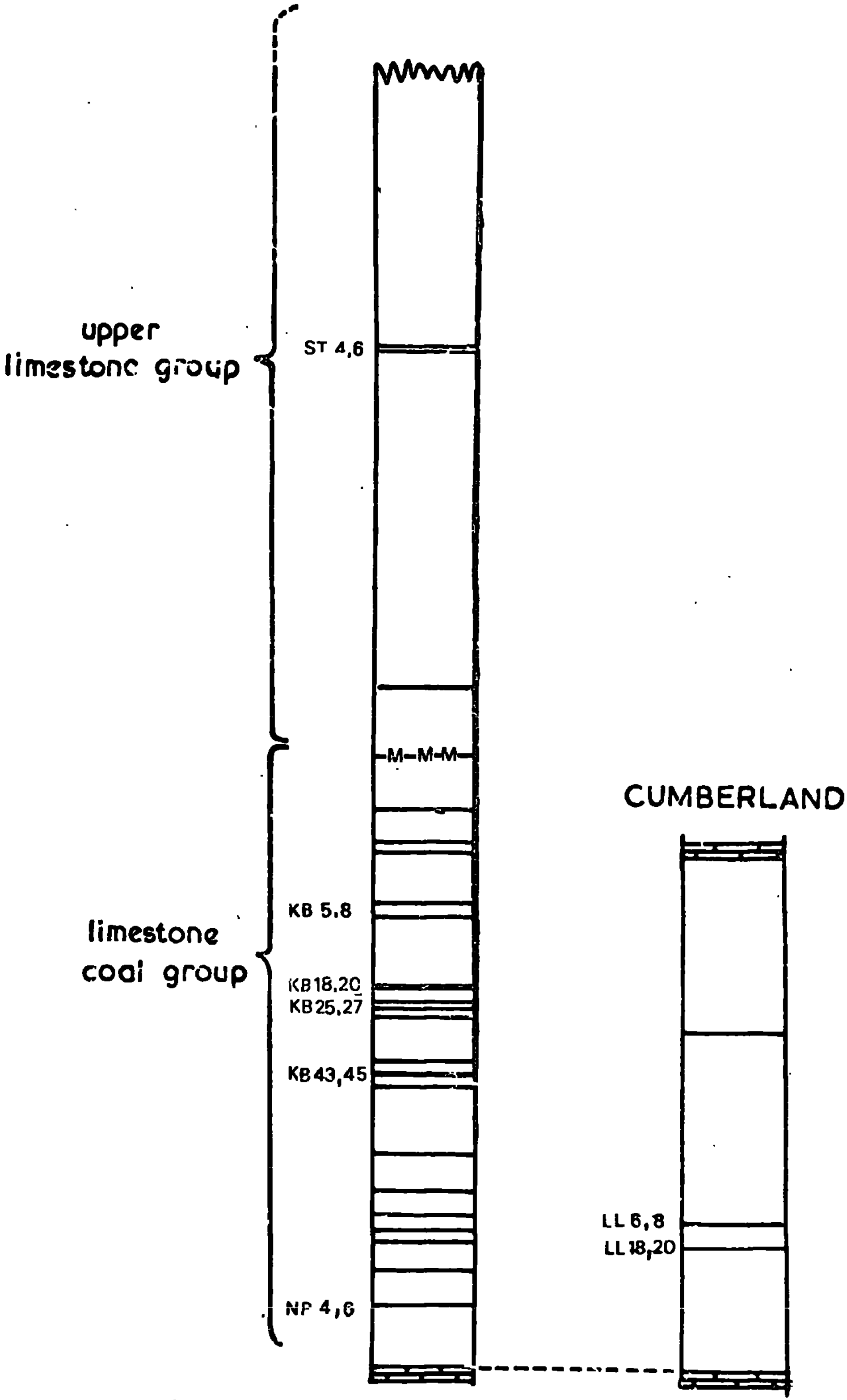


FIG.1·7 STRATIGRAPHIC SECTIONS continued



1.6 REFERENCES TO CHAPTER ONE

BENNISON, G. A., and WRIGHT, A. E., (1969), The Geological History of the British Isles., Edward Arnold Ltd. Lond.

ENNOS, F. R., and SCOTT, A., (1924), Refractory materials : fireclays. Analyses and physical tests., Mem. Geol. Surv., Spec. Rept Min. Res. Gt. Britain, Vol XVIII.

GREENSMITH, J. T., (1965), Petology of the sedimentary rocks., by Hatch and Rastall, 4th Edition, George Allen and Urwin Ltd., Lond.

GRIM, R. E., and ALLEN, V. T., (1938), Petrology of the Pennsylvanian underclays of Illinois., Bull. Geol. Soc. Am., 49, 1483 - 1513.

HUDDLE, J. W., and PATTERSON, S. M. (1961), Origin of Pennsylvanian underclay and related seat rocks., Bull. Geol. Soc. Am., 72, 1643 - 1660.

HUDSON, R. G., (1924), On the rhythmic succession of the Yoredale series in Wensleydale., Proc. Yorks. Geol. Soc., 20, 125 - 135.

KELLER, W. D., (1956), Clay minerals as influenced by their environment of formation., Bull. Am. Ass. Petrol. Geol., 40, 2689 - 2710.

MARSHALL, A. E. and SMITH, A. H. V., (1965), Assemblages of microspores from some Upper Carboniferous coals and their associated sediments in the Yorkshire Coalfield., Palaeontology, 7, 656 - 673.

MOORE, L. R., (1968), Some sediments closely associated with coal seams., In, Coal and coal bearing strata., Ed. Murchison and Westoll, Oliver and Boyd, Edin.

NICHOLLS, G. D., and LORING, D. H., (1962), The geochemistry of some British Carboniferous sediments., Geochim. Cosmochim. Acta, 26, 181 - 223.

PEPPERS, R. A., (1964), Spores in strata of late Pennsylvanian cyclothems in the Illinois basin., Bull. Geol. Soc. Am., 75, 823 - 832.

SCHULTZ, L. G., (1958), The petrology of underclays., Bull. Geol. Soc. Am., 69, 363 - 402.

TAYLOR, R. K., and SPEARS, D. A., (1967), An unusual carbonate band in the East Pennine Coalfield (England)., Sedimentology, 9, 55 - 73.

WILLIS, L. J., (1951), A palaeogeographical atlas., Blackie, Lond.

WILSON, M. J., (1965), The origin and significance of South Wales underclays., J. Sed. Pet., 35, 91 - 99.

CHAPTER TWO

MINERALOGY

2.1 GENERAL REMARKS

The mineralogy of both seatearths and roof rocks is fairly restricted and the major components may be summarised as follows :-

(a) Carbonate. Usually present as siderite nodules and for the most part in minor quantities.

(b) Carbonaceous matter. Present as coaly partings and plant remains preserved as carbonaceous films. Carbon will be considered as a member of the mineral assemblage.

(c) Quartz. Quartz is almost invariably a major component in both roof and floor measures.

(d) Clay minerals. The usual assemblage of clay minerals is illite and/or kaolinite, together with minor chlorite. Illite is used in a very broad sense to include sedimentary mica, hydromica, illite s.s., and mixed layer minerals of which illite is usually the major component. Illite terminology is discussed by YODER and EUGSTER (1955).

The variations from roof to floor will be discussed in Chapter five, the variations within roofs in Chapter four, and the variation in seatearths in Chapter three. This chapter is concerned with the mineral components themselves rather than their variations. Three methods were used to investigate the mineralogy :-

(a) X-ray diffraction.

(b) Differential thermal analysis.

(c) Thin section examination.

Methods (a) and (b) were used to examine the clay mineralogy and method (c) was used to examine the texture of the sediments.

In addition to the three methods listed several heavy mineral separates were obtained and a number of grain size distribution curves were constructed. Quantitative mineralogic analyses were carried out on some 14 roof rocks and 48 seatearths for the following components :- siderite, carbon, quartz, chlorite, illite, and kaolinite. Table 2.1 summarises the quantitative data for roof rocks and Table 2.2 the data for seatearths. Appendix I gives details of the methods employed for quantitative analysis.

2.2 CARBONATE

Tables 2.1 and 2.2 indicate that carbonate is usually a minor phase. The quantitative determination of carbonate was made by recalculation of the chemically determined CO_2 content into the siderite molecule, since the level of carbonate was too low for quantitative X-ray determination. Calcite, ankerite/dolomite, and siderite were, however, all detected by the presence of their strongest reflections, corresponding to the "d" spacings of 3.03Å, 2.89Å, and 2.79Å respectively, in various samples. However, the siderite reflection was in general the strongest and definitely by far the most frequently occurring. All carbonate was recalculated as siderite since meaningful partition of the CO_2 between the various phases proved impossible. The usual occurrence of siderite, especially in seatearths, was as nodular concretions consisting of siderite, coarse grained (0.05 mm) well crystallised laths of kaolinite, and often pyrite.

2.3 CARBONACEOUS MATTER

The carbonaceous matter in both roof and floor measures consists of coaly partings and plant remains, preserved as carbonaceous films. Rootlets are commonly found in seatearths and Stigmaria is the common fossil plant. Carbon was quantitatively determined by the chemical method outlined in Appendix I. Separation of carbonaceous matter from several sediments by a floatation method was carried out. The carbonaceous separates consisted of coal and fossil wood.

2.4 QUARTZ

All samples examined contained quartz, usually as a major component of the mineral assemblage. Thin section examination revealed that the grain size of the quartz was its least constant property. The shape and degree of abrasion of the quartz grains was also variable and further details of these variations will be discussed in Chapter five. Tables 2.1 and 2.2 show the wide variations in quartz content of the sediments examined.

2.5 CLAY MINERALS

Probably the singularly most interesting and important feature of the sediments examined was their clay mineralogy. The assemblages encountered are illite and/or kaolinite with minor chlorite, using illite in the broad sense previously defined. Examination of the clay mineralogy was carried out essentially by X-ray diffraction. Each sample was run from 4 - 64° two theta using Cu K α radiation and machine conditions essentially similar to those outlined in Appendix I. for the quantitative work.

2.51 CHLORITE

Chlorite is the least abundant of the clay minerals present in the majority of samples examined. However, it may be of considerable genetic significance in any theory to explain the origin of seatearths. Samples in which chlorite was suspected from the preliminary X-ray scan were heated to 450°C for 30 mins. and then re-run. A further period of heating, at 550°C for 60 mins., was carried out and the sample re-run for a second time. This procedure is similar to that suggested by SCHULTZ (1958) for distinguishing between chlorite and vermiculite. Preliminary recognition of chlorite was based on the presence of a 14, 7, and 4.7 Å peak corresponding to 001, 002, and 003 reflections. Vermiculite also gives a similar set of peaks and kaolinite contributes to a 7 Å reflection. Further interferences could be present due to montmorillonite or chamosite but such minerals are less likely to occur. On heating at 450°C both vermiculite and montmorillonite undergo a dehydration and collapse of the structure. Disappearance of the 14 Å peak would indicate either of these minerals to be present. In the case of vermiculite the 14 Å is very strong and the other basal reflections relatively weak thus reduction of the 001 intensity on heated samples and subsequent reversible rehydration is probably sufficient for the positive identification of vermiculite. Proof of vermiculite in this way, however, does not preclude the existence of chlorite and the second heating at 550°C is necessary. Such heating tends to destroy kaolinite in addition to vermiculite and montmorillonite and any reflections at 14, 7, and 4.7 Å indicated the presence of chlorite. The relative intensities of 001, 002, and 003 peaks in chlorite are a function of the chemistry of the mineral and BRINDLEY (1961) indicates that low intensity for the odd reflections (001, 003) indicates Fe-rich as opposed to Mg-rich chlorite. Measurements of relative intensities after and prior to heating in both natural and standard chlorites indicated that the chlorites in the samples were probably Mg-rich, as would be expected in the environment. Two tests were carried out to confirm this conclusion and, in fact, prove the validity of the quantitative calibration of chlorite. First, the natural chlorite proved resistant to acid attack which indicates that they were Mg-rich. Chamosite would give a similar reaction but has only a 7 Å peak. The second test was to measure the powder pattern of a separate of natural chlorite. A chlorite rich fraction was separated from sample BS27 relatively easily due to the large size of the chlorite compared to the other clays. The powder pattern is given in Table 2.3 and compared with a penninite. The similarity of the patterns is striking and the Mg-rich nature of the natural chlorite is thus established. The examination of samples for chlorite revealed the following major points :-

(a) The chlorite is of larger grain size than other clays (except muscovite) and grains 1-2 mm in diameter have been found in some samples. Similarly large chlorite was found in the Mansfied Marine band sediments by TAYLOR (1970).

(b) Tables 2.1 and 2.2 show that chlorite is the least abundant clay mineral in the sediments investigated.

(c) The natural chlorites encountered are Mg-rich. The dehydration temperature determined by differential thermal analysis on the BS27 separate was about 560°C which is in the range for Mg-chlorites quoted by CAILIERE and HENIN (1957).

(d) Vermiculite in very small amounts is suspected in samples NP4, NP6, LL6, LL8, LL18, and LL20. A small fall in the 001 14Å intensity was observed on heating to 400°C. BRINDLEY (1961) indicates that an increase in intensity of this peak normally occurs on heating chlorite, due to structural rearrangement.

2.52 KAOLINITE

Kaolinite is probably the most abundant mineral in the samples examined but shows the least amount of variation in its X-ray diffraction and differential thermal analysis patterns. Differential thermal analysis proved a useful auxillary technique. When low concentrations of kaolinite were suspected, or when a test to see that heating to 550° C for 60 mins, was sufficient to destroy kaolinite was needed. SCHULTZ (1958) found that Pennsylvanian underclays contained a disordered "fireclay" kaolinite as described by BRINDLEY and ROBINSON (1947). MURRAY and LYONS (1956) listed the distinguishing features of these b-axis disordered minerals. The most useful differences are :-

(a) The non-resolution of the 4.12 - 4.17Å doublet.

(b) The broad 2.5 Å peak replacing the triplet 2.55 - 2.52 - 2.49 Å.

(c) The broad 2.3 Å peak replacing the triplet 2.37 - 2.33 - 2.28 Å.

Fig. 2.1 shows the pattern differences diagramatically. WILSON (1965) found that the two triplets were often resolved in the South Wales underclays but the doublet was not resolved. WILSON (1965) concluded that the mineral in his samples was partially disordered. In the present study the two triplets were always resolved when the intensity of such reflections was sufficient. In some cases, for example, sample TB5, the doublet was resolved but in others, for example, sample BS27, resolution did not occur. It is concluded that the sediments examined contain a kaolinite of a slightly disordered nature. The degree of disorder varies between samples. In many cases it was difficult to determine the degree of disorder since the concentration of kaolinite varied and other clay mineral peaks produced interferences. The resolution of the diffractometer is also critical in the application of such tests. Interpretation of patterns was therefore restricted to kaolinite-rich samples. Extremely well crystalline kaolinite was found in association with siderite nodules and microscopic examination revealed that such kaolinite was coarsely crystalline. Examination of kaolinite in the sediments revealed the following points :-

(a) The kaolinites, in general, suffer from only slight b-axis disorder. This conclusion is in line with the findings of WILSON (1965).

(b) Coarse grained, well crystalline, kaolinite is found in association with siderite nodules.

(c) The "fireclay" kaolinite reported by SCHULTZ (1958) from Pennsylvanian underclays would appear to be non-typical of seatearths.

2.53 ILLITE

The term illite has been used, for convenience, to cover a wide range of minerals and when used in this sense is the most variable feature of the clay mineralogy of the sediments examined. Quantitatively illite is only slightly less important than kaolinite. Fig. 2.2 shows the variation in appearance of the basal reflections of minerals included under the term illite.

Trace (a) shows the diffraction pattern from 8 to 10° two theta for sample BS4 which is a micaceous sandstone. The 10 Å peak is that of a fairly fresh coarse grained muscovite mica. The mica was separated and examined optically. The optical properties were consistent with the identification as muscovite. Under the microscope inclusions of rutile, zircon, and opaques were visible.

Trace (b) shows the diffraction chart for a very fine grained micaceous mineral found in sample TB5. Microscopic examination was impossible due to the fine size of the mineral (<2μ) and this property proved an obstacle to separation. The peak is only very slightly broadened relative to trace (a) and only slight signs of assymetry are visible. The mineral is interpreted as being a hydromica.

Trace (c) shows the diffraction chart for a mineral present in sample FB2. The mineral is interpreted as illite s.s. The peak is broad indicating disorder due to mis-matching of layers and is also assymetrical towards low two theta indicating some interlayering. The trace is typical of minerals normally referred to as illite.

Trace (d) shows a mineral in which interlayering is very strongly developed. The sample is BS8. The assymetry towards low two theta is very marked and the height to width ratio is very low. This ratio has shown a progressive decrease through the preceeding traces and may be used a parameter to define relative degrees of interlayering and disorder.

Trace (e) shows the very broad diffuse band indicative of the extreme of disorder and interlayering. The mineral is present in sample KB27. It is interesting that sample KB27 is a very carbonaceous shaley seatearth.

Trace (f) shows a further extreme of interlayering resulting in a peak shift. The mineral is present in sample NP4 and shows the following reactions to various treatments :-

(i) Natural spacing 10.9 Å, ranging over 10 - 14 Å.

(ii) Water saturation causes peak to broaden over the range 9 - 17 Å.

(iii) Heating to 110°C causes a fall in spacing to about 10.5 Å but rapid rehydration occurs.

(iv) Heating to 400°C causes irreversible collapse to a 9.8 Å spacing.

(v) Glycolation causes expansion to about 12.3 Å but the peak is broad (10 - 16 Å) and rather ragged.

(vi) Potassium saturation leaves the natural spacing virtually unaltered at 10.9 Å.

(vii) Magnesium saturation causes expansion to 11.9 Å.

(viii) Further ions were used to saturate the clay. Na, Ca, and Ba saturation give spacings of 12.3, 12.2 and 11.1 Å respectively.

(ix) Differential thermal analysis gave a curve consistent with an interlayered illite - montmorillonite. (COLE and HOSKING, 1957).

The reactions to the various treatments are consistent with an approximate 1 : 1 mixture of illite (10 Å) and potassium bentonite (12.4 Å). The graphs of MACEWAN et al. (1961) indicate about 40% bentonite. Table 2.4 gives details of the expansions on saturation with various ions, heating reactions, and glycolation. Fig. 2.3 shows a differential thermal curve obtained on a separate enriched in the mineral. Minerals with similar properties have been reported by FRANCIS (1961), from kaolinised tuffs in Fife, TREWIN (1968), from thin bands in the Namurian of Derbyshire, and SPEARS (1970) from the Stafford tonstein. In all cases the authors suggest that the mineral is of volcanic origin. In addition to sample NP4, a similar mineral is present in samples NP6, LL6, LL8, LL18, and LL20. It is interesting to note that all these samples occur in a very restricted statigraphic range.

Trace (g) shows two "illite" minerals in the same sample. Sample LL8 is interpreted as containing a hydromica and a mixed layer illite/bentonite.

Fig. 2.2 illustrates the problems involved in the quantitative estimation of illite. The standard mineral used lay approximately between traces (c) and (d) and was considered to be representative of the "average" illite.

Tables 2.5 and 2.6 shows the classification of illites found in the roof and floor samples respectively into the seven groups a-g. Error in the quantitative estimation is likely to be largest for samples least like (c) and (d). However, each phase in the mineralogical analysis was determined independently and total analyses were always between 90-110%. The mineralogical totals, prior to normalisation, for 124 determinations show that there is a slight bias towards low totals and that illite-rich samples tend to give lower totals. The errors in the assumption of a single illite standard are thought to be responsible for the errors in the analytical totals, to a large extent.

Having seen the huge variations in the illite components, the similarities must be discussed. First, the 060 illite reflection was always close to 1.50 Å indicating that all the illites, for which the 060 peak was sufficiently intense to be measured, were dioctahedral. Because of line interferences due to various minerals in the diagnostic region 20 - 35° two theta, it was not always possible to determine the illite polymorph. The coarse micaceous separates from samples BS4 and LL8 were identified as the 2M polymorph. Other illite-rich samples appear to be more closely related to the 1Md polymorph described by YODER and EUGSTER (1955). Tables 2.5 and 2.6 shows details of the polymorphs for samples in which a reasonable estimate could be made.

2.6 HEAVY MINERALS

Heavy mineral separates were obtained from a few seatearth samples. All samples contained apatite, pyrite, zircon, rutile, and opaques. Other minerals sometimes present were fluorite, barytes, and tourmaline. Very little qualitative work was carried out on heavy minerals other than the initial determination of the common phases.

TABLE 2.1

QUANTITATIVE MINERALOGICAL ANALYSES OF 14 ROOF ROCKS

SAMPLE	C	CBT	QZ	CHL	ILL	KAOL	T.C.
LL1	0.4	1.6	62	3	27	6	36
LL2	0.4	1.5	58	4	30	6	40
LL3	0.2	1.3	60	4	28	6	38
LL4	0.5	1.0	66	3	24	6	33
LL5	0.6	6.3	57	3	27	6	36
TB1	0.7	0.1	56	3	25	14	42
TB2	0.4	0.2	31	5	40	24	69
TB3	1.8	0.1	62	3	20	13	36
BS2	0.8	3.1	51	4	20	21	45
BS4	1.3	7.4	44	4	21	23	48
BS12	1.3	4.3	8	6	37	44	87
BS14	0.4	2.8	9	6	38	44	88
BS20	1.0	3.2	20	8	31	37	76
BS22	1.2	0.1	23	8	31	38	77

TABLE 2.2

QUANTITATIVE MINERALOGICAL ANALYSES OF 42 SEATEARTHS

SAMPLE	C	CBT	QZ	CHL	ILL	KAOL	T.C.
DY5	1.8	2.6	16	10	37	33	80
DY6	0.4	2.7	22	10	34	31	75
DY3	2.4	2.5	11	11	38	35	84
DY4	0.7	2.2	44	9	25	20	54
DY1	1.2	2.2	14	14	31	38	83
DY2	0.8	1.3	30	10	24	34	68
FB1	0.4	1.3	13	3	67	16	86
FB2	0.1	1.3	15	3	65	15	83
FB3	0.6	1.1	11	3	67	17	87
FB4	0.7	0.9	10	3	68	17	88
FB5	0.6	0.9	13	2	73	10	85
FB6	0.3	1.0	15	3	63	17	83
FB7	0.2	0.9	8	1	15	75	91
FB8	0.1	0.7	9	1	16	73	90
FB9	1.0	0.5	21	1	27	50	78
FB10	1.1	0.8	14	1	29	54	84
FB11	0.1	0.7	24	-	14	61	75
FB12	0.1	0.4	44	-	9	46	55
TB5	0.3	0.3	14	-	18	67	85
TB7	0.1	0.3	15	-	22	63	85
BS6	2.4	0.3	15	1	28	53	82
BS8	2.4	0.4	20	2	24	52	78
BS16	2.4	0.5	22	3	16	56	75
BS18	0.7	0.3	22	3	20	54	77
BS25	0.6	0.7	22	10	22	45	77
BS27	0.5	0.6	22	9	25	43	77
ST4	10.9	1.9	18	-	10	59	69
ST6	1.5	1.6	20	-	5	72	77
KB5	4.1	0.7	7	2	12	75	89
KB8	8.3	0.7	4	2	12	73	87
KB18	3.8	0.6	20	-	11	64	75
KB20	1.0	0.6	27	-	12	59	71
KB25	3.4	0.9	7	2	14	73	89
KB27	31.3	0.3	2	1	10	56	67
KB43	1.0	0.3	23	1	8	67	76
KB45	2.6	0.3	32	1	9	56	66
LL6	4.4	0.4	21	1	45	28	74
LL8	6.4	1.2	21	1	45	26	72
LL18	0.8	1.5	23	4	43	28	75
LL20	0.7	9.9	17	4	43	25	72
NP4	3.0	1.1	27	12	56	1	69
NP6	1.7	0.9	31	13	52	1	66

TABLE 2.3

COMPARISON OF POWDER PATTERNS FOR CHLORITES

PENNINITE*			SEPARATE BS27	
d (Å)	I/I°	hkl	d (Å)	I/I°
14.3	6	001	14.2	5
7.18	10	002	7.15	10
4.79	10	003	4.78	6
4.61	2	020	4.60	1
3.592	10	004	3.58	10
2.873	6	005	2.87	6
2.590	3	$131;20\bar{2}$	2.60	2
2.548	4	$13\bar{2};201$	2.54	3
2.449	4	$1\bar{3}2;20\bar{3}$	2.44	3
2.392	3	$13\bar{3};202$	2.40	3
		006		

* After BRINDLEY and ROBINSON (1951)

TABLE 2.4

EXPANSIONS OF INTERLAYER MINERAL WHEN SUBJECTED TO VARIOUS TREATMENTS

d (Å)	Treatment
10.9	Natural mineral from sample NP4.
9 - 17	Water saturation.
10.5	Heating to 110°C, rapid rehydration occurs.
9.8	Heating to 400°C, collapse is irreversible.
12.3	Glycolation.
10.9	K^+ saturation.
11.9	Mg^{2+} saturation.
12.3	Na^+ saturation.
12.2	Ca^{2+} saturation.
11.1	Ba^{2+} saturation, diffuse peak.

TABLE 2.5

CLASSIFICATION OF ILLITES IN ROOF ROCKS.

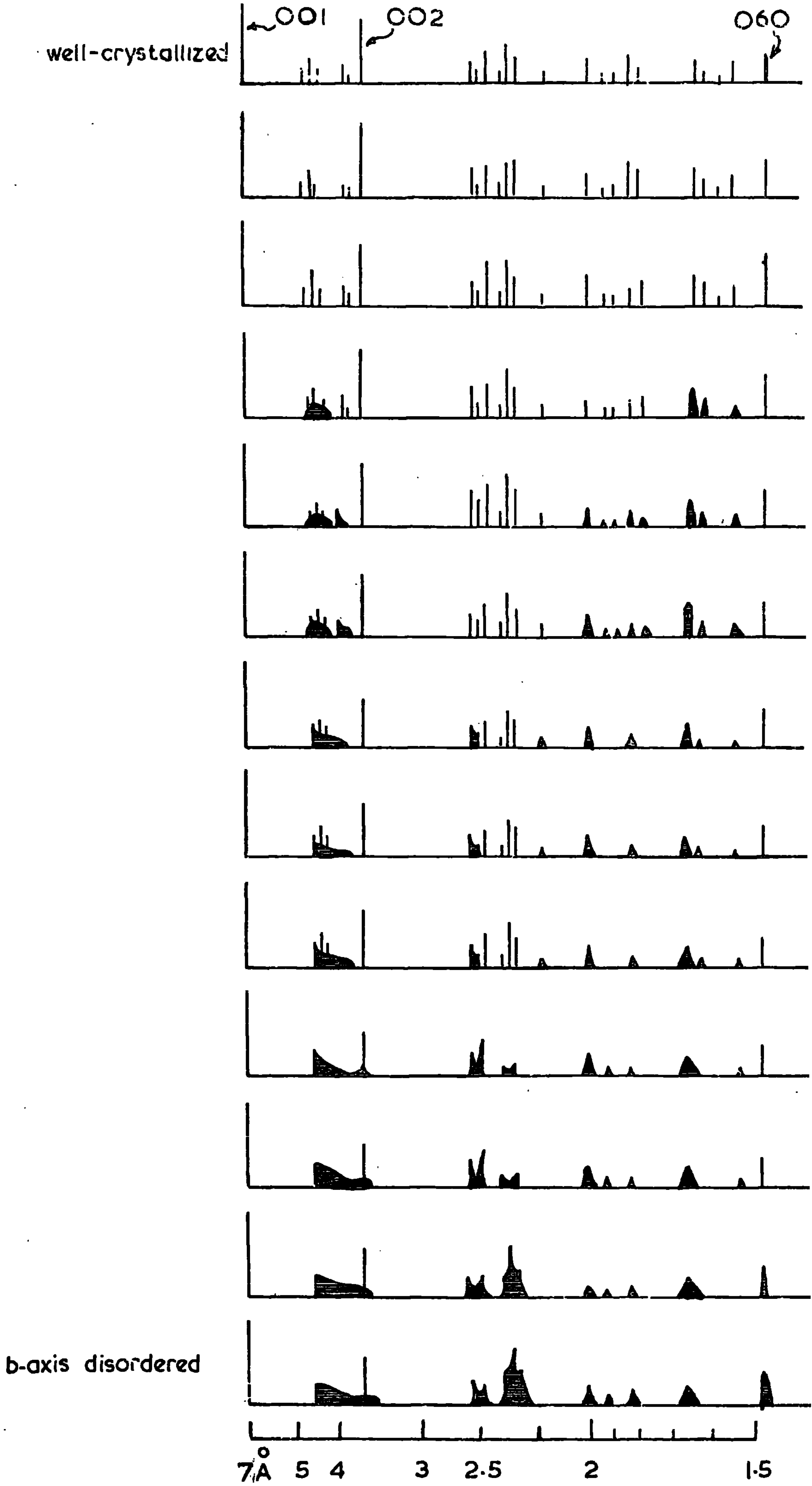
SAMPLE	CLASSIFICATION	POLYMORPH	CONCENTRATION
LL1	g	?	27
LL2	g	?	30
LL3	g	?	28
LL4	g	?	24
LL5	g	?	27
LL13	g	?	n.d.
LL16	g	?	n.d.
BS2	a-b	2M	20
BS4	a-b	2M	21
BS12	b-c	2M	37
BS14	b-c	2M	38
BS20	c-d	2M	31
BS22	c-d	2M	31
TB1	a-b	2M	25
TB2	a-b	2M	40
TB3	a-b	2M	20
ST1	c	?	n.d.
ST2	c	?	n.d.
NP1	c and f	?	n.d.
NP3	c and f	?	n.d.
KB2	c	?	n.d.
KB3	c	?	n.d.
KB13	c	?	n.d.
KB15	c	?	n.d.
KB21	c-d	?	n.d.
KB23	c-d	?	n.d.
KB37	c-d	?	n.d.
KB39	c-d	?	n.d.

TABLE 2.6

CLASSIFICATION OF ILLITES IN SEATEARTHS

SAMPLE	CLASSIFICATION	POLYMORPH	CONCENTRATION %
DY5	c	2M	37
DY6	c	2M	34
DY3	c-d	2M	38
DY4	c-d	2M?	25
DY1	c-d	2M	31
DY2	c-d	2M?	24
FB1	c	2M	67
FB2	c	2M	65
FB3	c	2M	67
FB4	c	2M	68
FB5	c	2M	73
FB6	c	2M	63
FB7	d	?	15
FB8	d	?	16
FB9	d	2M?	27
FB10	d	2M?	29
FB11	e	?	14
FB12	e	?	9
TB5	b	2M?	18
TB7	b	2M?	22
BS6	d	2M?	28
BS8	d	2M?	24
BS16	d	?	16
BS18	d	?	20
BS25	d-e	?	22
BS27	d-e	?	25
ST4	e	?	10
ST6	e	?	6
KB5	d	?	12
KB8	d	?	12
KB18	d	?	11
KB20	d	?	12
KB25	e	?	14
KB27	e	?	10
KB43	e	?	8
KB45	e	?	9
LL6	g	?	45
LL8	g	?	45
LL18	g	?	43
LL20	g	?	43
NP4	f	1Md	56
NP6	f	1Md	52

FIG. 2·1 DIAGRAMATIC REPRESENTATION OF X.R.D. DIAGRAMS FOR KAOLINITES. (AFTER MURRAY AND LYONS (1956))



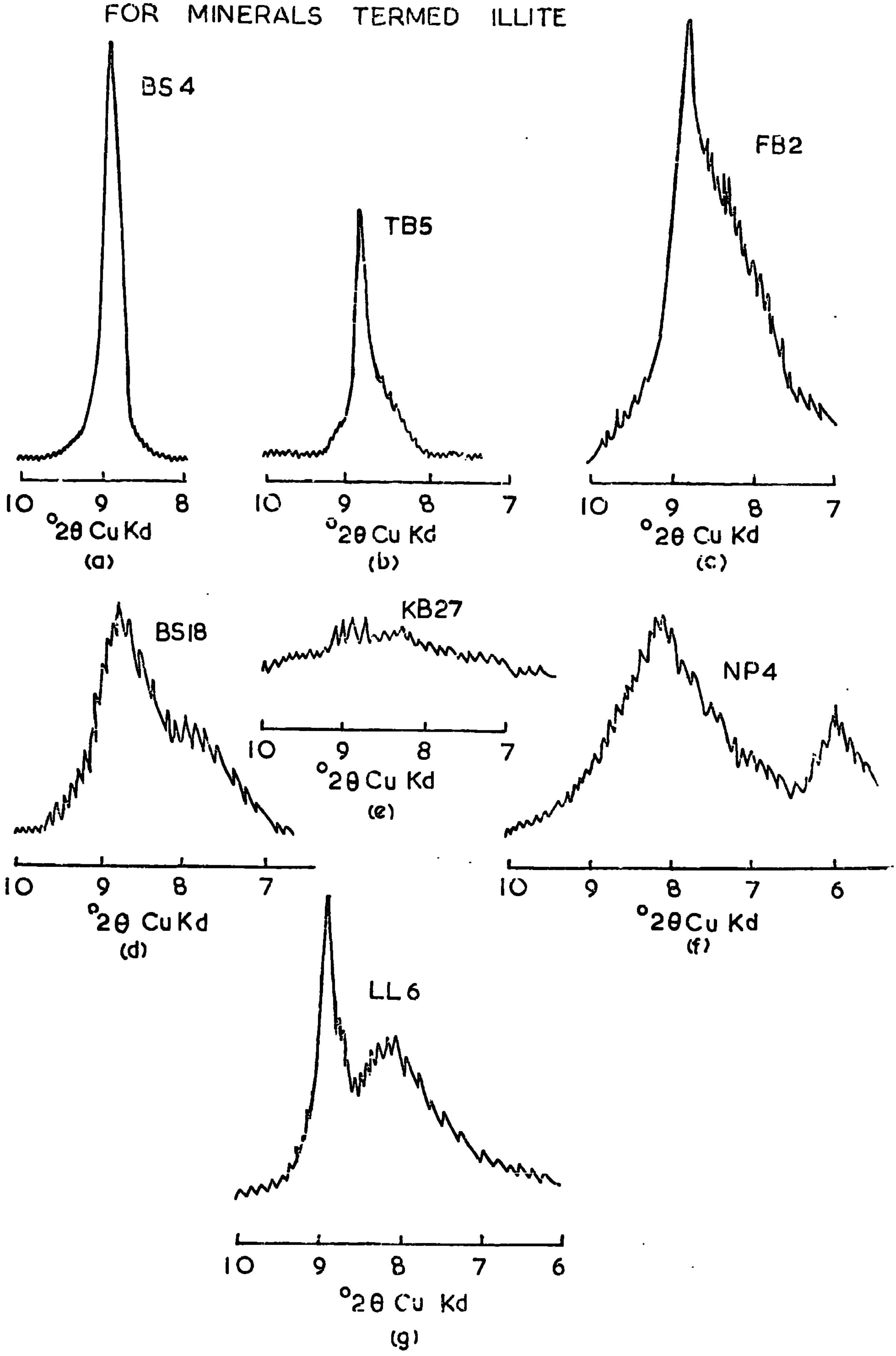
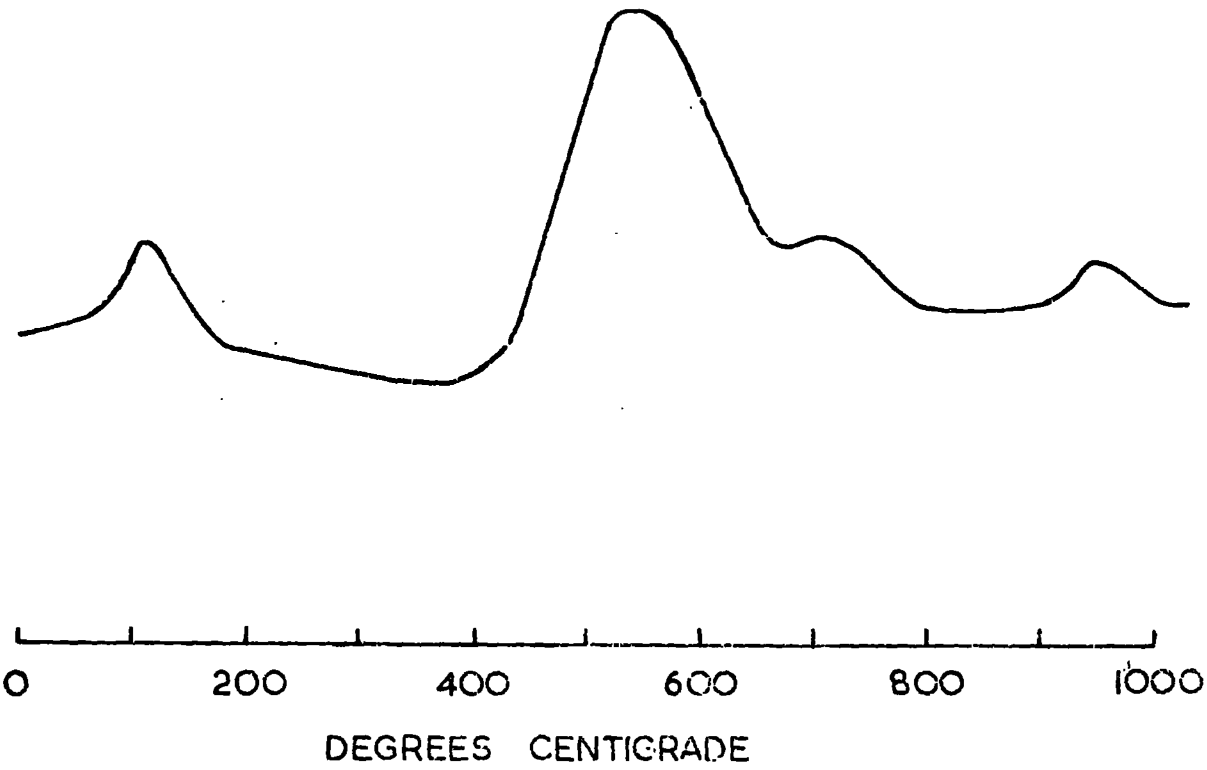


FIG. 2·2 VARIATION IN APPEARANCE OF BASAL REFLECTIONS FOR MINERALS TERMED ILLITE

FIG.2·3 DIFFERENTIAL THERMAL CURVE OF INTERLAYERED MINERAL



K$^+$ saturated mineral. Heating rate 10°C / min

2.7 REFERENCES TO CHAPTER TWO

BRINDLEY, G. W., (1961), Chlorite minerals, Ed. G. Brown, Mem. Min. Soc. Lond., Chapter 6.

BRINDLEY, G. W., and ROBINSON, K., (1947), X-ray studies of some kaolinitic fireclays., Trans. Brit. Ceram. Soc., 46 49 - 62.

CAILLERE, S., and HENIN, S., The chlorite and serpentine minerals, In, The differential thermal investigation of clays, Ed. R. C. Mackenzie, Mem. Min. Soc. Lond., Chapter 8.

COLE, W. S., and HOSKING, J. S., (1957), Clay mineral mixtures and interstratified minerals., In, The differential thermal investigation of clays, Ed. R. C. Mackenzie, Mem. Min. Soc. Lond., Chapter 10.

FRANCIS, E. H., (1961), Thin beds of graded kaolinitised tuff and tuffaceous siltstones in the Carboniferous of Fife., Bull. Geol. Surv. Gt. Brit., No, 17, 191 - 215.

MACEWAN, E. M. C., RUIZ AMIL, A., and BROWN, G., (1961), Interstratified clay minerals., In, The X-ray identification and crystal structures of clay minerals, Ed. G. Brown, Mem. Min. Soc. Lond., Chapter 11.

MURRAY, H. H., and LYONS, S. C., (1956), Degree of crystal perfection of kaolinite., Ed. A. Swineford, Clay and clay minerals, 31 - 40.

SCHULTZ, L. G., (1958), Petrology of underclays., Bull. Geol. Soc. Amer., 69, 363 - 402.

SPEARS, D. A., (1970), A kaolinite mudstone (tonstein) in the British Coal Measures., Jour. Sed. Pet., 40, 386 - 394.

TAYLOR, R. K., (1971), The petrology of the Mansfield Marine Band, Proc. Yorks. Geol. Soc., In Press.

TREWIN, N. H., (1968), Potassium bentonites in the Namurian of Staffordshire and Derbyshire., Proc. Yorks. Geol. Soc., 37, 73 - 91.

WILSON, M. J., (1965), The origin and geological significance of South Wales underclays., Jour. Sed. Pet., 35, 91 - 99.

YODER, H. S., and EUGSTER, H. P., (1955), Synthetic and natural muscovites., Geochim. Coschim. Acta, 8, 225 - 280.

CHAPTER THREE

CHEMICAL AND MINERALOGICAL VARIATION WITHIN SEATEARTHS

3.1 DISTRIBUTION OF MINERALS IN SEATEARTHS

The mineralogy of seatearths is defined essentially by five mineral species and organic carbon. They are :- kaolinite, illite, quartz, chlorite, carbon, and siderite. The first three of these are found to make up 92 percent, on average, of any seatearth and the mineralogy of seatearths is essentially confined to the system kaolinite - illite - quartz. The qualitative mineralogy has been discussed in Chapter two, and the frequency distributions of the various minerals in the 42 analysed Upper Carboniferous seatearths are shown in Figs. 3.1a-c. The distributions are plotted assuming both normal and lognormal models. All the relevant statistics are given in Table 3.1. The histograms shown in the figures are plotted in terms of standard deviations about the mean for the horizontal axis. Frequency is represented by the vertical axis. From Table 3.1 it can be seen that the distributions of the minerals are rarely in good agreement with either the normal or lognormal distribution model. Only organic carbon shows a good fit to the lognormal model, however, the distributions of siderite, chlorite, quartz and illite show a better fit to the lognormal rather than normal model. Total clay and kaolinite show distributions more closely normal than lognormal. Very little is known about the frequency distributions of minerals in sedimentary rocks and since very many simple statistical tests assume that the population being tested is normally distributed conclusions drawn from such tests can be entirely erroneous. From the present data it is concluded that minor mineral components (e.g. siderite, chlorite, and organic carbon) have frequency distributions approaching lognormality whereas major components (e.g. total clay and kaolinite) tend to fit the normal distribution model. Components of intermediate importance have intermediate distributions (e.g. quartz and illite). RODIONOV (1965) has investigated the frequency distributions of elements and minerals in igneous rocks and concludes:-

(a) The vast majority of minerals in igneous rocks are approximately lognormally distributed.

(b) Minerals which are approximately normally distributed are, characteristically, the result of superimposed processes.

SHAW (1961) suggests that the mineral distributions in sediments will be complex since the minerals result from many interacting processes. The data for seatearths tends to support this theory.

3.2 DISTRIBUTION OF CHEMICAL COMPONENTS IN SEATEARTHS

Frequency distribution histograms have been plotted for 29 chemical components, in the same way as those for the minerals. The frequency distribution histograms for major and minor components are given in Figs. 3.2a-e and 3.3a-f respectively. The relevant statistics are given in Tables 3.2 and 3.3. The chi squared statistic of Pearson is generally accepted as the most reliable of the three parameters, assymetry, kurtosis, and chi squared, given in the tables. On the basis of this statistic it can be seen that TiO_2, Al_2O_3, P_2O_5, Mn, Nb, and Pb fail to fit either of the two proposed models. TiO_2, Mn, and Nb, however, fit the lognormal model if a single extreme sample is discarded in each case. The sample size (42) was too small to reflect the true distribution of these components. P_2O_5 fails to fit either model, mainly because the chosen sample interval ($\frac{1}{3}$ standard deviation) was less than the precision of the determination. Thus, the recorded variance of P_2O_5 was largely error variance. Pb fails because 32 of 42 samples contained Pb below the detection limit of the analytical method. The lack of fit shown by Al_2O_3 probably results partially because of its high error variance, and partially because Al_2O_3 contents are the products of a very complex series of processes. It is concluded that SiO_2, Al_2O_3, CaO, P_2O_5, Ni, Y, and Zr tend towards normal distribution whereas TiO_2, Fe_2O_3, MgO, Na_2O, K_2O, S, C, H_2O^+, H_2O^-, CO_2, Ba, Cr, Cu, La, Mn, Nb, Rb, Sc, Sr, V, and Zn are better approximated by the lognormal frequency distribution model. In deciding on the best model all three statistics were taken into consideration. Many variables can be attributed to either model but almost all components showed reasonable correspondence with the lognormal model. This is consistent with the findings of RODIONOV (1965) for igneous rocks. ONDRICK and GRIFFITHS (1969) found that most components followed the lognormal distribution in 119 samples of greywacke. They also found that few components showed very good fits to either normal or lognormal models; this is also true of the seatearth data where only S, C, and Cu fitted a particular model according to all three statistics. Having determined that the lognormal distribution was followed by most components the data was transformed to logarithms prior to further statistical analysis.

3.3 RELATIONSHIP BETWEEN CHEMISTRY AND MINERALOGY IN SEATEARTHS

Qualitative mineralogy of seatearths was dealt with in Chapter two. Quantitatively only three minerals are important in seatearths :- quartz, illite, and kaolinite. Chlorite, siderite, and carbonaceous matter are normally present in small but significant amounts. Pyrite, apatite, rutile, and calcite are also present but the total of these components rarely exceeds 2 percent. The only other mineral phase which may be present is feldspar and although none was detected by X-ray diffraction its presence cannot be discounted. DIXON et al. (1970) report an average of about 2 percent feldspar in seatearths from the East Midlands. Fig. 3.4 shows the 42 seatearths examined in this study plotted in the triangle quartz - (illite + chlorite) - kaolinite. Data from NICHOLLS and LORING (1962) and DIXON et al. (1970) are plotted for comparison.

The wide mineralogical variation present in seatearths is not strongly reflected in their major-component geochemistry. SiO_2, Al_2O_3, and total water make up about 90 percent of a seatearth and Fig. 3.5 illustrates the rather restricted variation of these major chemical components. Other major components show more variation but the variance of almost all chemical components within seatearths is very much less than that encountered in roof rocks.

In order to assess the control of major mineral components on the chemistry of seatearths stepwise multiple regression methods were used. 29 chemical components were treated as dependent variables and 7 mineral components as independent variables. In practice the components of the mineralogical analyses were far from independent as illustrated in Table 3.4, which is based on logarithmic data. The correlations between the "independent" variables were taken into consideration when interpreting the results of the analysis. SHIMP et al. (1969) have used the same procedure to predict trace element contents from mineralogy in marine and non-marine sediments. For the present data prediction of both major and trace components is attempted. Table 3.5 gives details of the stepwise multiple regression procedure. Only "independent" variables which significantly improve the multiple correlation coefficient were included.

Most major components can be adequately predicted by the mineralogy. The exceptions are TiO_2, CaO, S, and P_2O_5. These inadequacies could perhaps be explained if rutile, pyrite, apatite, and perhaps calcite had been included in the mineralogical analyses. Fe_2O_3 and MgO are particularly interesting in that the multiple correlation coefficient of Fe_2O_3 shows a much greater increase than that of MgO with the addition of siderite to the regression. C and CO_2 were used in computing the mineralogical analyses hence the excellence of their prediction.

The prediction of trace element contents from the mineralogy is much less certain than that of major elements. Ba, Cr, Cu, Mn, Rb, Sc, Sr, V, Zn and Zr are reasonably predictable and are essentially elements which are associated with major mineral phases. Of the remaining elements Nb is thought to be associated with rutile, Ni and Pb with pyrite, while La and Y may be related to detrital heavy minerals which are controlled by provenance. The correlations suggest that Ba, Cu, Rb, and Zn are essentially associated with illite, where they presumably replace K. Sr also shows a secondary association with illite, as does Pb. Cr and V show strong associations with kaolinite and probably replace Al^{3+} in the lattice. Cu, Pb, Rb, and Zn show secondary associations with kaolinite which are thought to reflect surface adsorption. Mn is strongly associated with chlorite, although the influence of siderite is noticeably more important than in the case of Fe. Mn, Ni, Sr, Zn, La, and Y show coherence with siderite. Mn may be readily explained as a replacement for Fe in the lattice and Ni and Zn are of similar sizes to substitute for the ferrous ion. Sr, however, is a relatively large ion and only substitutes in the aragonite structure to a significant extent. X-ray diffraction charts of siderite rich samples show that small amounts of carbonate other than siderite are present and since CO_2 content has been recalculated to siderite Sr may well be associated with a minor carbonate phase. La and Y are of similar sizes to Sr and could replace this element. However, the association of these elements with siderite is rather tenuous and only a very small proportion of their variance is accounted for in this way. Zr appears to be the only trace element for which quartz is a significant predictor in the positive sense. This is thought to be a reflection of the covariance of detrital quartz and zircon.

Carbon appears only to be useful in the prediction of Pb and the analytical data for this element is poor. The form of the carbon in the sediments is macroscopic plant remains and TOURTELOT (1964) also found very few minor elements were associated with this form of carbonaceous debris.

So far negative coefficients have been ignored since these represent indirect associations. The negative association of C with Ba, for example, may represent an environmental factor. Thus Ba retention in the sediment is favoured by a process which results in a lower carbon content. Oxidation is such a process, rate of deposition perhaps is another. Many elements show a negative association with quartz (La, Sc, Sr, V) and since quartz may roughly indicate rate of deposition it could be infered that the accumulation of these elements in the sediments may be favoured by slow deposition. Since leaching would tend to remove chlorite and illite it is argueable that Cr, Cu, La, Nb, Pb, Sc, and Zr which show negative associations with these minerals, may be retained during leaching. Although no direct conclusions can be drawn from these associations they will be born in mind for future interpretation of the origin and genesis of seatearths. Sc is the only element to show a significant association with total clay. NORMAN and HASKIN (1968) have noted the covariance of Sc with ferric iron and CARROLL (1958) has discussed the role of clay minerals in the transportation of Fe. It is thought that the association of Sc and total clay may be a function of the transportation of iron oxides/hydroxides as coatings around clay minerals. Sc may be reatined by the clays during diagenesis whereas Fe is reduced and takes its place in diagenetic siderite and pyrite.

The stepwise multiple regression of the data showed that 75 percent of the variance of the major chemical components and 47 percent of that of trace elements could be explained in terms of the mineralogical analyses. Thus mineralogy is a very important factor in determining both the major and trace element geochemistry of seatearths. The importance of mineralogy is even greater after removal of error variance. If an arbitary 10 percent error variance is assumed very little of the major element geochemistry remains unexplained.

3.4 COMPARISON WITH PREVIOUS DATA ON SEATEARTHS

Since the major element geochemistry and mineralogy of seatearths are so closely linked, comparison of the present work with that of previous authors can be made equally well on either basis. DIXON et al. (1970) give an average mineralogical composition for Lower Coal Measures' seatearths from the East Midland Coalfields and an average chemical composition for 45 British Carboniferous seatearths was obtained from the data of ENNOS and SCOTT (1924). Table 3.6 shows the present data compared with the published data mentioned above. The major element data for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, total water, and CO_2 show excellent agreement and the MgO figures are reasonably similar. CaO, K_2O, Na_2O, P_2O_5, S and C show very marked differences. These differences may be readily explained in terms of mineralogical variations. The data of ENNOS and SCOTT (1924) suggests that their average seatearth is less illitic (though with a similar Na/K ratio), contains significantly less organic matter, and has a significantly greater phosphate content. The latter difference may result from error or differences in analytical technique. The discrepancies between the average mineralogical composition given by this work and that of DIXON et al. (1970) is large. However, the difference in major element geochemistry of the two mineralogical compositions would be quite small. Before discussing the source of the deviations it must be noted that the average compsition given by DIXON et al. is comfortably within the range of compositional variation found in this work. The deviations are attributed to :-

(a) DIXON et al. (1970) include only seatearths from the Lower Coal Measures of the East Midlands. The present work involves seatearths from most Northern Coalfields and includes horizons from the base of the Namurian to the Similis-Pulchra Zone of the Coal Measures. Thus the data of DIXON et al. (1970) may be considered as a subset of the present data, not a comparable set.

(b) The mineralogical analyses were carried out in different laboratories by different methods and the analytical precision of both methods should be considered in the comparison. When this is considered almost all the differences could result from laboratory bias.

From the above discussion it is apparent that the sample obtained in this study is comparable with that obtained by previous workers and the similarity of the major element data is thought to indicate that a representative sample suitable for statistical analysis has been collected.

3.5 R-MODE FACTOR ANALYSIS OF SEATEARTHS

In previous sections it has been shown that the data for major elements shows little variance, this tends to make this data unsuitable for factor analysis, a technique which involves the analysis of variance. The mineral composition of seatearths, however, is highly variable (and consistent with the major element data) and it was therefore decided to factor analyse the mineralogical data, together with the trace element data, for the 42 seatearths involved in the study. Pb was excluded from analysis since it rarely exceeds the analytical detection limit (See Appendix I). 21 variables, chlorite, illite, kaolinite, total clay, siderite, carbon, quartz, Ba, Cr, Cu, La, Mn, Nb, Ni, Rb, Sc, Sr, V, Y, Zn, and Zr, were included and the data was transformed to a logarithmic base prior to factor analysis. Table 3.7 shows the analytical data for the 42 seatearths. 8 factors were extracted which explained 87.5 percent of the variance of the data. Table 3.8 shows the eigenvalues extracted from the correlation matrix. A varimax rotation was carried out and a subsequent series of five promax solutions obtained. Fig. 3.6 shows the behaviour of factor loadings, which account for more than 10 percent of the variance of an element, on rotation. The promax loadings have been normalised for the purposes of this figure, unlike those of Figure 4.7. Fig 3.7 illustrates the important loadings of the factors after rotation.

Factor one has a strong positive loading for Ni and two lesser negative loadings for Cu and Zr. The factor shows only one significant correlation which is a small positive one with factor five (carbon v quartz). Factor one is interpreted as a Ni v detritals factor. The Zr loading is thought to represent inorganic detritus since Zr is related to both quartz (as covarient zircon) and clay minerals (as included zircon). The Cu loading may indicate that Cu associates with the clay minerals rather than the sulphide phase that the Ni loading is thought to represent. The correlation with factor five indicates that Ni accumulation is favoured in carbonaceous sediments, however, since the carbonaceous matter in seatearths is essentially macro plant remains adsorption of Ni is thought to be unlikely. The major element data shows S to be quite strongly covarient with C and it is thought that the Ni loading represents a sulphide phase. Factor three is very similar to factor one but the correlation matrix (Table 3.9) shows the two factors to be independent. The interpretation of factor one is almost entirely speculative and no evidence is available to either confirm or deny it. However, the factor represents only a very small part of the total variance of the data.

Factor two has strong positive loadings for kaolinite and Cr and a lesser positive loading for La. Illite and Sr show strong negative loadings and Ba, Rb, and chlorite have moderate loadings in the same sense. The factor has a strong negative correlation with fator three (Zn v detritals) and a lesser negative loading with factor four (rare earths). Factors one and five (carbon v quartz) show a small positive correlation. Factor two is interpreted as a degree of leaching factor. It is thought to represent the destruction of illite and chlorite by leaching to form the more stable clay mineral kaolinite. The loadings of Cr and La are thought to indicate that Cr^{3+} and La^{3+} replace Al in the clay mineral lattice and are thus preserved in the leached sediment. Sr, Ba, and Rb are thought to be removed by the action of leaching. The relative strengths of the loadings of Sr, Ba, and Rb are consistent with the results expressed in Chapter five on the relative ease with which these elements are leached. Fig. 3.8 shows factor scores for factor two plotted against the weathering potential index devised by REICHE (1943). The index is based on the major element composition of the rock and is given by :-

$$W.P.I. = \frac{100 \times \text{moles}(Na_2O + K_2O + CaO + MgO - H_2O)}{\text{moles}(Na_2O + K_2O + CaO + MgO + SiO_2 + Al_2O_3 + Fe_2O_3)}$$

The correlation obtained is reasonable and tends to confirm the interpretation of factor two. Factor two accounts for a substantial part of the total variance of the data.

Factor three has a strong positive loading for Zn and a lesser positive loading for Rb. Zr and Sc show moderate negative loadings. The factor has a moderate positive correlation with factor four (rare earths) and also with factor seven (clay v quartz). Factor three is interpreted as a Zn v detritals factor. The loadings of Zr and Sc are thought to represent detritals (as explained for factor one). Zn shows a covariance with Pb (not included in the factor analysis) which indicates the posibility of a Pb/Zn mineralising fluid. If such a fluid passed through the sediments then some mechanism to "fix" the Zn is necessary. The strong correlation with factor two indicates that the less leached sediments were more receptive and it is tentatively suggested that illite may have been responsible for the retention of Zn. The loading of Rb on factor three can thus be explained. As for factor one the interpretation is highly speculative, however, once again only a small amount of the total variance of the data is involved.

Factor four has positive loadings for Y, La, Sr, and to a lesser extent Rb. Zr shows a slight negative loading which decreases in significance on rotation. Y, La, and Sr are similar in that they all replace Ca in apatite, however, the P content of the sediments is very low and cannot be used to explain the variation of these elements. Fig. 3.9 shows the variation of factor loadings for factor four with the stratigraphy. The scores are consistently low in the Lower Westphalian. All the lower Westphalian samples were drawn from Northumberland and Durham whereas those higher in the sequence were from Yorkshire and those in the Namurian mainly from Scotland. It is concluded that factor four is a function of provenance. It can be argued that the samples with low factor scores were deposited some distance from the crystalline igneous source rocks of stable continental blocks and that the major source of Y, La, and Sr would be acid igneous intrusives or metamorphic terrains. Factor four is interpreted as a provenance factor related to acid igneous source material. The positive correlation with factor seven (clay v quartz) is thought to indicate that clay minerals are responsible for the retention of Y, La, and Sr in the sediments.

Factor five has a very strong positive loading for C opposed by lesser loadings for Ba and quartz. The carbon/quartz balance is thought to be a function of several related factors :-

(a) Rate of deposition. Fast deposited sediments tend to contain greater amounts of coarse grained quartz.

(b) Oxidation. Carbonaceous matter is easily oxidised and is only preserved under reducing conditions or fast deposition when the carbon is rapidly buried.

(c) Proximity to shoreline. Carbonaceous sediments occur close to the source of the carbonaceous material, in this case the delta/swamp.

(c) is thought to be the dominant factor in this case. It is thought that (a) is also involved but the length of the last period of reworking and not the initial rate of deposition is the controlling factor. (b) is not thought to be a strong influence since Eh conditions for seatearth deposition were probably relatively constant and phisical abrasion of large particles of carbonaceous material is likely to have had more influence on the rate of oxidation than Eh. The amount of carbon in a seatearth is not a feature of the original sediment but rather of the last cycle of reworking before the coal was formed.

Factor six has a strong positive loading for Nb and lesser loadings for siderite, V, and quartz. The factor shows a single low positive correlation with factor two indicating that the factor is favoured in strongly leached sediments. Nb is covariant with the major component TiO_2 and is thought to substitute for Ti in the rutile lattice. The siderite loading is thought to be misleading since all carbonate was recalculated as siderite. Thus the loading will be considered as CO_2 rather than siderite to avoid erroneous conclusions. All the loadings on factor six are consistent with its interpretation as a detrital factor, however, the stratigraphic variations of the loadings are also of interest. Fig. 3.10 shows that the scores show a consistent and significant upward increase though the Upper Carboniferous. It is thought that factor six results from a consistent change of source material. Nb, V, Ti, and CO_2 are all typical of basic igneous rocks. During the Lower Carboniferous extensive flows of basaltic lavas occured in northern Britain. PRICE and DUFF (1969) have shown that tonsteins probably derive from volcanic ash and seatearths LL6, 8, 18, 20, NP4, 6 show evidence of volcanic addition. Factor six is thought to be due to the increasing amount of erosion of Lower Carboniferous lavas through the Upper Carboniferous period. The effect of progressive erosion of basic lavas is to some extent counteracted by the sampling procedure which gathered samples progressively southwards as the stratigraphic column was climbed. Factor six accounts for a comparatively small amount of the total variance of the data. From the preceding discussion it can be seen that the interpretation of factor six is based on rather tenuous evidence. The possibility of attributing factor six to analytical error has been examined and it is true that the

Nb and CO_2 were not the most precise determinations, however, such a conclusion evades rather than replaces interpretation. Factor loadings for factor six show a steady increase upwards through the Upper Carboniferous.

Factor seven has high positive loadings for total clay, Sc, and V and lesser loadings for Cu, Cr, and Rb. An opposed high loading for quartz is present and Zr has a lesser negative loading. A minor Zn loading in the negative sense is also present but is not regarded as significant since the determination of the element may be of relatively poor precision. Factor seven is clearly a clay v quartz factor. Zr loads with quartz, presumably indicating detrital zircon. The trace elements loading with total clay fall into two groups; Sc, V, and Cr, which presumably replace Al, and, Rb and Cu which are probably representative of adsorbed elements. The term rate of deposition is rather ambiguous when applied to seatearth deposition since these sediments are thought to have been deposited and re-deposited several times. The clay : quartz ratio, however, is probably determined by the relative grain sizes of the two phases and the relative ease with which they may be transported; particle shape is also effective in determining the ratio. The very limited variation of quartz and total clay in the sediments emphasises the similarity of conditions under which seatearths accumulated. Factor seven is, of course, an expression of the analytical "constant sum" and due to the limited variation in total clay, factor two may also be a result of this effect. The "constant sum", however, though inevitable, does reflect variations attributable to geological processes, and is a real property of all analytical data. Almost all petrological interpretation (triangular diagrams, tetrahedra etc) is based on forced constant sums, and, although care must be taken in interpretation, the constant sum in the present data is not thought to invalidate any of the interpretation. Factor seven is interpreted as a sorting factor related to the mean rate of deposition of the material present in the seatearth. Areal variation of seatearths may strongly effect the clay : quartz ratio but such variation through winnowing, etc., is not thought to seriously influence factor two which shows only a very slight negative correlation with factor seven (See Table 3.9). Factor seven shows significant positive correlations with factors three and four indicating that Zn etc. and La, Y, and Sr tend to be enriched, and the factors enhanced, in more argillaceous sediments. This is probably due to the fact that clay minerals carry the vast majority of the trace elements by inclusion, substitution or sorption.

Factor eight has high positive loadings for Mn, chlorite, and siderite. V and Ba have slight negative loadings and Cu also has a minor loading in this sense. The factor is thought to be essentially a chlorite factor. Siderite is thought to develop in chlorite rich sediments because iron is available. Siderite shows a significant positive correlation with chlorite and the correlation would probably be even stronger if siderite did not form at the expense of chlorite. During diagenesis chlorite, especially fine grained chlorite, is possibly destroyed and the Fe taken into siderite. Large grains of chlorite often have ragged edges and sometimes appear to be recrystallised. The covariance of Mg with chlorite is very much stronger than that of Fe and Mn, whereas for siderite the reverse is true. During diagenesis Fe and Mn may be taken up in diagenetic phases thus leaving essentially Mg -rich chlorites. Probe analysis of these "altered" chlorites would have proved interesting but clay minerals tend to "blow up" under the electron beam due to loss of structural water. Either only Mg-rich chlorites survive in sediments or chlorites are converted by diagenesis, in varying degrees, to Mg-rich forms. The opposed loadings of Ba, V, and Cu are slight but a consistent interpretation for these loadings can be found. Diagenetic siderite formation is often limited and preceded by sulphide formation. Since both sulphide and carbonate compete for Fe they will tend to show an antipathetic relationship. Both CURTIS (1969) and NICHOLLS and LORING (1962) report Ba, V, and Cu covarient with pyrite in Coal Measure sediments and this reasonably explains the opposed loadings of factor eight. Fig. 3.11 shows factor scores for factor eight plotted against Fe_2O_3 + MgO in order to demonstrate the association of these major components with diagenetic processes. Factor eight shows a significant negative correlation with factor seven. This is thought to reflect the covariance of coarse flakes of chlorite and detrital quartz, rather than clay. Coarse muscovite is also found but this makes up only a small proportion of the total "illite" content and shows no significant loadings in the factor pattern.

To summarise, the eight factors extracted, were :-

(1) Ni v Cu factor, possibly related to diagenetic sulphide formation?

(2) leaching factor controlling the composition of the clay mineral fraction of the sediments.

(3) A Zn ? mineralisation factor.

(4) A provenance factor indicating acid source rocks

(5) A proximity to palaeoshoreline factor.

(6) A ? provenance factor indicating basic source rocks.

(7) A sorting factor controlling the clay : quartz ratio.

(8) A chlorite factor related to diagenesis.

As indicated, factors one, three, and six are the subject of rather speculative interpretation. The important factors are two, five, seven, and eight.

3.6 STRATIGRAPHIC VARIATION IN SEATEARTHS

Two rather minor factors (four and six) in the factor analysis were interpreted as having stratigraphical significance, however, the most important stratigraphic variation is that shown by the leaching factor, factor two. Fig. 3.12 shows the factor scores for this factor plotted against stratigraphic horizon. WILSON (1965) found a similar variation in South Wales seatearths and interpreted an increase in chlorite and illite in higher Coal Measures sediments as a function of palaeoclimate. WILSON (1965) argued that lower rainfall and higher temperatures would result in less leached source material. The stratigraphical variation may result in several ways :-

(a) Change in palaeoclimate.

(b) Change in source of material.

(c) Change in degree of weathering at source.

(d) Change in degree of weathering in the basin of deposition.

All these changes probably occur, however, it is thought that (c) and (d) perhaps induced by (a) are essentially responsible for the variations. Rate of accumulation could also effect the chlorite content and increasingly coarse material may yeild increasing chlorite contents. The origin and genesis of seatearths and their lateral and stratigraphic variations will be discussed in detail in Chapter six.

TABLE 3.1

SUMMARY STATISTICS FOR MINERAL FREQUENCY DISTRIBUTIONS

MINERAL	CHLOR	KAOL	ILL	T.CLAY	QZ	CARBON	SID
MEAN	3.67	48.9	30.1	77.6	18.6	2.54	1.19
MAX	14	76	73	91	44	31.3	9.92
MIN	0	1	5	53	2	0.09	0.26
S.DEV	4.13	21.6	19.6	8.77	9.01	5.06	1.52
ASSYM.N	1.09	-0.27	0.77	-0.73	0.81	4.61	4.55
L	-0.39	-2.38	-0.11	-1.09	-1.31	0.08	0.62
KURT. N	2.73	1.92	2.36	3.38	4.13	26.0	26.2
L	1.93	9.16	2.03	4.38	5.76	2.80	3.72
CHISQ.N	20.1	3.74	4.52	6.29	11.4	60.1	42.7
L	5.05	29.7	4.22	7.29	4.73	4.99	1.08

Underlined parameters are those which do not discount the proposed distribution at the 95% significance level.

L = Lognormal (base e)

N = Normal

TABLE 3.2

SUMMARY STATISTICS FOR MAJOR COMPONENT FREQUENCY DISTRIBUTIONS

COMPONENT	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O
MEAN	54.1	1.19	24.5	2.71	1.05	0.16	0.32
MAX	64.2	3.68	30.1	7.25	1.88	0.39	0.53
MIN	33.2	0.84	18.3	1.18	0.35	0.02	0.10
S.DEV	5.06	0.45	3.30	1.27	0.43	0.09	0.11
ASSYM.N	-1.49	4.17	$\underline{0.01}$	1.33	0.48	0.87	$-\underline{0.18}$
L	-2.33	$\underline{0.08}$	$-\underline{0.17}$	0.47	$-\underline{0.02}$	-0.99	-0.86
KURT. N	8.26	22.9	1.81	4.88	1.86	3.51	2.08
L	12.1	11.3	2.00	2.33	2.10	2.29	$\underline{2.95}$
CHISQ.N	$\underline{5.34}$	38.0	14.3	16.9	20.6	$\underline{7.19}$	$\underline{1.83}$
L	$\underline{7.58}$	17.0	14.3	$\underline{3.29}$	$\underline{10.8}$	$\underline{9.61}$	$\underline{4.57}$

COMPONENT	K_2O	S	P_2O_5	C	H_2O^+	H_2O^-	CO_2
MEAN	2.91	0.43	0.04	2.54	8.69	0.93	0.45
MAX	5.19	2.74	0.09	31.3	11.6	2.09	3.76
MIN	0.98	0.01	0.01	0.09	5.24	0.18	0.10
S.DEV	1.11	0.60	0.02	5.02	1.78	0.57	0.58
ASSYM.N	0.62	2.40	0.87	4.61	$-\underline{0.17}$	0.71	4.54
L	-0.45	$-\underline{0.14}$	-0.26	$\underline{0.08}$	-0.45	-0.28	0.61
KURT. N	$\underline{2.74}$	8.20	$\underline{3.25}$	26.0	1.87	2.28	26.1
L	$\underline{3.38}$	$\underline{3.01}$	2.26	$\underline{2.80}$	2.14	2.42	3.72
CHISQ.N	$\underline{10.3}$	57.6	19.4	60.1	$\underline{6.22}$	$\underline{9.71}$	42.7
L	$\underline{7.24}$	$\underline{3.58}$	17.3	$\underline{4.99}$	$\underline{6.49}$	$\underline{9.98}$	$\underline{1.08}$

Underlined parameters are those which do not discount the proposed distribution at the 95% significance level.

L = Lognormal (base e)

N = Normal

TABLE 3.3

SUMMARY STATISTICS FOR TRACE ELEMENT FREQUENCY DISTRIBUTIONS

COMPONENT	Ba	Cr	Cu	La	Mn	Ni	Nb	Pb
MEAN	586	239	26	53	143	58	21	14
MAX	1620	445	68	106	558	91	72	57
MIN	65	147	6	30	31	17	7	12
S.DEV	352	61	15	17	133	18	11	7
ASSYM.N	1.11	1.13	1.23	0.89	1.63	-0.04	2.87	4.78
L	-0.80	0.34	0.16	0.13	0.64	-0.90	0.65	3.46
KURT. N	4.26	4.80	3.84	3.94	4.71	2.04	12.9	27.0
L	3.81	3.11	2.72	2.45	2.29	4.08	5.28	15.8
CHISQ.N	4.37	2.45	15.3	17.1	48.6	6.31	32.7	103
L	7.69	6.23	10.9	4.63	22.0	8.84	24.9	104

COMPONENT	Rb	Sc	Sr	V	Y	Zn	Zr
MEAN	137	14	125	203	28	71	320
MAX	260	24	260	362	51	774	612
MIN	27	8	37	107	14	10	145
S.DEV	66	3	64	49	9	121	149
ASSYM.N	0.40	0.32	0.65	1.06	0.24	4.83	0.62
L	-0.83	-0.41	-0.02	0.18	-0.29	1.19	0.18
KURT. N	2.08	3.62	2.16	4.68	2.37	27.5	2.04
L	3.70	2.93	2.08	3.68	2.01	5.31	1.66
CHISQ.N	14.6	1.04	11.3	4.08	6.44	52.9	7.27
L	10.4	6.05	4.18	1.77	9.52	10.2	10.6

Underlined parameters are those which do not discount the proposed distribution at the 95% significance level.

L = Lognormal (base e)

N = Normal

TABLE 3.4

CORRELATIONS BETWEEN "INDEPENDENT" VARIABLES IN THE STEPWISE MULTIPLE REGRESSION ANALYSIS

	Chlor	Ill	Kaol	T.Clay	Qz	Sid	Carbon
Chlor	1.00						
Ill	0.62	1.00					
Kaol	-0.52	-0.68	1.00				
T.Clay	0.05	0.23	0.22	1.00			
Qz	0.06	0.07	-0.27	-0.59	1.00		
Sid	0.47	0.38	-0.29	-0.03	0.07	1.00	
Carbon	0.04	-0.20	0.01	-0.16	-0.03	-0.03	1.00

TABLE 3.5

SUMMARY OF STEPWISE MULTIPLE REGRESSION PROCEDURE

Dep. Var.	Step	Ind. Var.	Sign	Cum. Var.	MRC	FR
SiO_2	1	Quartz	+	0.681	0.825	85.352
	2	Total Clay	+	0.782	0.881	69.801
TiO_2	1	Illite	-	0.420	0.648	29.016
	2	Total Clay	+	0.452	0.662	16.106
	3	Quartz	+	0.506	0.693	12.982
Al_2O_3	1	Kaolinite	+	0.335	0.579	20.186
	2	Quartz	+	0.474	0.679	17.566
	3	Siderite	-	0.566	0.737	16.523
Fe_2O_3	1	Chlorite	+	0.543	0.737	47.435
	2	Siderite	+	0.686	0.824	42.677
MgO	1	Chlorite	+	0.677	0.823	83.779
	2	Siderite	+	0.721	0.845	50.435
CaO	1	Carbon	+	0.209	0.458	10.600
	2	Illite	+	0.429	0.644	14.672
	3	Siderite	+	0.486	0.678	11.984
K_2O	1	Illite	+	0.786	0.887	147.104
	2	Kaolinite	+	0.857	0.924	116.773
Na_2O	1	Illite	+	0.565	0.752	51.927
	2	Quartz	+	0.814	0.900	85.611
S	1	Carbon	+	0.446	0.668	32.223
	2	Illite	+	0.559	0.740	24.753
P_2O_5	1	Chlorite	+	0.365	0.604	22.971
	2	Kaolinite	-	0.429	0.644	14.632
	3	Carbon	+	0.491	0.682	12.233
	4	Siderite	+	0.553	0.719	11.430
C	1	Carbon	+	1.000	1.000	-
H_2O^+	1	Kaolinite	+	0.646	0.804	73.125
	2	Illite	+	0.691	0.826	43.568
H_2O^-	1	Illite	+	0.916	0.957	433.728
CO_2	1	Siderite	+	1.000	1.000	-

TABLE 3.5 (CONTINUED)

SUMMARY OF STEPWISE MULTIPLE REGRESSION PROCEDURE

Dep. Var.	Step	Ind. Var.	Sign	Cum. Var.	MRC	FR
Ba	1	Illite	+	0.470	0.685	35.457
	2	Carbon	-	0.645	0.798	35.413
Cr	1	Kaolinite	+	0.399	0.631	26.509
	2	Chlorite	-	0.495	0.694	19.077
Cu	1	Illite	+	0.179	0.423	8.700
	2	Chlorite	-	0.334	0.564	9.788
	3	Kaolinite	+	0.438	0.640	9.872
La	1	Quartz	-	0.159	0.399	7.569
	2	Illite	-	0.230	0.459	5.832
	3	Siderite	+	0.357	0.570	7.043
Mn	1	Chlorite	+	0.429	0.655	30.044
	2	Siderite	+	0.540	0.727	22.873
Ni	1	Quartz	-	0.084	0.289	3.658
	2	Siderite	+	0.171	0.388	4.036
Nb	1	Siderite	+	0.117	0.342	5.312
	2	Illite	-	0.323	0.553	9.309
	3	Carbon	-	0.396	0.605	8.320
Pb	1	Carbon	+	0.065	0.254	2.759
	2	Illite	+	0.141	0.345	3.191
	3	Chlorite	-	0.236	0.444	3.922
	4	Quartz	+	0.277	0.470	3.552
	5	Kaolinite	+	0.356	0.586	3.987
Rb	1	Illite	+	0.580	0.762	55.317
	2	Kaolinite	+	0.706	0.836	46.716
Sc	1	Total Clay	+	0.380	0.616	24.514
	2	Chlorite	-	0.544	0.730	23.234
	3	Quartz	-	0.606	0.765	19.409
Sr	1	Siderite	+	0.286	0.534	15.988
	2	Illite	+	0.401	0.622	13.076
	3	Quartz	-	0.403	0.691	12.801
V	1	Kaolinite	+	0.301	0.549	17.242
	2	Quartz	-	0.443	0.655	15.496

TABLE 3.5 (CONTINUED)

SUMMARY OF STEPWISE MULTIPLE REGRESSION PROCEDURE

Dep. Var.	Step	Ind. Var.	Sign	Cum. Var.	MRC	FR
Y	1	Carbon	-	0.086	0.286	3.555
	2	Total Clay	+	0.133	0.334	2.990
	3	Siderite	+	0.188	0.382	2.930
Zn	1	Illite	+	0.317	0.563	18.563
	2	Siderite	+	0.376	0.601	11.760
	3	Kaolinite	+	0.433	0.636	9.692
	4	Total Clay	-	0.587	0.745	13.160
Zr	1	Quartz	+	0.333	0.577	20.014
	2	Illite	-	0.550	0.734	23.867
	3	Kaolinite	-	0.673	0.810	26.047
	4	Siderite	-	0.714	0.832	23.102

Dep. Var. = Dependent Variable.

Ind. Var. = Independent Variable.

Cum. Var. = Cummulative proportion of variance.

MRC = Multiple Regression Coefficient.

FR = f-test for significance of adding new terms.

TABLE 3.6

COMPARISON OF THE AVERAGE SEATEARTH FROM THE PRESENT STUDY WITH PREVIOUS WORK

Element		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O
Mean	A	58.5	1.26	24.6	2.46	0.74	0.27	1.97
S.Dev		7.93	0.40	5.44	1.47	0.33	0.16	1.11
Max		76.6	3.36	36.0	7.36	1.77	0.78	4.46
Min		44.7	0.81	14.8	0.66	0.20	0.06	0.14
Mean	B	54.1	1.19	24.5	2.71	1.05	0.16	2.91
S.Dev		5.06	0.45	3.30	1.27	0.43	0.09	1.11
Max		64.2	3.68	30.2	7.25	1.88	0.39	5.19
Min		33.2	0.84	18.3	1.18	0.35	0.02	0.98
Diff		-4.4	-0.07	-0.1	0.25	0.31	-0.11	0.94
t-test		3.11	0.76	0.10	0.85	3.75*	3.99*	3.95*

Element		Na_2O	S	P_2O_5	C	H_2O^+	H_2O^-	CO_2
Mean	A	0.17	0.10	0.09	0.45	7.39	1.84	0.35
S.Dev		0.13	0.18	0.04	0.32	2.20	0.65	0.70
Max		0.48	1.15	0.23	1.25	12.17	3.93	3.44
Min		0.01	0.01	0.05	0.01	3.93	0.58	0.01
Mean	B	0.32	0.43	0.04	2.54	8.69	0.93	0.45
S.Dev		0.11	0.60	0.02	5.02	1.79	0.57	0.58
Max		0.53	2.74	0.09	33.3	11.59	2.09	3.76
Min		0.10	0.01	0.01	0.09	5.24	0.18	0.10
Diff		0.15	0.33	-0.05	2.09	1.30	-0.91	0.10
t-test		5.83*	3.42*	7.54*	2.69	3.03+	6.95*+	0.73

Mineral		Chlor	Ill	Kaol	T.Clay	Quartz	Sid
Mean	C	2	38	25	65	33	1
Mean	B	4	30	44	78	19	1

A Mean of 45 major element analyses after ENNOS and SCOTT (1924)

B Mean of 42 major element and mineralogical analyses (This work)

C Mean seatearth for E.Midlands Coalfield after DIXON et al. (1970)

* Difference significant

\+ Total water shows no significant difference

TABLE 3.7

ANALYTICAL DATA FOR 42 SEATEARTHS

SAMPLE	SiO_2	TiO	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	S	P_2O_5
DY5	54.9	0.93	22.1	3.79	1.59	0.27	3.86	0.40	0.44	0.04
DY6	58.9	0.96	18.6	4.87	1.76	0.21	3.91	0.44	0.28	0.03
DY3	52.0	0.90	22.9	4.42	1.50	0.18	3.74	0.43	0.85	0.04
DY4	59.0	0.88	21.0	4.29	1.61	0.17	2.75	0.53	2.14	0.07
DY1	55.0	1.06	21.8	4.66	1.47	0.17	3.30	0.37	0.24	0.08
DY2	64.2	0.86	18.3	2.91	1.09	0.14	2.63	0.40	0.22	0.05
FB1	56.1	1.03	21.9	3.30	1.52	0.13	5.19	0.47	0.10	0.02
FB2	57.0	1.08	22.4	3.42	1.53	0.08	5.00	0.45	0.03	0.03
FB3	56.6	0.95	23.0	2.96	1.30	0.16	5.10	0.44	0.23	0.04
FB4	55.2	0.90	22.4	4.08	1.56	0.17	5.18	0.39	0.32	0.09
FB5	55.6	0.93	24.4	2.48	1.08	0.16	5.10	0.45	0.23	0.05
FB6	56.6	1.10	24.0	2.35	1.05	0.18	4.70	0.35	0.20	0.05
FB7	52.4	1.27	28.7	1.92	0.57	0.03	2.11	0.19	0.10	0.01
FB8	51.7	1.24	28.5	2.96	0.90	0.04	2.55	0.20	0.04	0.02
FB9	54.1	1.18	24.7	2.97	1.03	0.03	2.69	0.25	0.35	0.01
FB10	52.4	1.17	27.0	2.56	0.66	0.09	2.84	0.27	0.31	0.02
FB11	51.3	1.21	30.1	2.09	0.63	0.09	2.15	0.29	0.01	0.02
FB12	62.6	1.58	23.1	1.18	0.35	0.02	1.06	0.23	0.01	0.01
TB5	53.7	1.12	28.9	1.32	0.57	0.10	2.29	0.22	0.12	0.01
TB7	53.3	1.13	28.5	1.54	0.66	0.12	2.87	0.27	0.13	0.02
BS6	51.8	1.10	27.9	1.80	0.79	0.18	2.84	0.28	0.06	0.02
BS8	52.4	1.17	28.1	1.62	0.77	0.17	2.59	0.28	0.14	0.02
BS16	53.3	1.83	27.5	1.80	0.72	0.13	2.11	0.24	0.06	0.02
BS18	53.4	1.28	2.89	1.65	0.63	0.13	2.38	0.26	0.05	0.02
BS25	56.5	1.06	22.3	4.38	1.79	0.17	2.66	0.31	0.09	0.03
BS27	55.9	1.14	23.4	4.62	1.84	0.24	2.44	0.31	0.07	0.03
ST4	50.0	1.89	21.4	2.05	0.79	0.21	1.04	0.14	0.37	0.03
ST6	51.4	3.68	28.3	1.64	0.74	0.24	0.98	0.13	0.12	0.04
KB5	48.1	1.37	29.0	2.07	0.78	0.10	1.77	0.13	0.28	0.02
KB8	43.5	1.18	27.5	2.03	0.80	0.12	2.01	0.14	2.74	0.03
KB18	55.4	1.19	24.8	1.61	0.69	0.10	2.05	0.30	0.08	0.02
KB20	60.4	1.07	23.0	1.42	0.65	0.07	2.37	0.35	0.05	0.01
KB25	48.9	1.35	28.6	1.64	1.37	0.15	2.40	0.17	0.32	0.04
KB27	33.2	0.98	19.8	1.95	0.60	0.17	1.90	0.10	1.47	0.04
KB43	55.2	1.31	27.9	1.84	0.79	0.13	2.11	0.29	0.20	0.04
KB45	56.8	1.05	23.6	2.04	0.76	0.10	2.05	0.33	0.55	0.01
LL6	54.2	1.16	23.5	1.86	0.70	0.33	3.77	0.43	0.88	0.05
LL8	52.4	1.07	22.2	1.99	0.70	0.38	3.69	0.45	2.03	0.06
LL18	55.1	1.06	26.5	1.69	1.05	0.39	3.44	0.43	0.27	0.05
LL20	50.7	0.93	22.5	7.25	1.27	0.36	3.23	0.36	0.20	0.05
NP4	60.4	0.84	19.1	3.39	1.88	0.28	2.21	0.35	0.70	0.05
NP6	60.3	0.92	19.9	3.46	1.54	0.14	2.95	0.44	0.93	0.08

TABLE 3.7 (CONTINUED)

ANALYTICAL DATA FOR 42 SEATEARTHS

SAMPLE	C	H_2O^+	H_2O^-	CO_2	La	Ba	Cu	Ni	Zn	Rb	Sr
DY5	1.80	7.83	1.08	0.98	62	548	17	74	58	221	207
DY6	0.43	7.55	1.01	1.02	56	555	19	91	77	221	183
DY3	2.38	8.49	1.15	0.94	35	520	41	81	83	240	145
DY4	0.65	5.24	0.75	0.85	51	357	6	70	90	132	85
DY1	1.22	8.79	0.99	0.84	65	547	31	82	129	197	170
DY2	0.81	7.14	0.75	0.48	55	420	20	45	69	152	88
FB1	0.35	7.54	1.84	0.50	51	1620	12	78	41	260	218
FB2	0.10	6.40	1.99	0.48	41	1605	28	76	42	255	217
FB3	0.60	6.21	2.09	0.40	44	810	53	75	44	250	230
FB4	0.69	6.64	2.09	0.32	38	1145	45	72	46	238	260
FB5	0.60	6.47	2.03	0.35	55	750	51	52	60	237	250
FB6	0.29	6.92	1.80	0.37	46	830	25	46	31	217	223
FB7	0.15	11.55	0.63	0.35	56	835	18	51	24	105	128
FB8	0.10	10.87	0.57	0.62	66	850	32	82	41	130	140
FB9	0.99	10.49	1.05	0.20	55	810	47	51	43	126	145
FB10	1.11	10.26	0.94	0.30	68	1150	65	51	30	155	148
FB11	0.10	11.29	0.44	0.26	35	800	30	45	40	70	70
FB12	0.09	9.28	0.28	0.15	53	700	20	45	40	30	100
TB5	0.29	10.53	0.70	0.10	30	317	16	42	44	89	37
TB7	0.11	10.48	0.73	0.10	50	490	33	71	31	128	48
BS6	2.41	10.02	0.71	0.10	63	530	27	49	49	139	67
BS8	2.42	9.38	0.76	0.15	37	520	16	40	24	113	77
BS16	2.38	9.22	0.47	0.21	33	430	11	70	29	79	67
BS18	0.71	9.99	0.44	0.12	34	352	17	49	46	90	51
BS25	0.59	9.37	0.50	0.27	33	385	12	40	82	c67	42
BS27	0.51	8.72	0.60	0.21	52	345	16	51	70	80	62
ST4	10.92	10.26	0.20	0.74	56	145	15	77	14	27	71
ST6	1.50	10.57	0.18	0.60	55	110	10	82	10	27	77
KB5	4.11	11.59	0.44	0.25	66	292	20	62	29	77	81
KB8	8.30	11.03	0.37	0.26	106	285	19	74	23	107	135
KB18	3.79	9.28	0.49	0.21	56	300	28	34	19	100	96
KB20	1.00	8.75	0.54	0.24	46	455	23	25	17	100	88
KB25	3.41	10.76	0.49	0.35	91	65	21	35	18	139	142
KB27	31.32	7.78	0.54	0.11	71	100	17	79	26	85	116
KB43	1.01	8.84	0.19	0.10	65	249	12	56	16	100	77
KB45	2.56	9.65	0.47	0.10	62	285	16	88	18	95	117
LL6	4.37	7.23	1.34	0.15	32	905	68	17	83	139	77
LL8	6.37	6.54	1.67	0.45	34	745	19	57	774	139	78
LL18	0.75	7.37	1.32	0.58	76	990	36	46	213	208	240
LL20	0.66	7.34	1.30	3.76	85	405	43	51	284	198	211
NP4	3.02	5.65	1.62	0.40	35	475	15	39	33	87	84
NP6	1.73	5.60	1.56	0.35	43	580	15	39	33	87	107

TABLE 3.7 (CONTINUED)

ANALYTICAL DATA FOR 42 SEATEARTHS

SAMPLE	Zr	Pb	Y	Nb	Cr	V	Sc	Mn	Chl	Ill	Kao	T.C	Qz	Sid
DY5	182	12	23	18	189	226	15	279	10	37	33	80	16	2.6
DY6	173	12	29	17	182	201	14	504	10	34	31	75	22	2.7
DY3	161	14	21	46	217	262	17	411	11	38	35	84	11	2.5
DY4	309	12	18	45	153	139	8	325	9	25	20	54	44	2.2
DY1	216	12	38	23	203	219	10	426	14	31	38	83	14	2.2
DY2	278	12	31	18	151	174	12	225	10	24	34	68	30	1.3
FB1	186	12	36	22	173	178	13	108	3	67	16	86	13	1.3
FB2	212	12	42	21	175	178	12	124	3	65	15	83	15	1.3
FB3	170	12	35	15	181	205	16	93	3	67	17	87	11	1.1
FB4	168	12	40	15	188	196	14	217	3	68	17	88	10	0.9
FB5	182	20	32	17	195	218	17	62	2	73	10	85	13	0.9
FB6	200	12	33	19	184	224	15	54	3	63	17	83	15	1.0
FB7	145	12	29	20	296	210	16	39	1	15	75	91	8	0.9
FB8	150	12	28	20	294	240	19	93	1	16	73	90	9	0.9
FB9	284	12	29	20	265	194	15	93	1	27	50	78	21	0.5
FB10	191	12	36	20	267	244	16	54	1	29	54	84	14	0.8
FB11	340	12	20	21	311	312	16	46	-	14	61	75	24	0.7
FB12	600	12	30	30	247	243	8	31	-	9	46	55	44	0.4
TB5	342	15	14	17	365	186	14	93	-	18	67	85	14	0.3
TB7	327	14	29	19	281	210	18	70	-	22	63	85	15	0.3
BS6	165	14	24	16	264	199	16	85	1	28	53	82	15	0.3
BS8	290	27	15	20	272	208	16	54	2	24	52	78	20	0.4
BS16	561	17	20	22	223	196	9	46	3	16	56	75	22	0.5
BS18	392	12	21	10	241	192	11	46	3	20	54	77	22	0.3
BS25	485	14	17	13	213	162	11	178	10	22	45	77	22	0.7
BS27	580	12	18	11	383	171	12	170	9	25	43	71	22	0.6
ST4	545	12	19	31	253	214	14	108	-	10	59	69	18	1.9
ST6	477	12	18	72	445	362	24	39	-	5	72	77	20	1.6
KB5	370	12	30	19	248	259	17	62	2	12	75	89	7	0.7
KB8	225	12	33	18	255	239	17	124	2	12	73	87	4	0.7
KB18	390	12	34	20	232	168	14	85	-	11	64	75	21	0.6
KB20	549	12	30	15	225	159	13	77	-	12	59	71	27	0.6
KB25	279	12	35	19	282	193	15	54	2	14	73	89	7	0.9
KB27	150	12	16	7	280	320	18	46	-	10	56	66	2	0.3
KB43	441	12	37	24	211	186	13	85	1	8	67	76	23	0.3
KB45	467	12	37	18	228	156	13	77	-	9	56	65	32	0.3
LL6	363	24	20	14	234	166	12	54	1	45	28	74	21	0.4
LL8	287	57	14	14	217	147	10	39	1	45	26	72	21	1.2
LL18	191	12	43	20	226	155	12	46	4	43	28	75	23	1.5
LL20	190	12	51	19	265	176	13	558	4	43	25	72	17	9.9
NP4	612	12	14	8	147	107	8	310	12	56	1	69	27	1.1
NP6	598	12	27	12	177	135	9	279	13	52	1	66	31	0.9

TABLE 3.8

EIGENVALUES EXTRACTED FROM SEATEARTH CORRELATION MATRIX

EIGENVALUE	PERCENTAGE OF VARIANCE	CUMMULATIVE PERCENTAGE
5.809	27.661	27.661
4.525	21.546	49.207
2.315	11.030	60.237
1.816	8.649	68.886
1.381	6.575	75.461
1.015	4.832	80.293
0.781	3.720	84.013
0.739	3.519	87.532
0.523	2.489	
0.433	2.062	
0.346	1.646	
0.321	1.528	
0.255	1.216	
0.184	0.878	
0.165	0.787	
0.138	0.655	
0.078	0.373	
0.053	0.253	
0.047	0.225	
0.044	0.208	
0.031	0.148	

TABLE 3.9

INTERFACTOR CORRELATIONS FOR PROMAX OBLIQUE MATRIX

KMIN = 6

FACTOR	1	2	3	4	5	6	7	8
1	1.00							
2	0.09	1.00						
3	0.01	-0.78	1.00					
4	0.24	-0.46	0.55	1.00				
5	0.39	0.44	-0.29	0.04	1.00			
6	0.18	-0.02	0.19	0.31	0.08	1.00		
7	0.19	-0.35	0.58	0.57	-0.01	0.30	1.00	
8	0.07	-0.17	-0.00	-0.12	0.05	0.22	-0.45	1.00

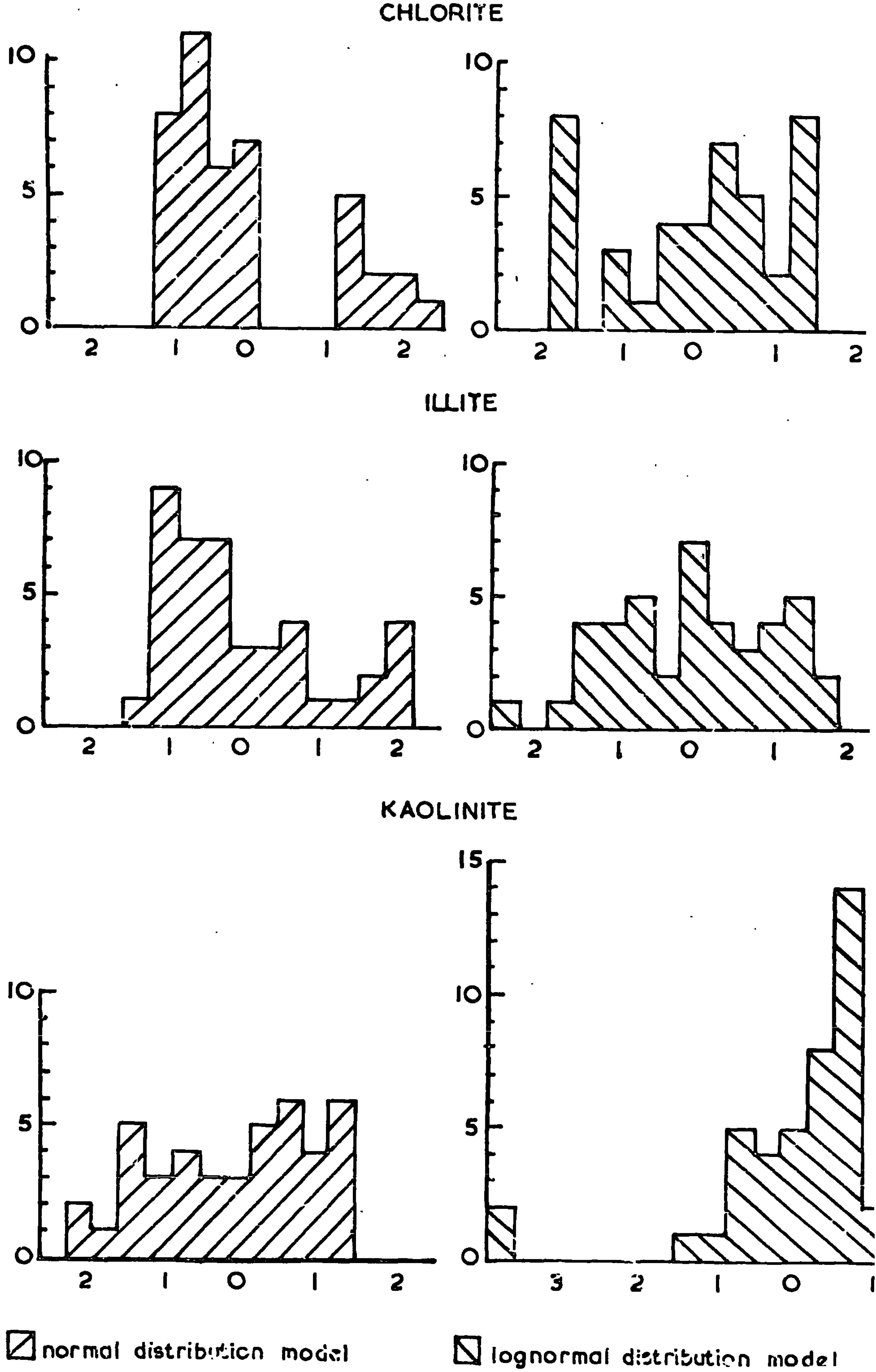
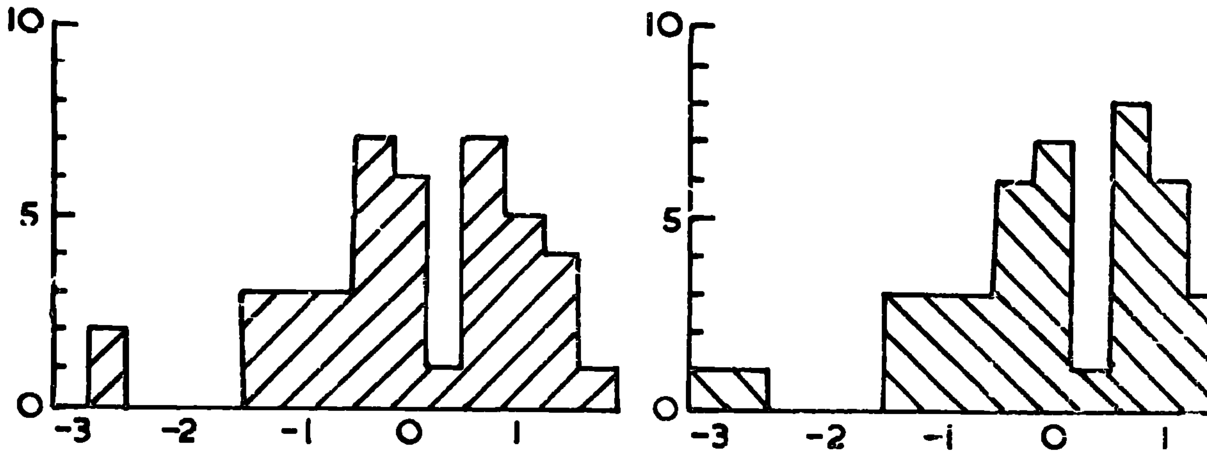


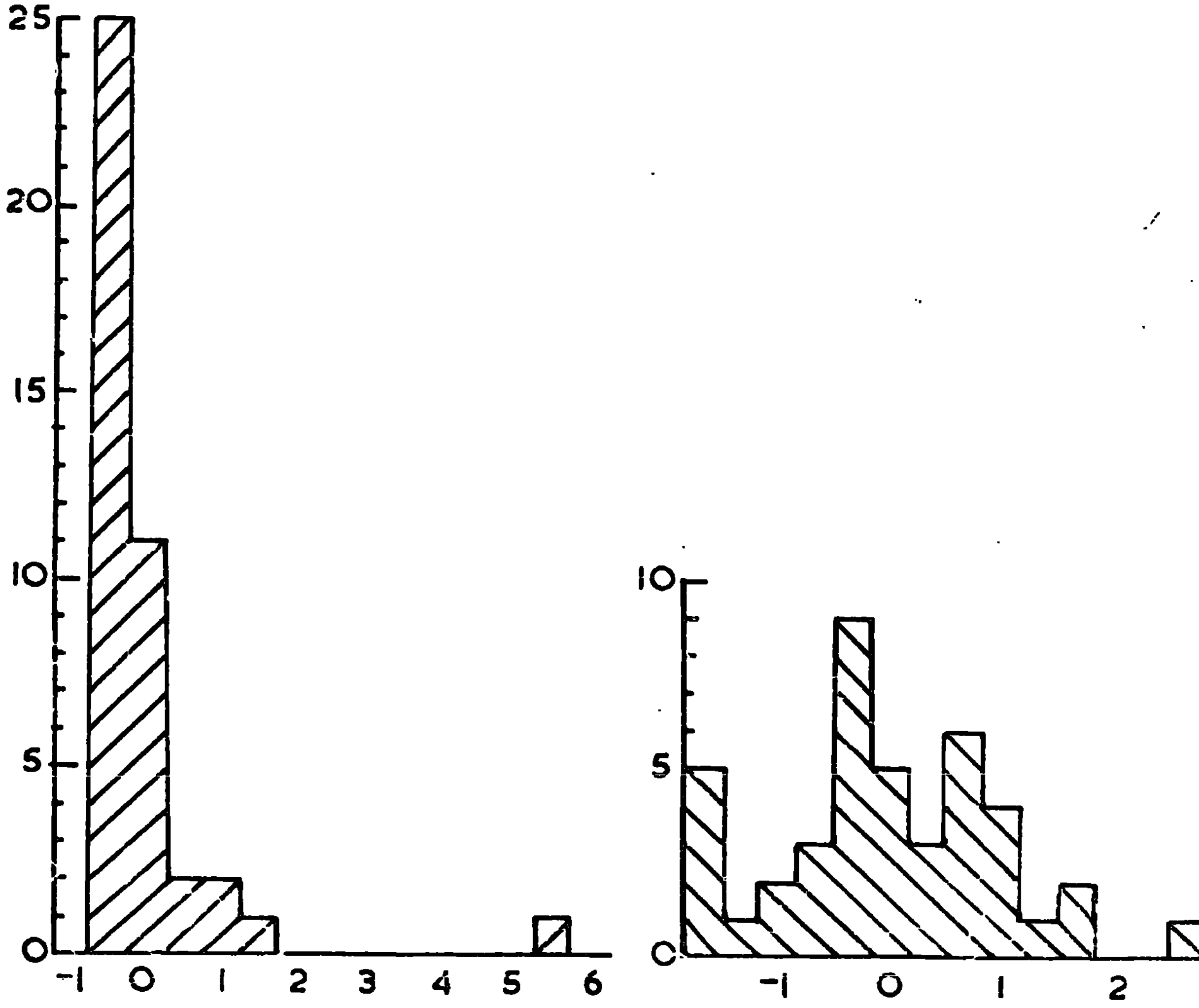
FIG.3·1a MINERAL FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

FIG. 3·1b. MINERAL FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS.

TOTAL CLAY



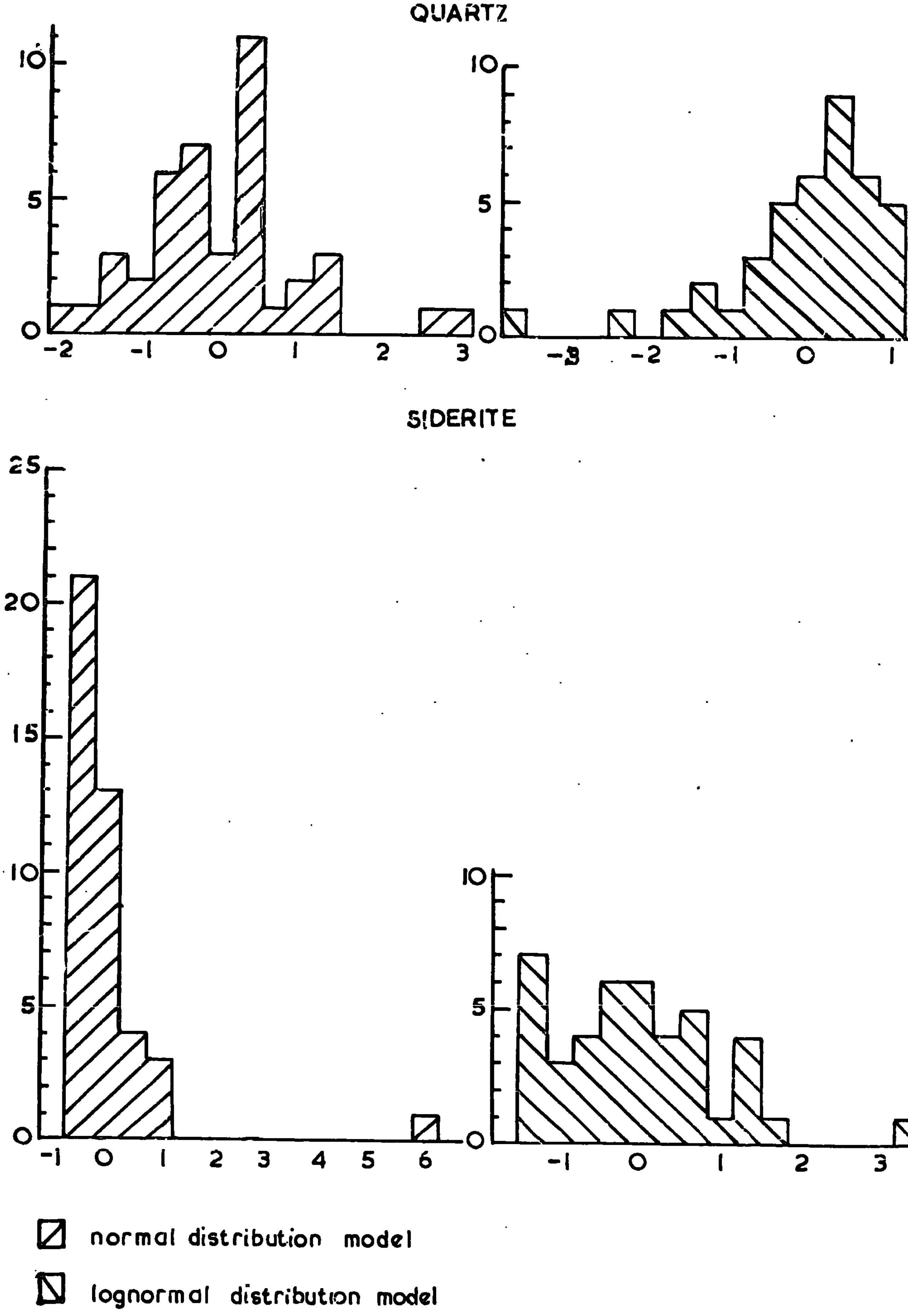
CARBONACEOUS MATTER



▨ normal distribution model

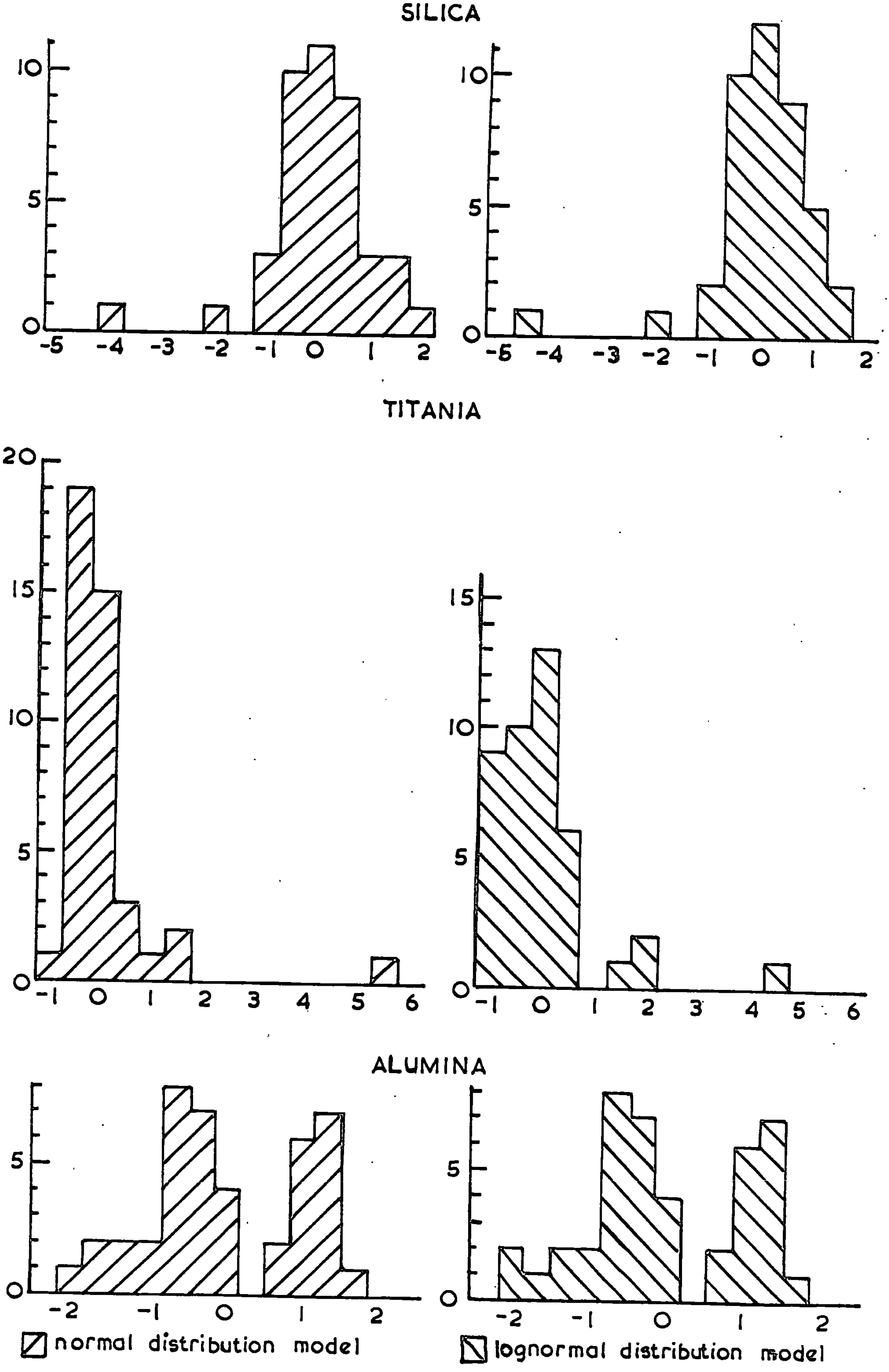
▧ lognormal distribution model

FIG.3·1c MINERAL FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS


QUARTZ

SIDERITE

FIG. 3·2a MAJOR ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS



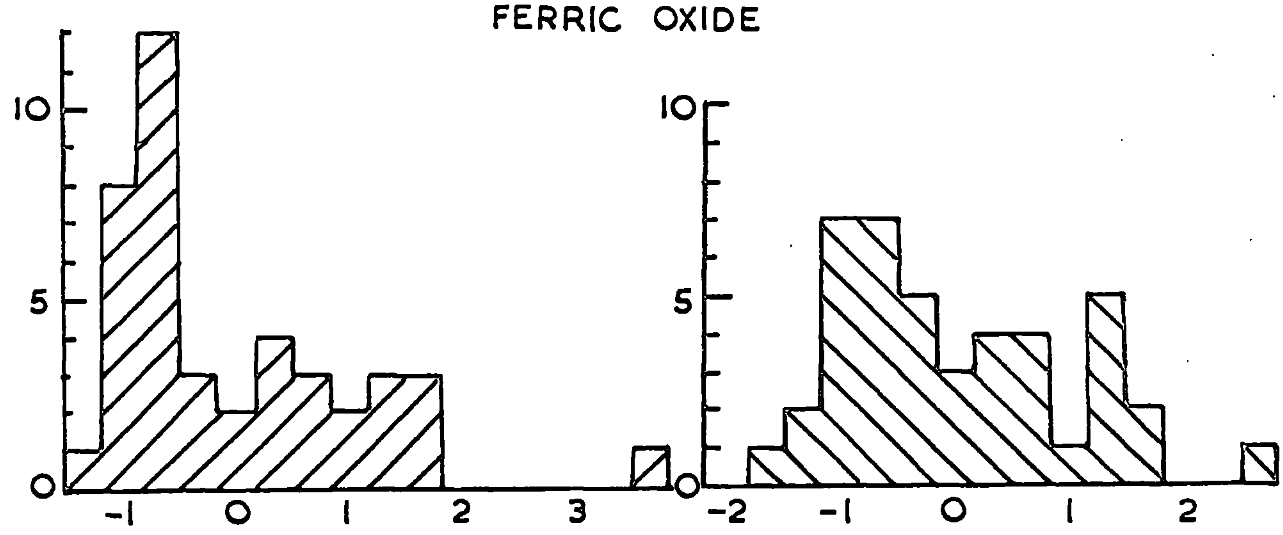
SILICA

TITANIA

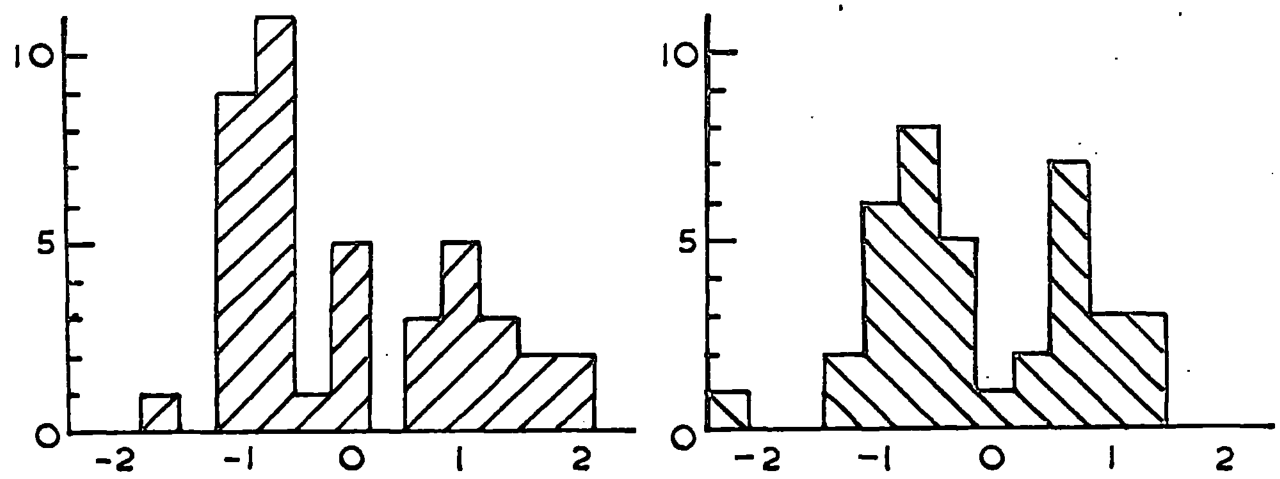
ALUMINA

FIG3.2b MAJOR ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

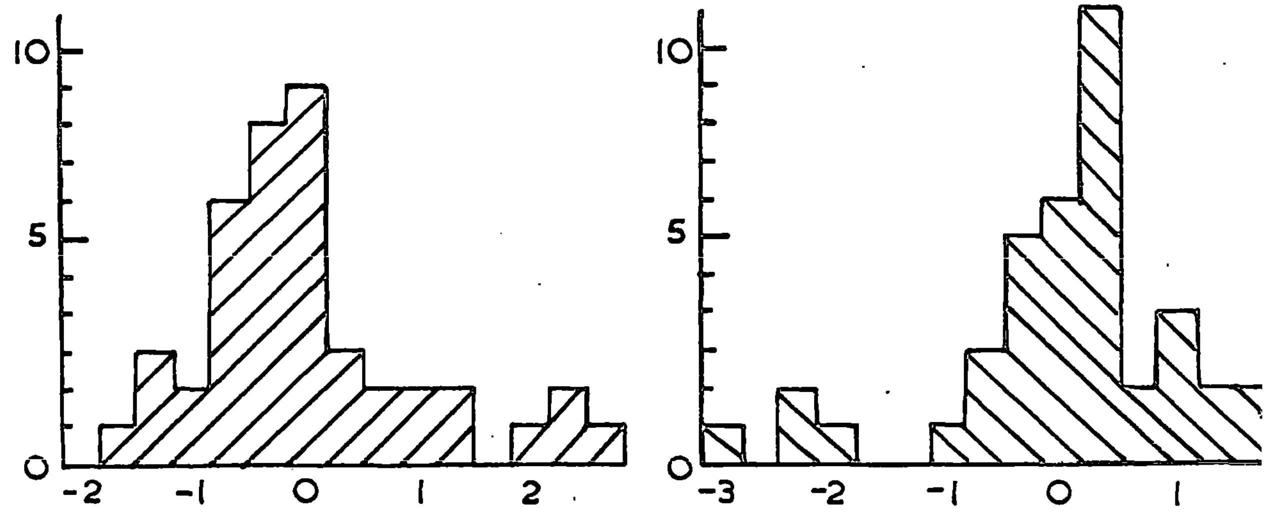
FERRIC OXIDE



MAGNESIA



LIME



▨ normal distribution model

▧ lognormal distribution model

FIG. 3·2c MAJOR ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

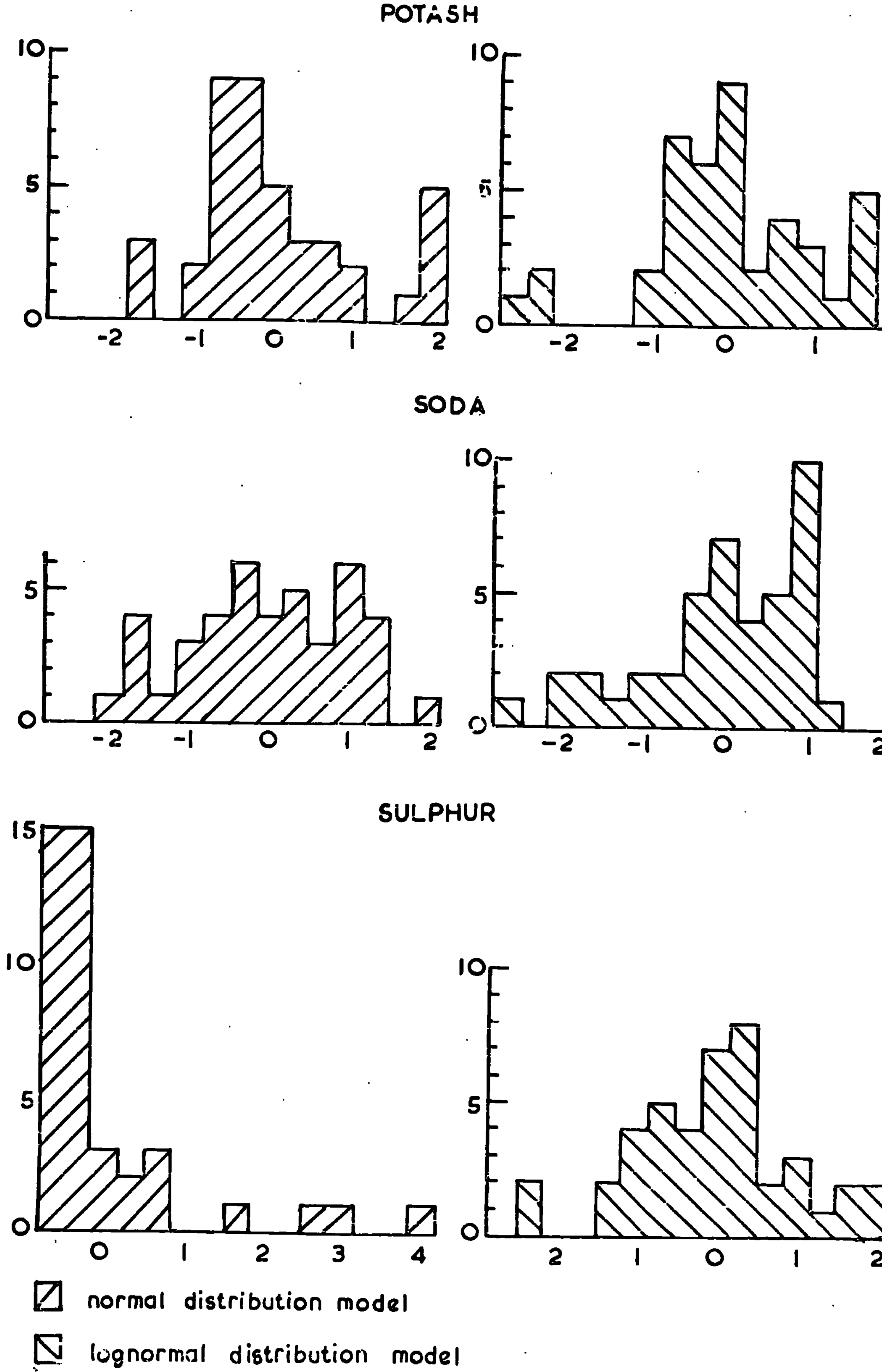


FIG. 3·2d MAJOR ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

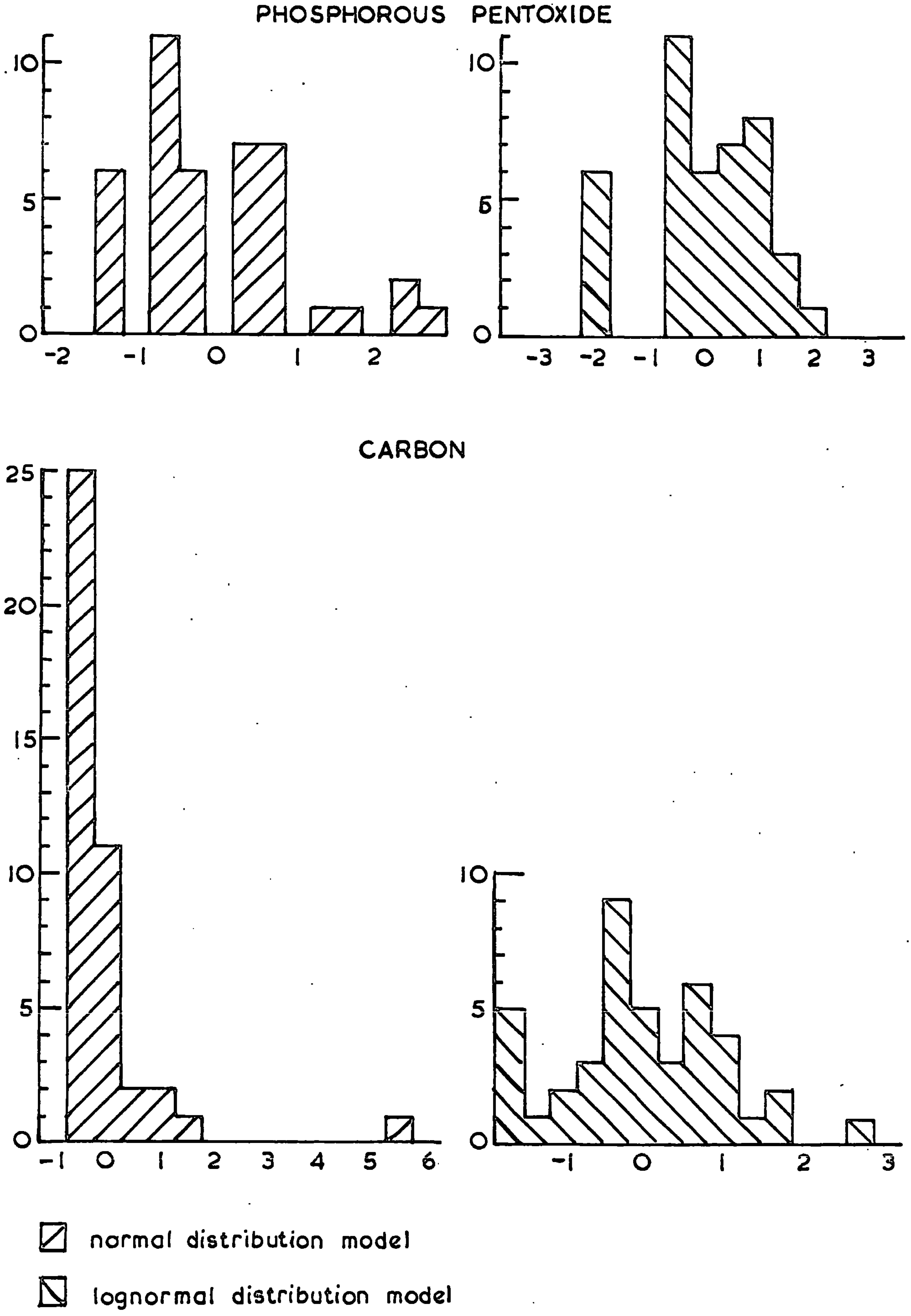


FIG. 3·2e MAJOR ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

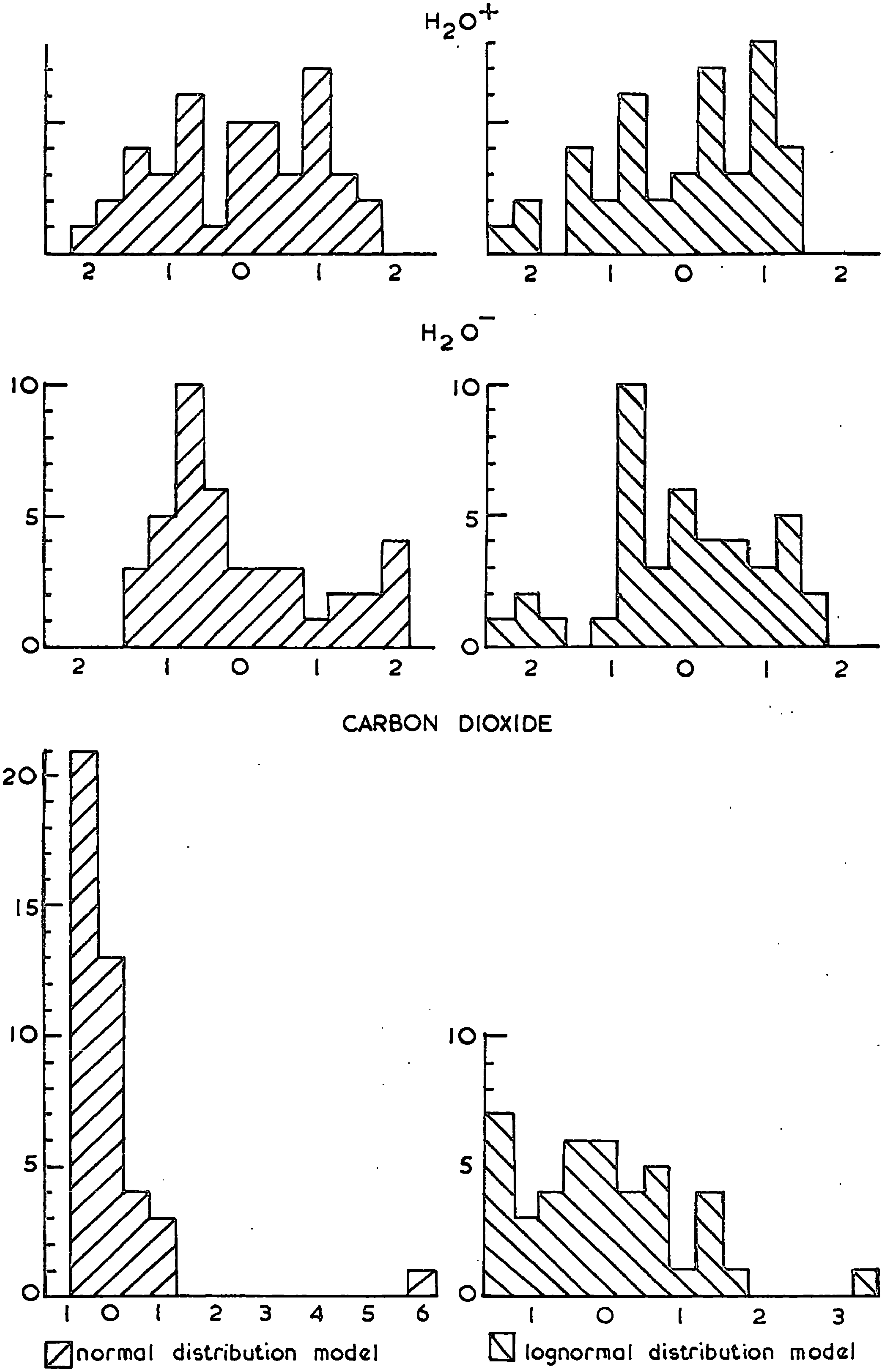


FIG.3·3a TRACE ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

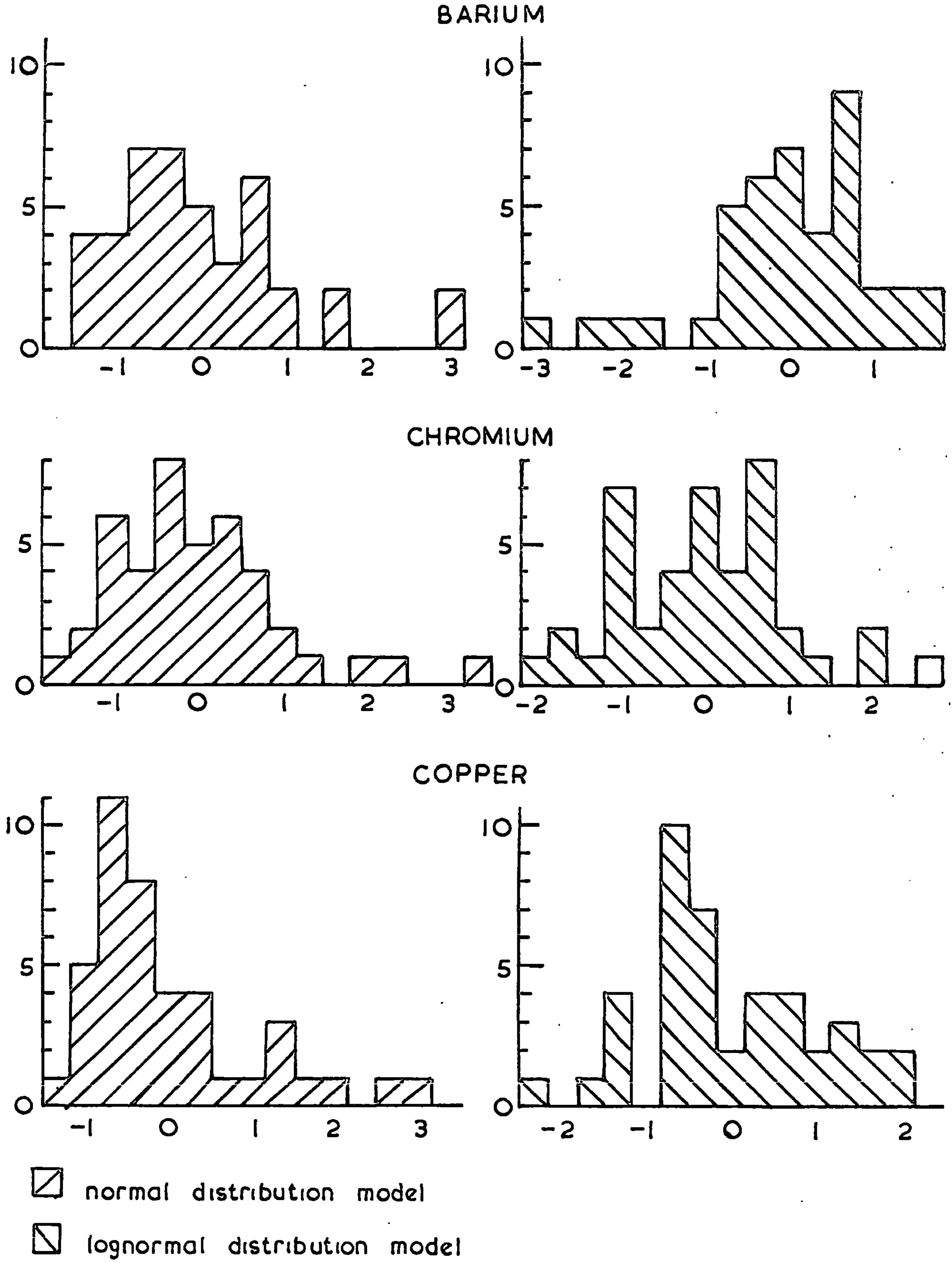


FIG. 3·3b TRACE ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

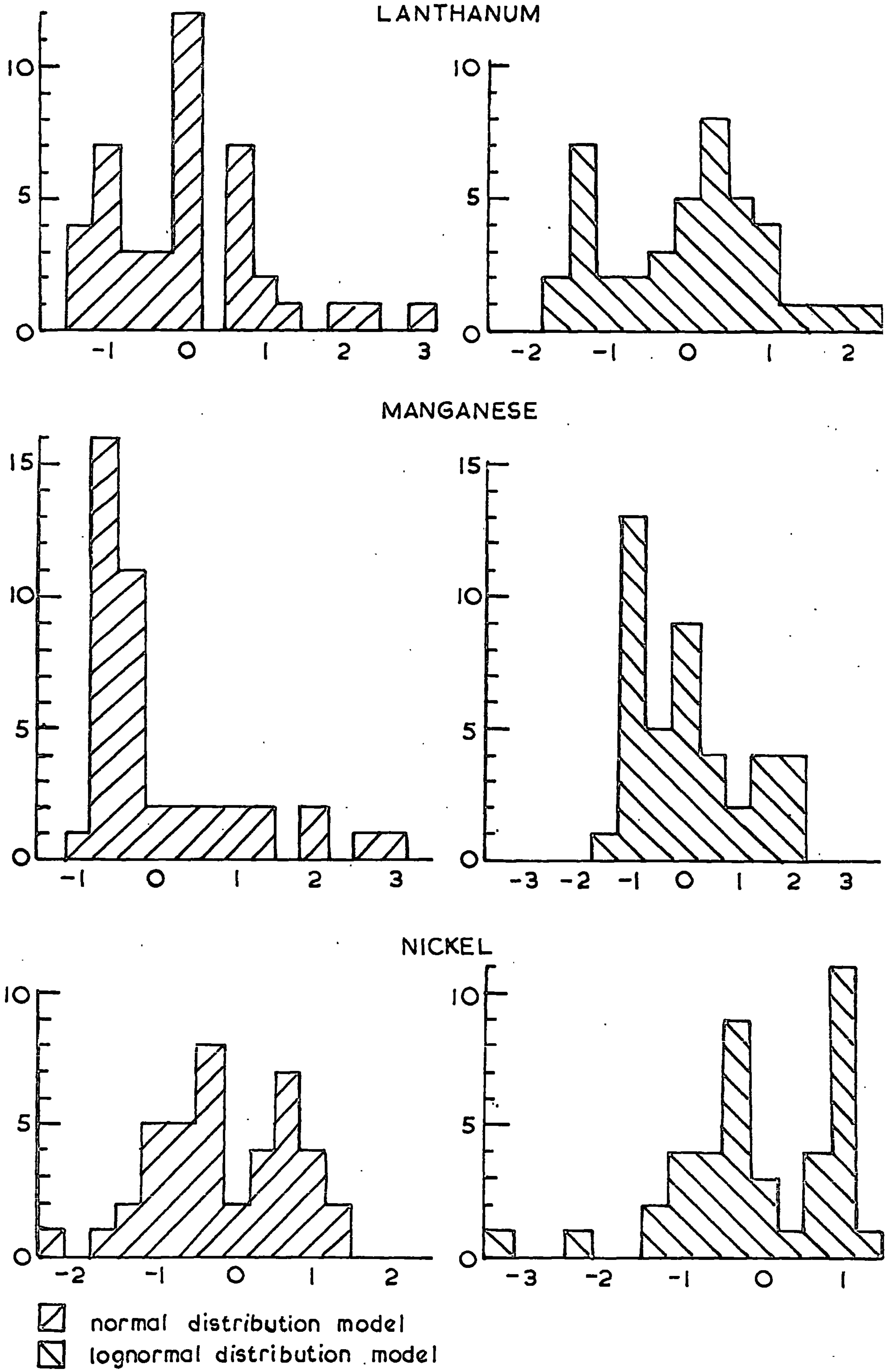


FIG 3 3c TRACE ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

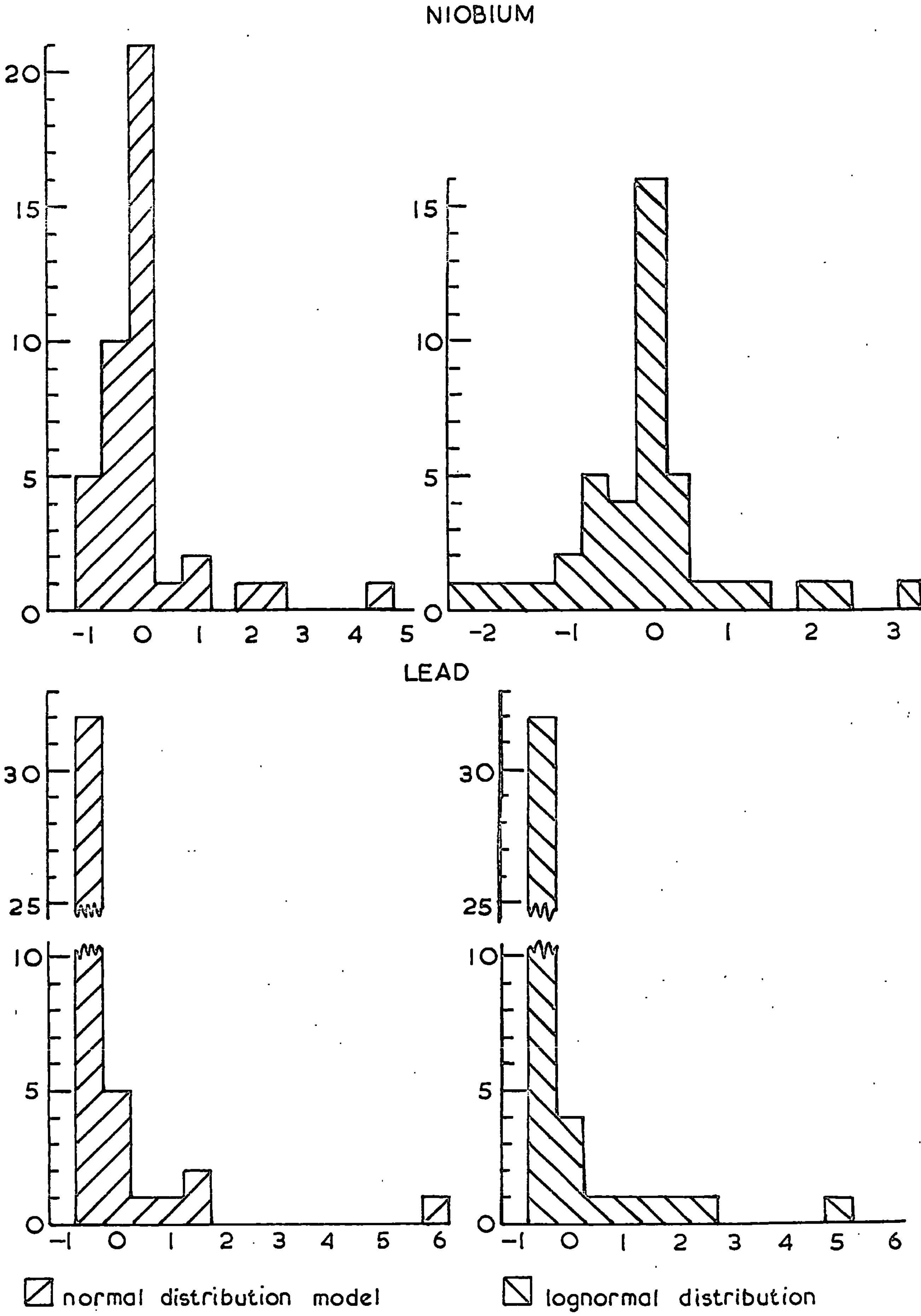


FIG. 3·3d TRACE ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

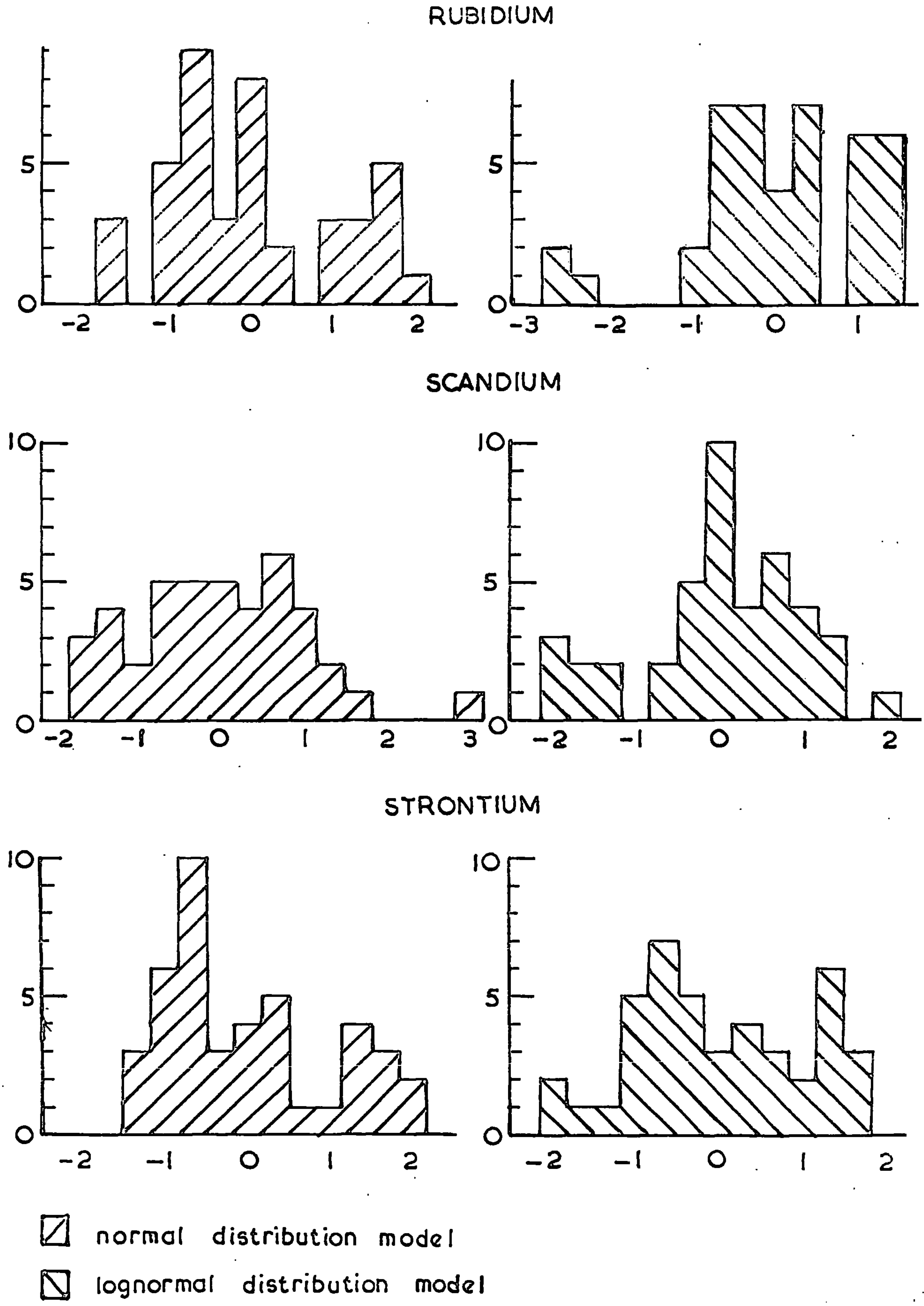
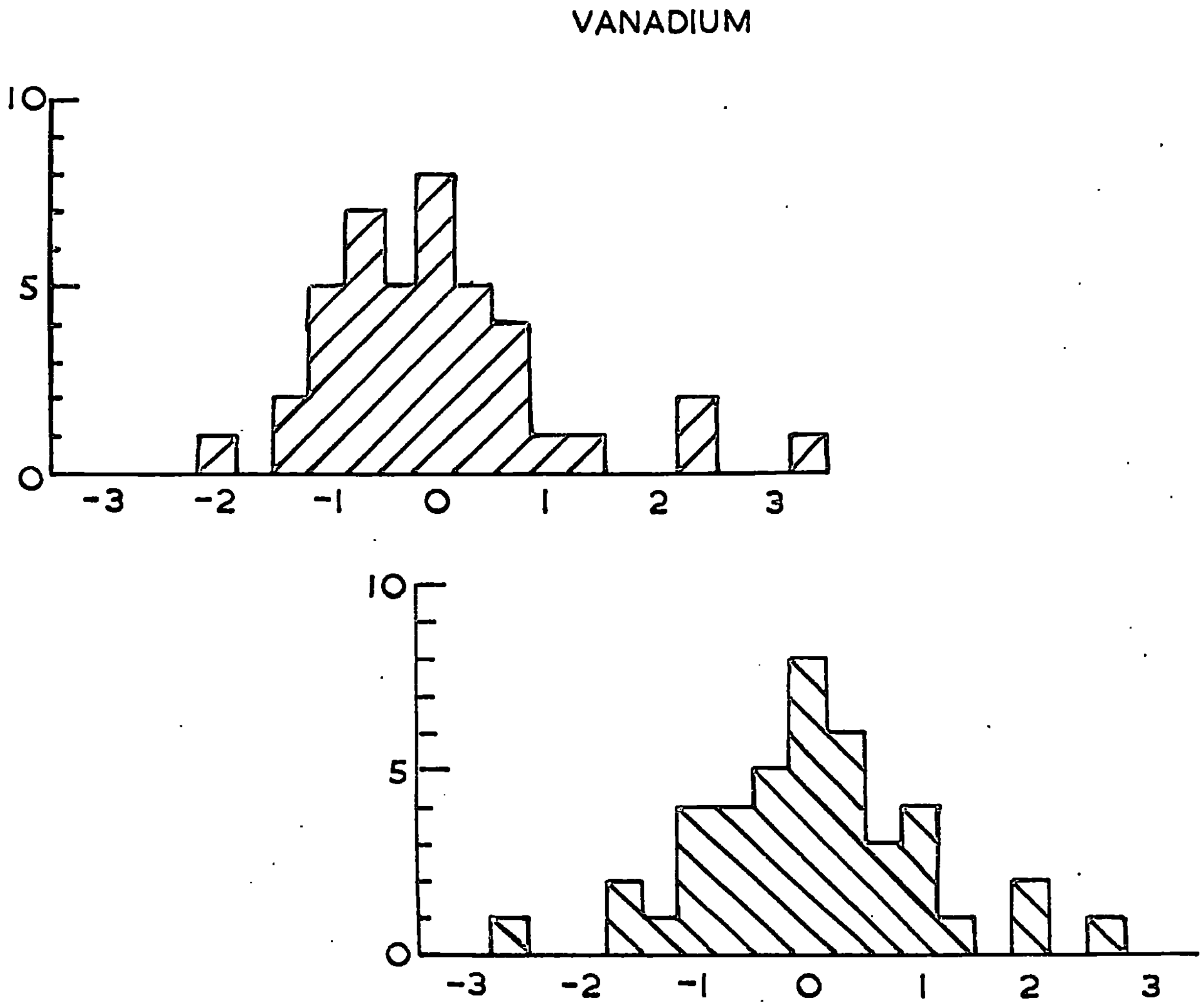
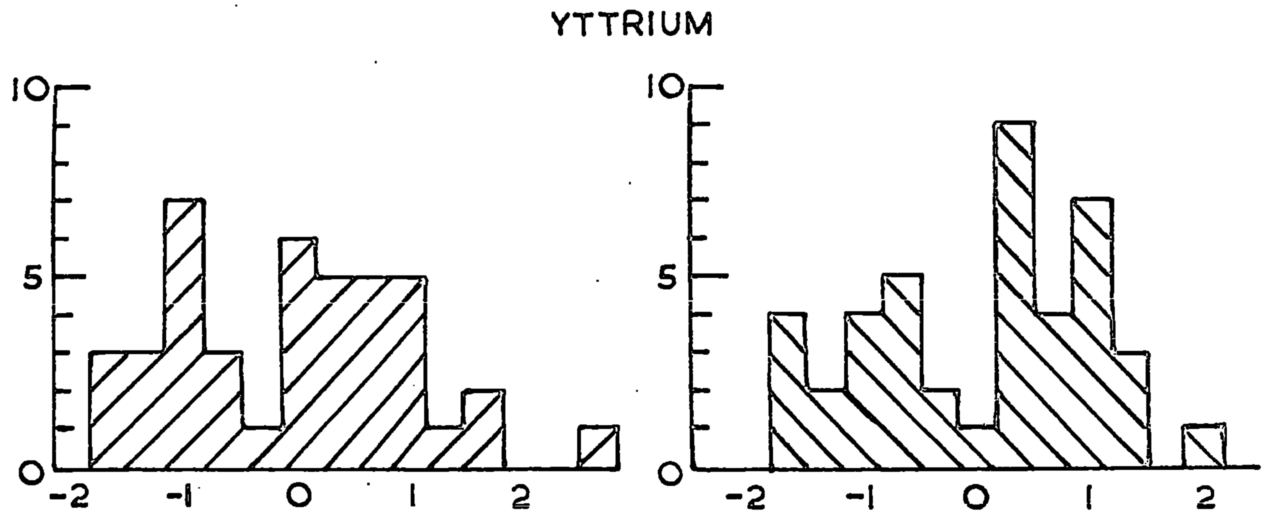


FIG.3.3e TRACE ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS





▨ normal distribution model

▧ lognormal distribution model

FIG. 3·3f TRACE ELEMENT FREQUENCY DISTRIBUTION HISTOGRAMS FOR 42 UPPER CARBONIFEROUS SEATEARTHS

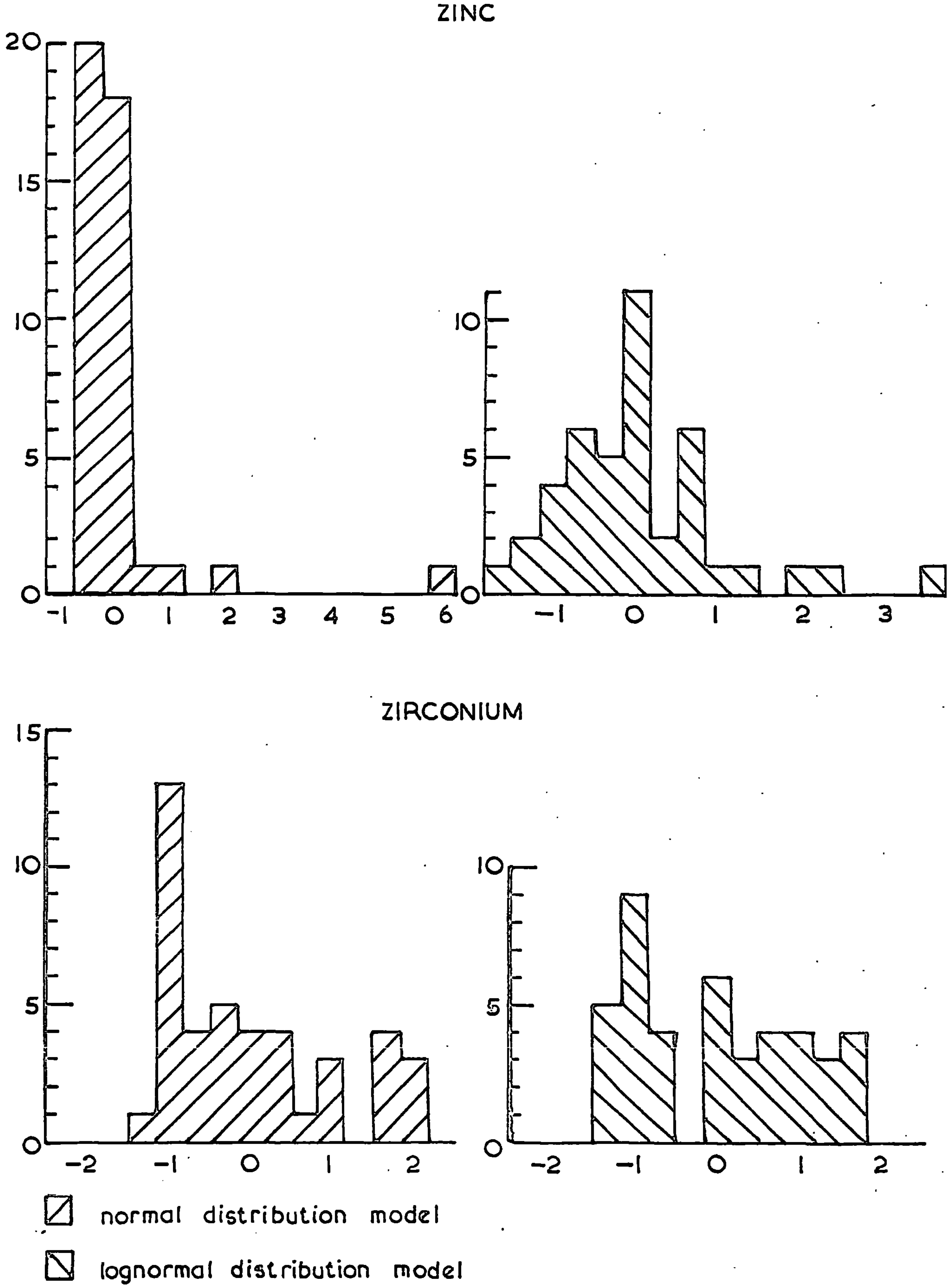


FIG. 3·4 VARIATION IN SEATEARTH MINERALOGY

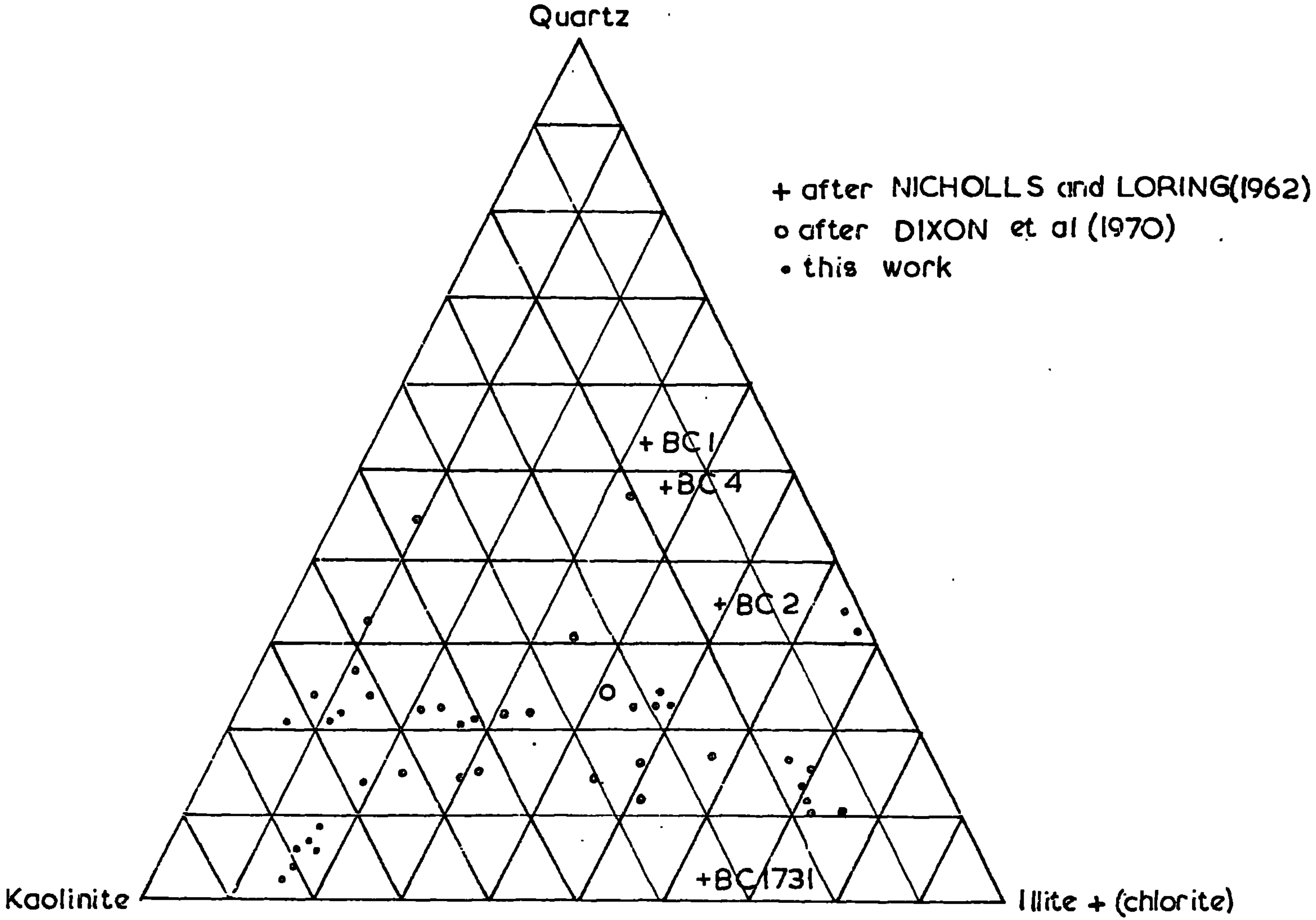


FIG.3.5 RESTRICTED VARIATION OF MAJOR COMPONENTS IN SEATEARTHS

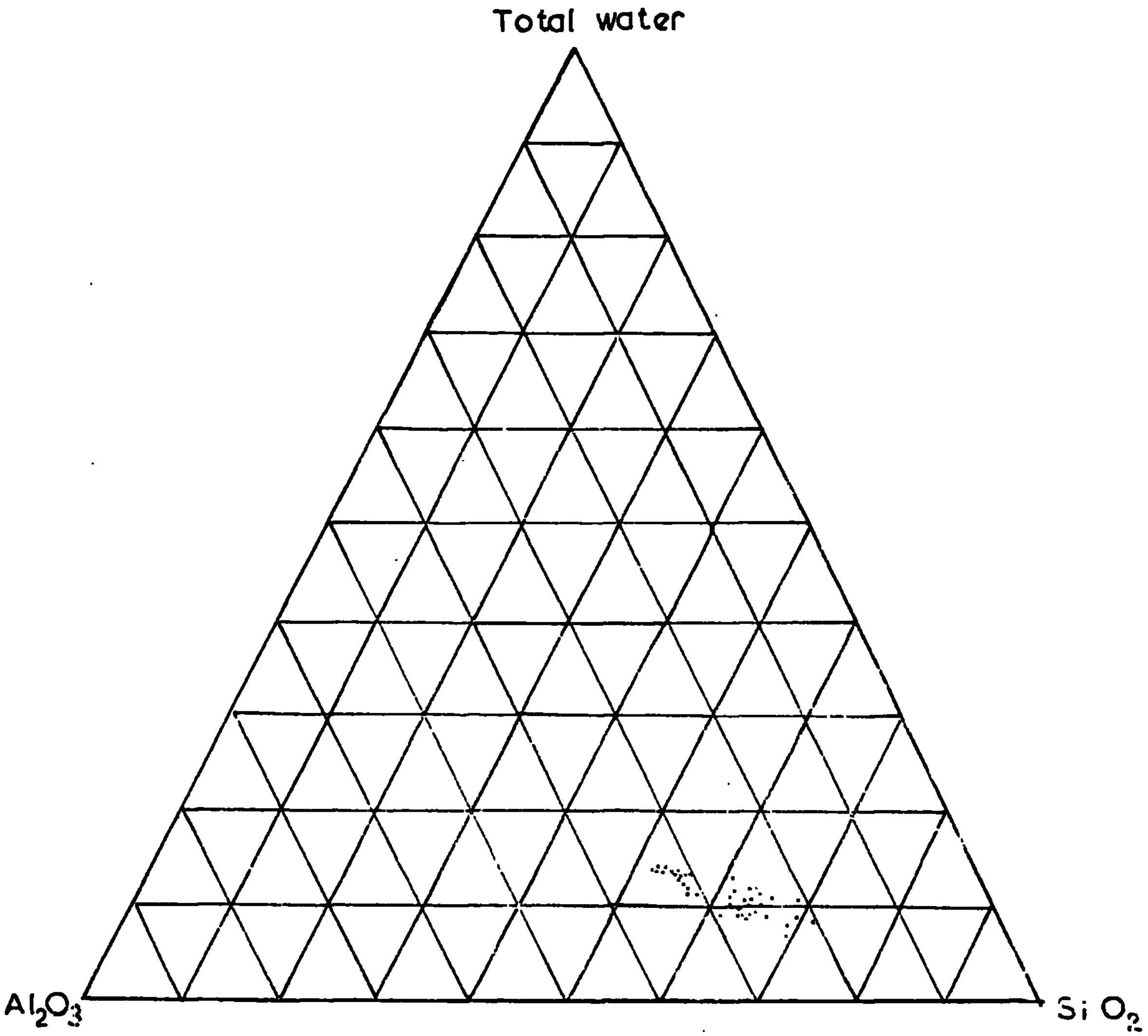


FIG. 3·6 VARIATIONS OF FACTOR LOADINGS ON ROTATION OF FACTOR AXES

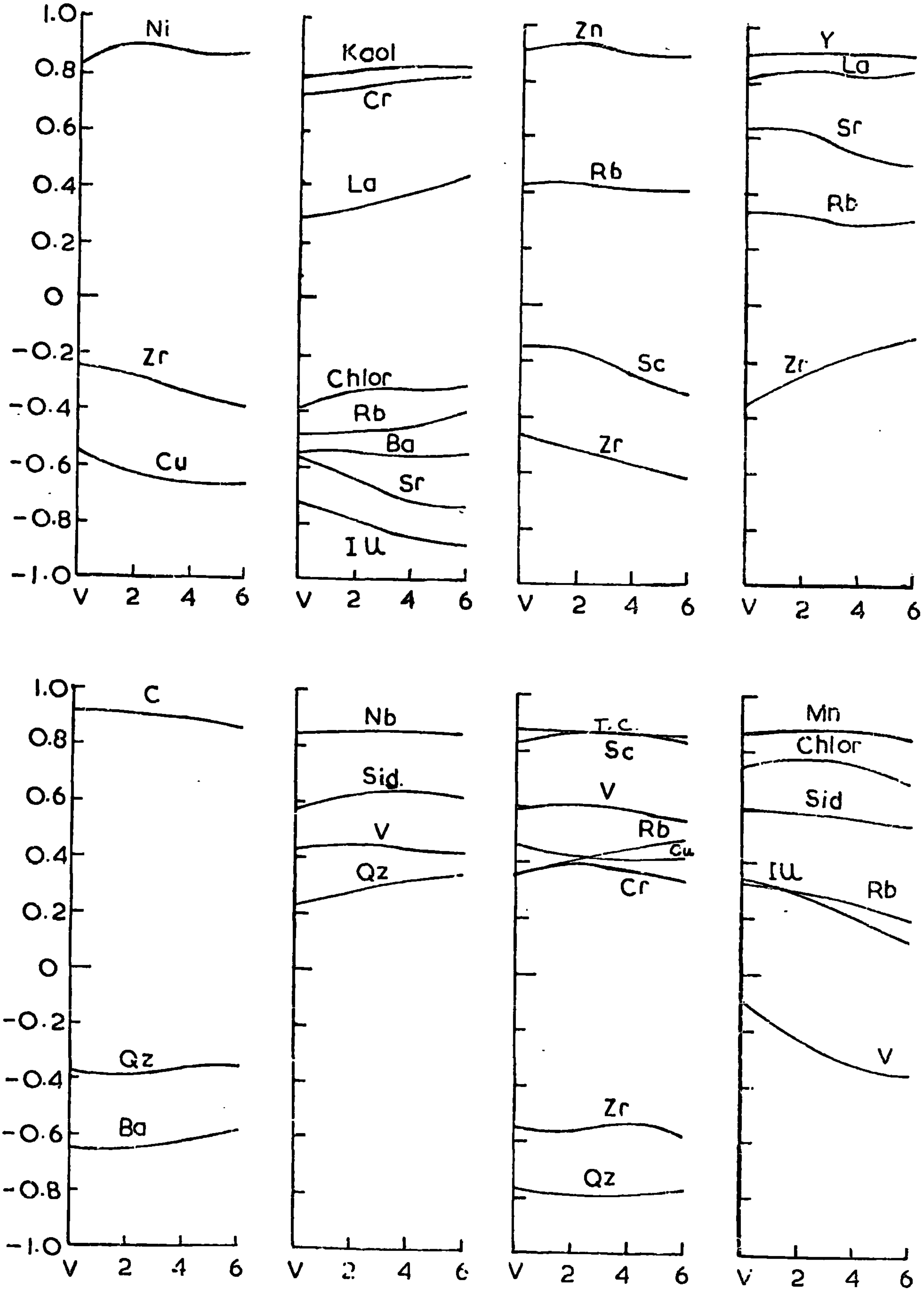


FIG. 3.7 SUMMARY OF FACTORS FOR KMIN=6 PROMAX OBLIQUE SOLUTION

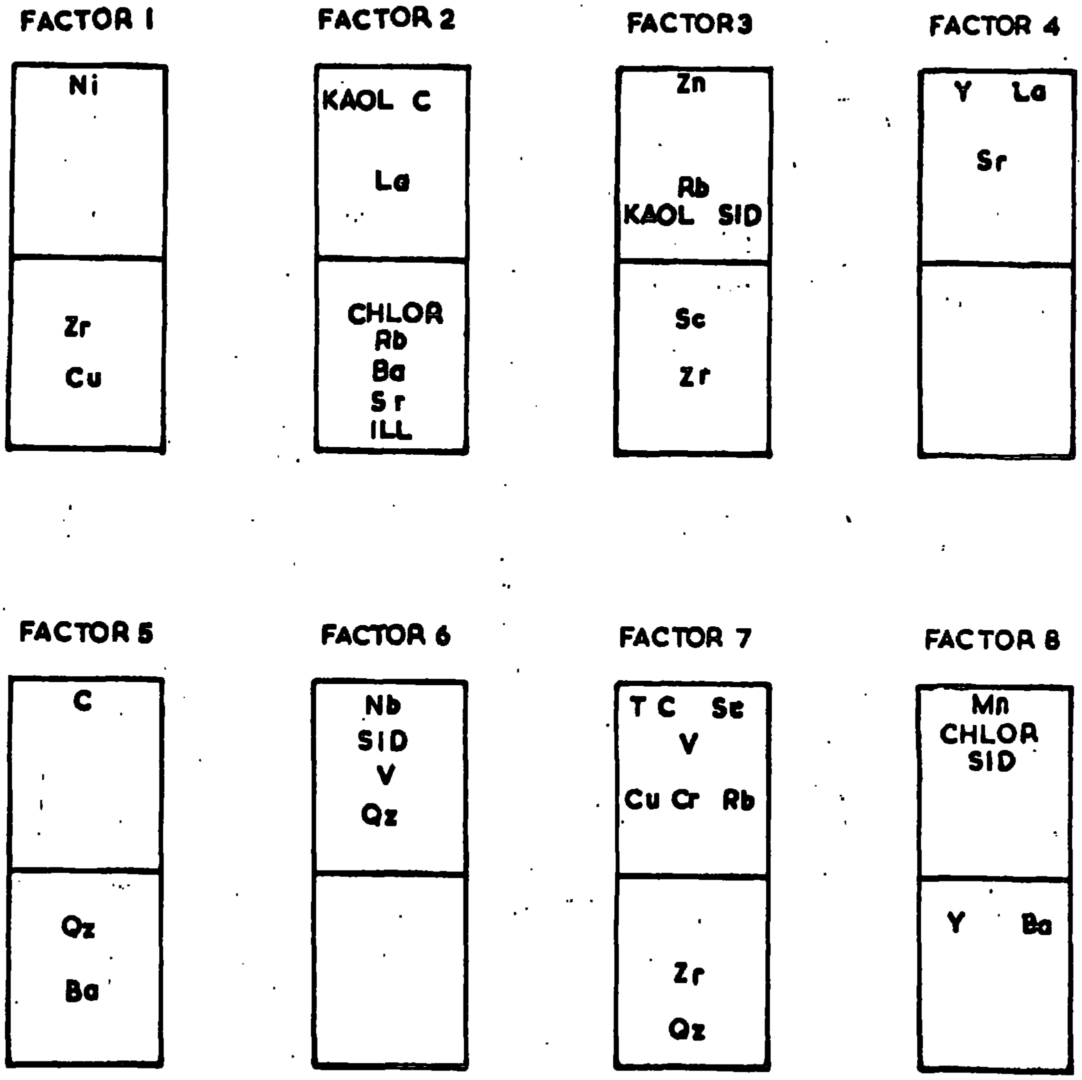


FIG. 3·8 FACTOR SCORES FOR FACTOR 2 v WEATHERING POTENTIAL INDEX OF REICHE (1943)

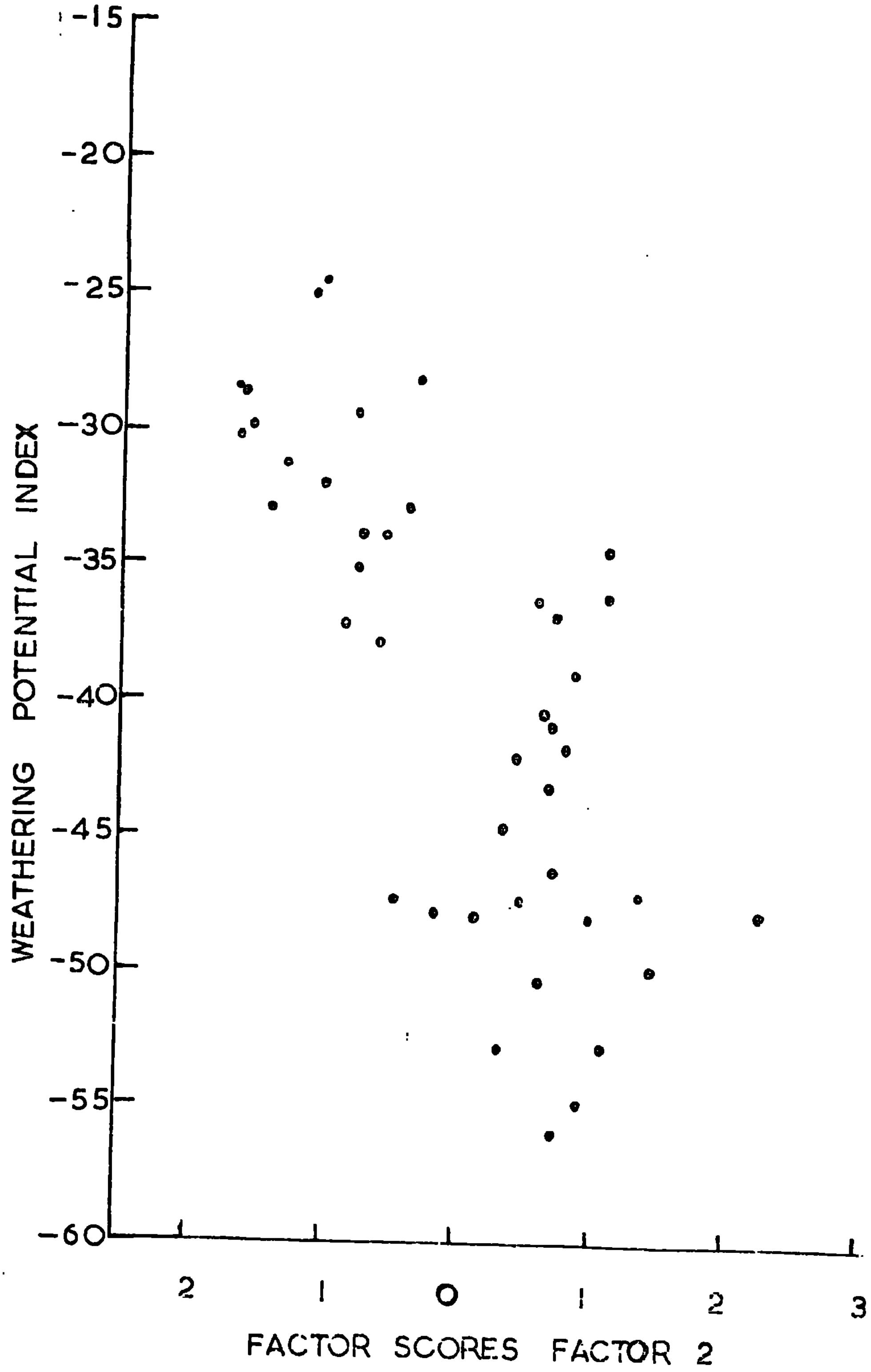


FIG. 3·9 VARIATION OF FACTOR SCORES FOR FACTOR FOUR WITH STRATIGRAPHY

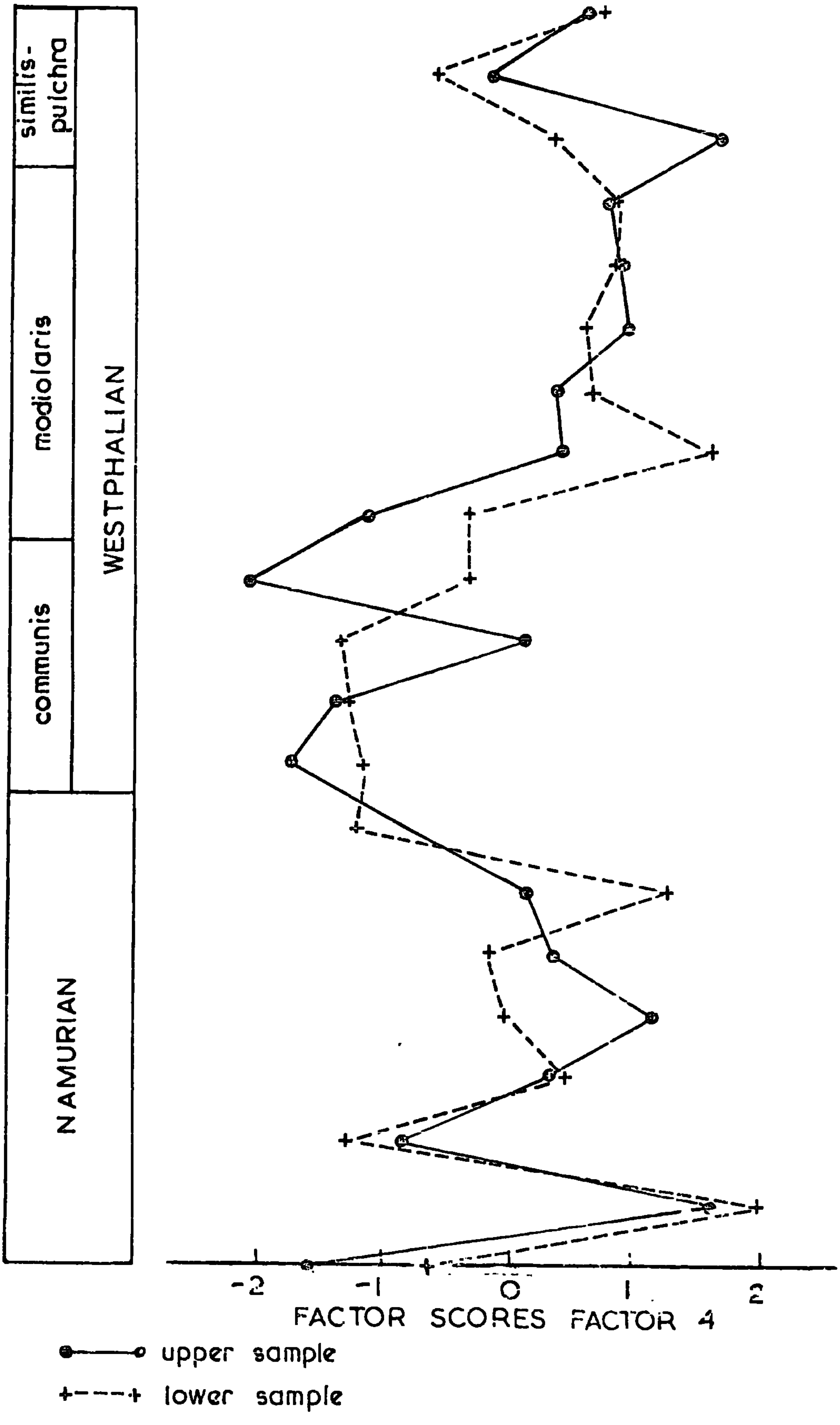
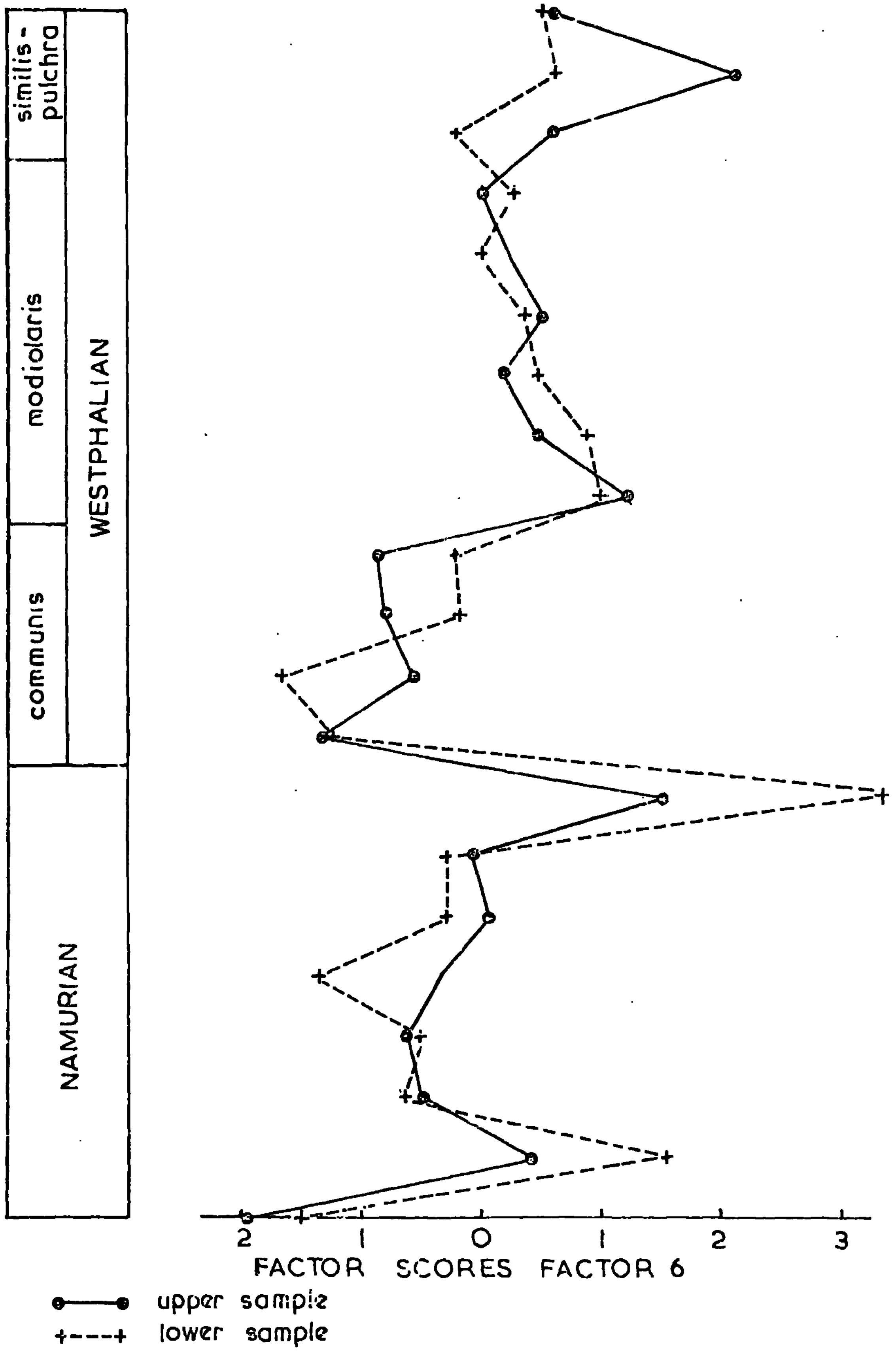


FIG. 3·10 VARIATION OF FACTOR SCORES FOR FACTOR SIX WITH STRATIGRAPHY



Spearman Rank Correlation for significance upward increase = 0·488
If samples LL 18, 20 and ST 4,6 are eliminated S.R.C. = 0·751

FIG. 3·11 FACTOR SCORES FOR FACTOR EIGHT v $Fe_2O_3 + MgO$

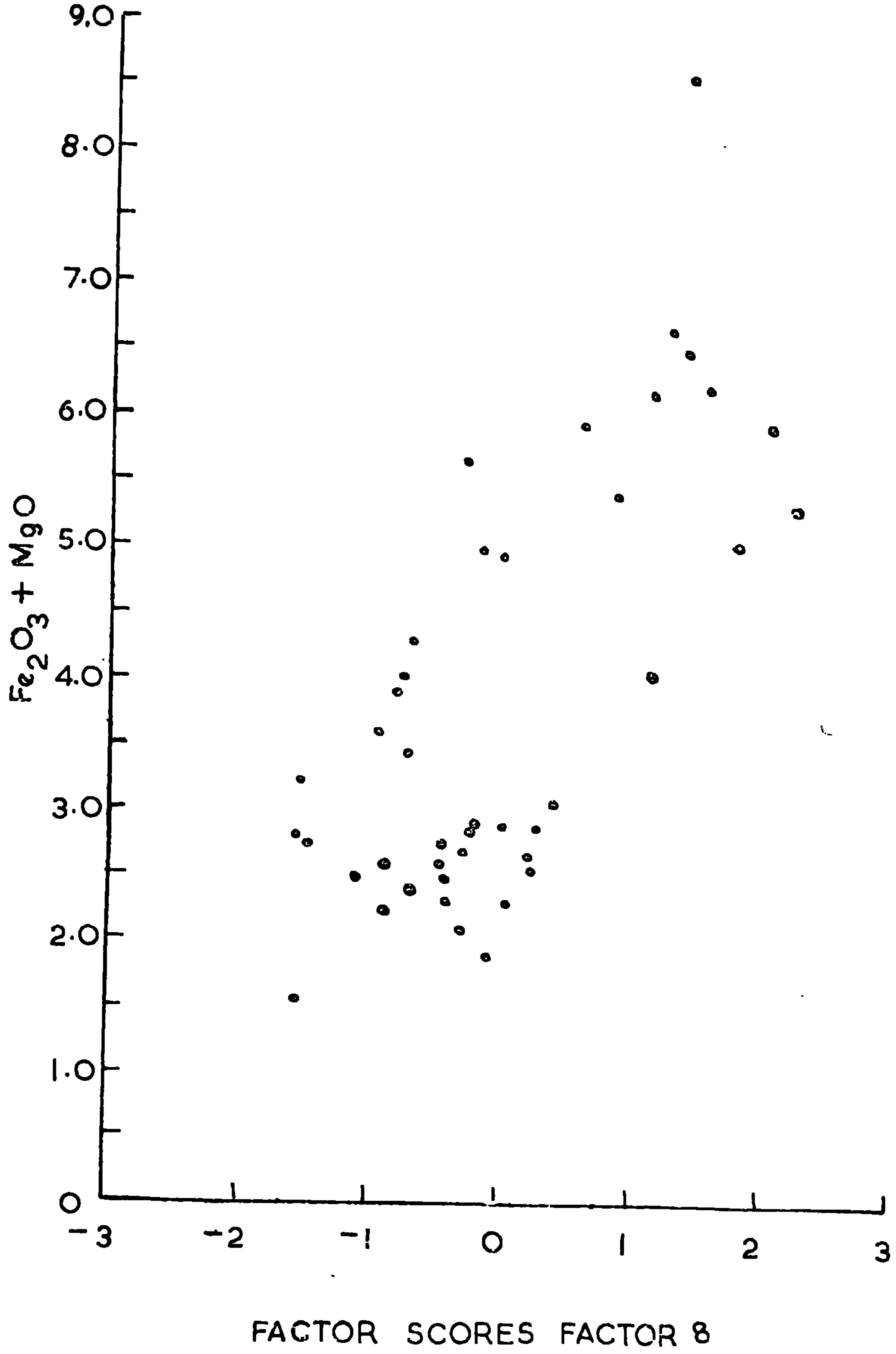
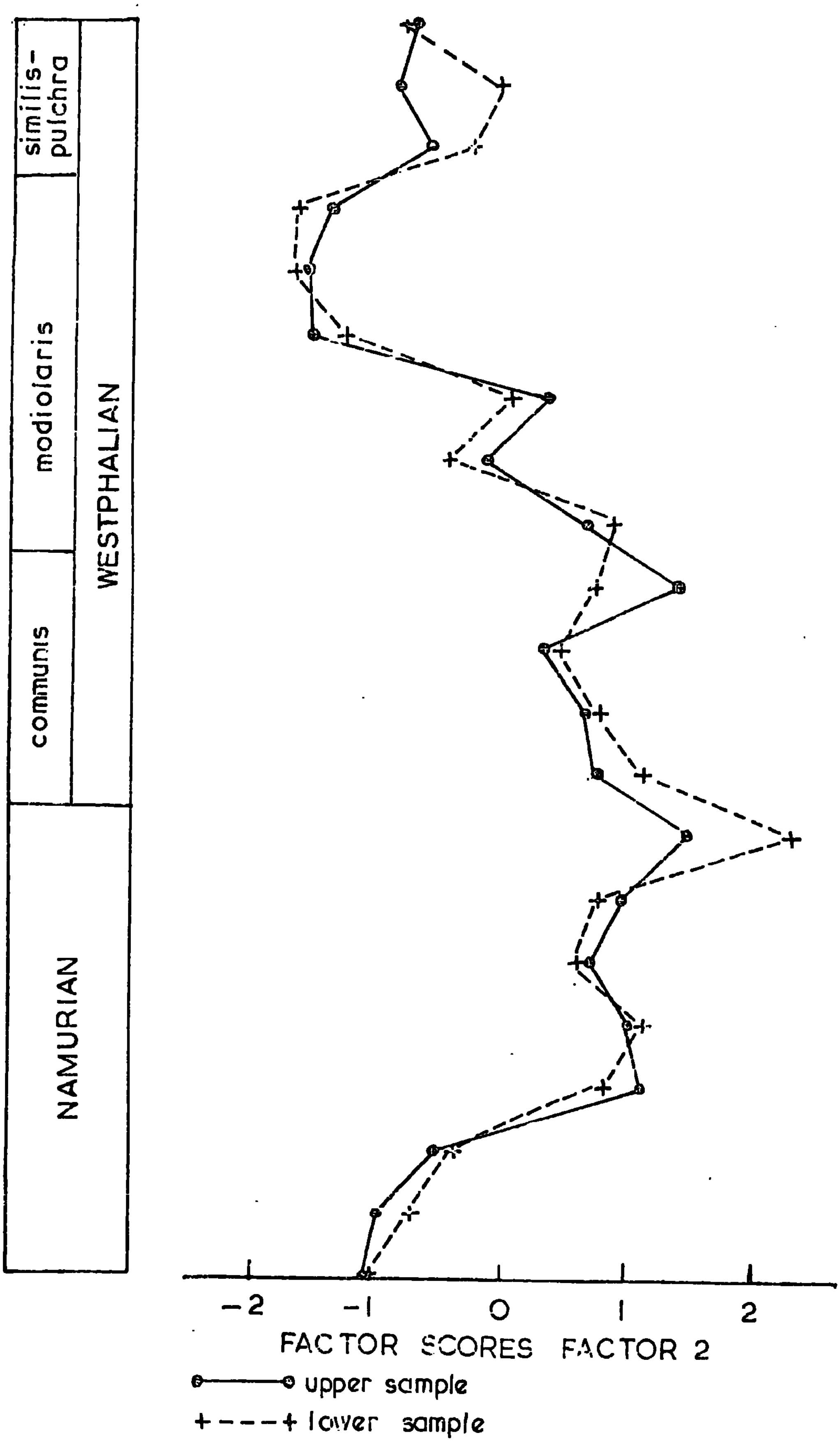


FIG. 3·12 VARIATIONS OF FACTOR SCORES FOR FACTOR TWO WITH STRATIGRAPHY.



3.7 REFERENCES TO CHAPTER THREE

CARROLL, D., (1958), The role of clay minerals in the transportation of iron., Geochim. Cosmochim. Acta, 14, 1 -27.

CURTIS, C. D., (1969), Trace element distribution in some British Carboniferous sediments, Geochim. Cosmochim. Acta, 33, 519 - 523.

DIXON, K., SKIPSEY, E., and WATTS, J. T., (1970), The distribution and composition of inorganic matter in British coals. Part 2: Aluminosilicate minerals in the coal seams of the East Midlands Coalfields., J. Inst. Fuel, 43, 124 - 128.

ENNOS, F. R., and SCOTT, A., (1924), Refractory materials : fireclays. Analyses and physical tests. Mem. Geol. Surv., Spec. Rept Min. Res. Gt. Britain, Vol XVIII.

NICHOLLS, G. D., and LORING, D. H., (1962), The geochemistry of some British Carboniferous sediments., Geochim. Cosmochim. Acta, 26, 181 - 223.

NORMAN, J. C., and HASKIN, L. A., (1968), The geochemistry of Sc: A comparison to the rare earths and Fe., Geochim. Cosmochim. Acta, 32, 93 - 108.

ONDRICK, C. W., and GRIFFITHS, J. C., (1969), Frequency distribution of elements in Rensselaer graywacke, Troy, New York. Bull. Geol. Soc. Am., 80, 509 - 518.

PRICE, N. B., and DUFF, P.McL.D., (1969), Mineralogy and chemistry of tonsteins from Carboniferous sequences in Great Britain., Sedimentology, 13, 45 - 69.

REICHE, P., (1943), Graphic representation of chemical weathering., J. Sed. Pet., 13, 58 - 68.

RODIONOV, D. A., (1965), Distribution functions of element and mineral contents of igneous rocks, Consultants Bureau, New York.

SHAW, D. N., (1961), Element distribution laws in geochemistry, Geochim. Cosmochim. Acta, 23, 116 - 134.

SHIMP, N. F., WITTERS, J., POTTER, P. E., and SCHLEICHER, J. A., Distinguishing marine and freshwater muds., J. Geol., 77, 566 - 580.

SPEARS, D. A., (1970), A kaolinite mudstone (tonstein) in the British Coal Measures., J. Sed. Pet., 40, 386 - 394.

TOURTELOT, H. A., (1964), Minor element composition and the organic carbon content of marine and nonmarine shales of Late Cretaceous age in the western interior of the United States: Geochim. Cosmochim. Acta, 28, 1579 - 1604.

WILSON, M. J., (1965), The origin and significance of South Wales underclays., J. Sed. Pet., 35, 91 - 99.

CHAPTER FOUR

VARIATIONS WITHIN ROOF ROCKS

4.1 GENERAL REMARKS

Roof rocks have only one essential property; that they were deposited above an organic accumulation which eventually became a coal seam. Unlike seatearths, roof rocks are not special sediments related to coal formation. They may be any of the normal precipitated and detrital sediments involved in the cyclothemic sedimentation associated with coal bearing strata. In Chapter one Figs. 1.1, 1.2, and 1.6 illustrated the wide variations found in roof rocks. Because of the very wide variation in these rocks any analysis of them is comparable with analysing the variations in cyclothemic sediments. The data of this study for 28 roof rocks shows largely the same sort of variations as previous studies of particular cyclothems. NICHOLLS and LORING (1962) carried out both mineralogical and chemical studies on the sediments of the Bersham cyclothem from the Middle Coal Measures of North Wales and SPEARS (1964) presented mineralogical and major element chemical data for the Mansfield Marine Band cyclothem from the Middle Coal Measures of South Yorkshire. Trace element data for the Mansfield cyclothem has been presented by CURTIS (1969). In addition to these data Dr. D. M. Hirst kindly made available some 49 unpublished analyses of Viséan sediments occurring between the Four Fathom and Great Limestones from the Rookhope borehole (See DUNHAM et al., 1965). Analysis of the variation in roof rocks was carried out in order to establish their relationship and significance with respect to seatearths.

4.2 MINERALOGICAL VARIATION

14 roof rocks were quantitatively analysed for mineralogy by the methods outlined in Appendix I. Table 4.1 compares these mineralogical analyses with those calculated by NICHOLLS and LORING (1962) for the Bersham cyclothem, this table illustrates the general similarity between the mineralogy of roof rocks and cyclothemic sediments. The mineralogical variation in the roof rocks is a little wider than that in the Bersham cyclothem. The data of Table 4.1 is dicussed more fully in Chapter five.

4.3 VARIATIONS IN MAJOR ELEMENT GEOCHEMISTRY

28 roof rocks were analyses for 15 chemical components, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, MnO, CaO, Na_2O, K_2O, S, P_2O_5, C, H_2O^+, H_2O^-, CO_2; the data is shown in Table 4.2; the analytical techniques being given in Appendix I. R-mode factor analysis was used to summarise the major element variation in the 28 roof rocks. Details of this method of data summary and interpretation are given in Appendix II. The data in Table 4.2 was transformed to logarithms (base 10) and a correlation matrix formed. This matrix is shown in Table 4.3. The reasons for the transform were discussed in Chapter three and Appendix II. Extraction of eigenvalues from the correlation matrix showed that 92.95 percent of the variance of the data could be explained in terms of six factors. The eigenvalues are given in Table 4.4 A principal components solution was computed and the orthogonal axes rotated to give the varimax solution shown in Table 4.5. The column headed communality represents the proportion of the variance of a particular variable explained by the matrix.

From these figures it is apparent that 80-97 percent of the variance of each variable has been explained. CaO contributes least to the matrix and SiO_2, TiO_2, and H_2O^- contribute most. SPENCER et al. (1968) suggested that the basic factors involved in sedimentary processes are not independent and therefore it could be difficult to assign physical significance to orthogonal factors (e.g. varimax factors). In order to permit correlations between factors a series of promax oblique factor solutions were computed by the method of HENDRICKSON and WHITE (1964). Table 4.6 shows the "best" oblique solution which remained stable on further rotation. Table 4.7 gives the correlations between the promax oblique factors. The only really significant correlation is that between factors 1 and 5 which permits separation of two simple factors from the more complex varimax factors. Table 4.8 gives the summary statistics for the 15 variables together with the error variances computed from the analytical precisions. The error variances are thought to be overestimates since three times the observed precision was used in their computation in order to rule out any possibility of severe underestimation which may result in attaching geochemical significance to factors resulting from analytical error. (See Appendix II). Table 4.8 indicates that the communalities in Table 4.5 may be justified in terms of "real" rather than error variance. Two properties of the present data bring this about :-

(a) The high total variance for most variables.

(b) The high analytical precision and therefore low error variance.

All subsequent interpretation is based on the factor matrix given in Table 4.6 and these factors are illustrated in Fig. 4.1 which presents a neat summary of the variations in the data of Table 4.2.

Factor 1 has high positive loadings for CaO and P_2O_5 and this indicates that the factor controls the variance of phosphate in the sediments which presumably occurs as apatite; in general four processes may be responsible for the variations in phosphate content :-

(a) Accumulation of free detrital inorganic apatite.

(b) Accumulation of detrital inorganic apatite as inclusions in clay minerals.

(c) Accumulation of organic detrital apatite. e.g. bones, teeth, phosphatic shells etc.

(d) Precipitation of phosphate from solution.

The correlations of factor 1 may give a clue to which of the above processes are important. Factor 1 shows a very slight positive correlation with factor 6 which would indicate that (b) is subsiduary to (a) and/or (c) since covariance with quartz, rather than clay, is implied. However, by far the most significant correlation of factor 1 is with factor 5. Factor 5 bears a high loading for CO_2 and it is well known that carbonate and phosphate are sensitive to environmental pH (e.g. See KRUMBEIN and GARRELS, 1952). If pH is invoked to explain this correlation then (d) must be considered as the important process in controlling phosphate variation.

Factor 2 involves a high positive loading for C and a lesser positive loading for S. A moderate CO_2 loading opposes those of C and S. The interpretation of this factor must therefore explain an increase in C and S at the expense of CO_2 and vice versa. The conversion of C to CO_2 is an oxidation reaction and is thus favoured by increasing Eh. Retention of S in sediments as S^{2-} rather than its removal in solution as SO_4^{2-} is also favoured by low Eh. Clearly factor 2 may be interpreted as an Eh control.

Factor 3 has a high positive loading for S and a lesser similar loading for C. Na_2O shows a moderate negative loading. Two explanations of factor 3 are reasonable in a sedimentary environment :-

(a) Factor 3 could be a function of rate of deposition since sulphide (pyrite) is commonly associated with slowly deposited sediments. Conversely high Na_2O contents in fast deposited sediments may be due to detrital albite or Na bearing clays (see NICHOLLS and LORING, 1960).

(b) Factor 3 may be related to pyrite formation in the diagenetic environment. Precipitation of diagenetic pyrite originally(as FeS, LOVE, 1967) from solutions enriched in S^{2-} would explain the S and Fe loadings. Na and Mg would probably be removed in solution during diagenesis, hence their loadings.

(a) is thought to be unlikely since factor 6 shows a clear clay v quartz relationship which is interpreted as a function of sorting and/or rate of deposition and factor 3 shows no strong correlation with this factor. The independence of factor 2 and 3 if (b) were the case could be explained if factor 3 represented sulphide ion activity. This would also explain the non correlation of factors 3 and 5, since factor 5 is thought to be related to diagenetic siderite. The Eh control of factor 2 is thought to link factors 3 and 5 and the three factors are all thought to be associated with diagenesis. Factor 3 is interpreted as a sulphide precipitation factor related to sulphide ion activity during diagenesis. The loading of C on factor 3 may indicate that preservation of C is favoured by diagenesis under conditions favourable to pyrite formation. Table 4.9 shows the factor loadings for each sample on each of the six factors. Pyrite was detected by X-ray diffraction in samples LL13, LL16, KB2, and KB21 and these samples show high scores on factor 3. The loadings of Fe and Mg were included in order to show their consistency with the interpretation, however, pyrite contributes only a trivial amount to the total variance of Fe and the loading is very low. The vast majority of the variance of Fe_2O_3 is dominated by siderite, pyrite and clay also contribute.

Factor 4 shows high positive loadings for K_2O and H_2O^- and a lesser positive loading for Na_2O. Fig. 4.2 shows factor scores for factor 4 plotted against illite content for 14 of the 28 sediments. It can be seen that while factor 4 clearly is related to the illite content, there is no significant correlation with factor 6, clay v quartz, and therefore the illite content appears to be independent of total clay. K^+ and Na^+ presumably occur as hydrated ions in intersheet positions in illite, thus explaining the three loadings. The non-loading of Al does not, of course, indicate its absence from illite, merely the fact that its variance is not significantly affected by illite content. Several explanations for factor 4 are possible :-

(a) Factor 4 is a function of provenance.

(b) Factor 4 is a function of stratigraphy.

(c) Factor 4 is a function of leaching.

All three explanations could account for a variation in illite content independent of total clay. Since the samples come from various geographical locations and various positions in the stratigraphic column (a) and (b) cannot be excluded. Leaching is thought to be trivial except for seatearths as shown in Chapter five. The mineralogical variations of the Bersham sediments shown in Table 4.1 also indicate that the clay fraction composition is fairly constant throughout the cyclothem a fact also demonstrated for the Mansfield Marine Band shales by SPEARS (1964). With the present data, however, factor 4 can only be called an "illite factor" since any more precise definition cannot be justified.

Factor 5 has high positive loadings for Fe_2O_3, MgO, MnO, and CO_2 and moderate negative loadings for SiO_2 and TiO_2. The positive loadings strongly suggest that siderite variation is controlled by this factor and Fig. 4.3 shows siderite content plotted against factor scores for factor 5. Factor 5 is thought to be a siderite diagenesis factor independent of factor 3 (sulphide diagenesis) but linked to this factor through factor 2 (Eh). The strong correlation with factor 1 (phosphate) suggests that factor 5 is also related to pH. The loadings of SiO_2 and TiO_2 are thought to represent detrital quartz and rutile and indicate that relatively slow deposition and argillaceous sediments favour diagenetic siderite formation. CARROLL (1958) indicated that iron may travel to the basin of deposition as oxide or hydroxide coatings on clay minerals and this probably explains the antipathy of detrital rutile and quartz to carbonate diagenesis since fast deposition would reduce the availability of iron.

Factor 6 involves high positive loadings for SiO_2 and a lesser positive loading for Na_2O. TiO_2, Al_2O_3, and H_2O^+ have high negative loadings and MgO has a moderate negative loading. Factor 6 is thought to illustrate the strong quartz v clay relationship which is thought to be a function of rate of depostion although sorting during transportation and depostition cannot be ruled out. The latter interpretation allows for post depositional Winnowing. However, grain size analysis tends to support the simple interpretation as rate of deposition. The Na_2O loading may reflect either detrital albite or Na in fast deposited clays (see NICHOLLS and LORING, 1960). Most of the variances of Al_2O_3 and H_2O^+ are thought to be related to lattice positions in clay minerals. Mg is thought to be especially associated with chlorite. The loading of TiO_2 may indicated that much of the variance of TiO_2 is explained by rutile inclusions in clay minerals. GOLDSCHMIDT (1954) suggested that Ti was unlikely to substitute in lattice positions of clays to a large extent. TiO_2 thus loads with detrital quartz on factor 5 but clay on factor 6 so reflecting its two occurrences as free detrital rutile and as rutile inclusions in clays. This division of TiO_2 is found also in many other sets of data examined and seems to be very common in sediments. The loading of Mg on factor 6 illustrates its partial independence from Fe and Mn Fig. 4.4 shows quartz content plotted against factor scores for factor 6 and Fig. 4.5 shows total clay content plotted against factor scores for factor 6. The basic control behind factor 6 is thought to be rate of deposition and many authors have pointed to this as a dominant control in sedimentary geochemistry. SPENCER et al. (1968), for example, find a similar factor in data for modern sediments from the Gulf of Paria . Thus, six factors explain the variance of major elements in roof rocks :-

(a) Phosphate, probably related to pH.

(b) Oxidation potential, probably related to diagenesis.

(c) Sulphur diagenesis, probably related to sulphide ion activity.

(d) an "illite factor", probably related to provenance in a palaeogeographical or stratigraphical sense.

(e) Carbonate diagenesis, related to the availability of iron and environmental pH.

(f) Rate of deposition, expressed as quartz versus clay.

From the foregoing analysis it can be seen that diagenetic processes are of considerable importance. Factors (a), (b), (c), and (e) are probably all related to conditions during diagenesis rather than deposition. Factors (d) and (f) are depositional factors. The interpretation of the factors for roof rocks agrees closely with those of NICHOLLS and LORING (1962) and SPEARS (1964).

The appearance of factor (b) appears to confirm the importance of sulphide ion activity as an independent variable during diagenesis as was suggested by CURTIS and SPEARS (1968). Factor (d) was not reported in the interpretation of the data on cyclothemic sediments and SPEARS (1964) suggested that the variation in the composition of the clay mineral fractions for both cyclothems was slight. This appears to support the interpretation of factor (d) as a function of provenance. The summary of the data by factor analysis has proved a considerable aid to interpretation and is a logical extension of the analysis of interelement correlations which is normally employed in treating analytical data.

4.4 TRACE ELEMENT GEOCHEMISTRY

Only 8 of the 28 roof rocks were analysed for trace elements. These samples were involved in the detailed sections discussed in Chapter five. Both CURTIS (1969) and NICHOLLS and LORING (1962) have published trace element analyses for the Mansfield and Bersham cyclothems respectively. Factor analysis of this data proved impossible for several reasons :-

(a) Insufficient samples were analysed.

(b) The two sets of data could not be combined since analyses made in different laboratories by different analysts cannot be closely compared.

(c) The precisions of the various variable is unknown and since the trace elements were determined by optical spectrography high precision is unlikely.

The Viseán samples supplied by Dr. D. M. Hirst, however, were of known precision and were all analysed by one analyst in one laboratory. Factor anlysis of this data will be discussed after a brief summary of the findings of CURTIS (1969) and NICHOLLS and LORING (1962) with respect to trace element variations in cyclothemic sediments. Both studies agree that trace elements are incorporated into cyclothemic sediments in five ways :-

(a) Detrital accumulation. NICHOLLS and LORING (1962) suggested that Zr and Cr were incorporated as detrital heavy mineral phases. CURTIS (1969) did not determine Zr and does not attribute Cr to this process.

(b) Sorption processes related to clay minerals, particularly illite. Both authors associate B, Ba, Ga, and Sr with clay variation. In addition NICHOLLS and LORING (1962) determined Li, Rb, and V and associate these elements with clays. CURTIS (1969) attributes much of the variation of Cr to clay. Pb was found to be covarient with clay in the Bersham sediments but not in the Mansfield strata.

(c) Adsorption onto organic matter. Ni and Co are found to be associated with organic carbon by both authors and CURTIS (1969) finds that Pb behaves in this way.

(d) Co-precipitation with siderite. Both authors find that Mn and Ni may be at least partially incorporated in this manner.

(e) Co-precipitation with pyrite. Pb, Ba, Co, are thought to be incorporated in this way by both authors. CURTIS (1969) indicates that Cu also is associated with pyrite and NICHOLLS and LORING (1962) attribute part of the variance of V to co-precipitation with iron in pyrite. The differences in major element geochemistry of the Bersham and Mansfield sediments are adequate to explain most of the differences in trace element content. The Bersham rocks are significantly richer in quartz and SPEARS (1964) showed that the alumina : combined silica ratio was significantly and consistently higher in the Bersham rocks. It is also found that Na/Al and K/Al ratios are significantly higher in the Mansfield sediments. These facts imply that the Bersham sediments contain a clay fraction with less illite than the Mansfield sediments. The Mansfield sediments contain pyrite as the dominant diagenetic phase (with the exception of the ankerite Marine Band itself) whereas in the Bersham sediments siderite predominates. Bearing in mind the three essential differences in major element geochemistry and mineralogy :-

(a) The Bersham sediments contain more quartz.

(b) The clay fraction of the Bersham rocks is less illitic, corresponding to the brackish, less marine, conditions of deposition indicated by the palaeontology.

(c) Siderite is the dominant diagenetic phase in the Bersham rocks but pyrite predominates in the Mansfield sediments.

The differences in mean trace element abundances in Table 4.10 are adequately explained. The enrichment of Cu, Mn, and Pb in the Mansfield sediments is, however, very marked and provenance may have a significant effect on these elements.

Returning to the Viseān sediments, the data was transformed to logarithms and a correlation matrix formed. Eigenvalues were extracted and six factors were found to account for 92.46 percent of the variance of the data for 25 variables. The communalities of all variables were computed and are given together with the varimax factor matrix in Table 4.11. The relatively low communalities for Na_2O, H_2O^+, H_2O^-, and Pb reflect the low variance and/or analytical precision of these variables. Fig. 4.6 illustrates the variation of factor loadings as the factor axes are rotated from varimax through various promax solutions. The subsequent interpretation is based on this diagramatic representation.

Factor 1 incorporates loadings for CO_2, CaO, and Sr. On rotation of the factor axes the loading for CO_2 increases slightly and those for CaO and Sr show slight decreases. Factor 1 is interpreted as calcium carbonate precipitation probably as original aragonite. The interfactor correlations for the most oblique solution (kmin= 5) shown in Table 4.12 indicate that factor 1 is strongly related to factor 5. The interpretation of factor 5 is as a function of proximity to shoreline and the correlation with factor 1 indicates that calcium carbonate precipitation increases with distance from shoreline. The factor scores for factor 1 accurately indicate those samples containing significant amounts of $CaCO_3$ by X-ray diffraction.

Factor 2 involves a large number of variables. Sr, C, Cu, V, Cr, MgO, Ba, Ni, TiO_2, Na_2O, Fe_2O_3, and F have positive loadings and H_2O^+ and SiO_2 have negative loadings as shown in Table 4.11 and illustrated in Fig. 4.6. On rotation of the factor axes loadings for TiO_2, Na_2O, Fe_2O_3, and F become insignificant but the loading for H_2O^+

strengthens to become significant. Loadings for Cu, V, Cr, MgO, Ba, Ni, and SiO_2 are relatively stable but C and Sr strengthen appreciably on rotation. Factor 2 is thought to be a function of rate of deposition and the factor scores for this factor are consistent with the lithological and palaeontological evidence of rate of deposition. Factor 2 correlates very strongly with factor 6 which is interpreted as a clay factor. The correlation indicates that slow deposition favours the deposition of argillaceous sediments. The loadings of factor 2 are thought to reflect elements associated with organic carbon (Cu, V, Cr, Ba, Ni) opposed to quartz (SiO_2). The loading of MgO on factor 2 may indicate that a chloritic or montmorillonitic clay component may be involved with the factor and it s accumulation is favoured by slow deposition. The loading of H_2O^+ with SiO_2 is puzzling. It may perhaps be a function of structural water in clay minerals indicating that low inorganic detrital supply involving both quartz and clay minerals favours accumulation of organic matter. However, the proportion of the variance of H_2O^+ involved in the factor is very low (less than 30 %) and analytical precision for this variable is not exceptionally high. Factor 2 involves a very strong loading for Sr indicating that Sr incorporation is favoured by slow deposition. SPENCER (1966) has indicated that Sr is replaced by K and Rb in clay minerals after deposition. Structural rearrangement of original aragonite to calcite also involves the expulsion of Sr. It is thus possible that a great deal of Sr may be removed from argillaceous and calcareous sediments after deposition and during diagenesis. It is tentatively suggested that organic carbon may act as a scavenger for Sr expelled from clay minerals and carbonates providing deposition is sufficiently slow for accumulation of fine grained organic matter with a large surface area. In general Sr is removed from illitic clays because its ionic size is not exactly suitable to intersheet structural positions. Montmorillonitic clays may adsorb significant amounts of Sr since their structures are less rigid than those of illites. The Sr loading is thought to be a function of adsorbtion by organic carbon and possibly montmorillonitic clay.

Factor 3 involves positive loadings for MnO, Fe_2O_3, MgO, H_2O^+, and C and negative loadings for CaO, SiO_2, and Na_2O. Fig. 4.7 shows that on rotation of the factor axes only the loadings for MnO, Fe_2O_3, and MgO remain significant. The MnO loading tends to strengthen slightly on rotation whereas those for Fe_2O_3 and MgO remain fairly stable. Factor 3 is interpreted as a diagenetic siderite factor and the factor scores for this factor can be correlated with the amount of siderite determined by X-ray diffraction (KAYE et al., 1966). Factor 3 shows a significant correlation with factor 5, proximity to shoreline, indicating that siderite is found in near shore sediments. The precipitation of Fe close to shoreline is a well established fact due to the sharp pH change from river water to sea water. Factor 3 also correlates with factor 6, clay, indicating that siderite formation is favoured by increasing clay content. Clearly this correlation may reflect the rôle of clay minerals in carrying iron oxides and hydroxides into the basin of deposition (CARROLL, 1958). Such iron may provide a source for diagenetic iron minerals. The absence of a CO_2 loading on factor 3 may be simply explained; most of the variance of CO_2 is dominated by calcium carbonate (Factor 1) rather than siderite.

Factor 4 involves loadings for S, Pb, F, and Na_2O. On rotation of the factor axes all the loadings remain relatively stable, however, the F loading is very close to being insignificant. Factor 4 is thought to reflect diagenetic pyrite with which Pb is covarient. The loading of Na_2O may reflect the removal of Na^+ in solution during diagenesis. The factor is virtually independent as was found for a similar factor in the 28 roof rocks. The loading of F may indicate Pb and F were introduced as mineralising fluids. However, the vast majority of the variance of F is dominated by clay and the covariance of the factor scores with pyrite indicate that the Pb was 'fixed' by pyrite during diagenesis.

Factor 5 incorporates loadings for CaO, TiO_2, Na_2O, and Zr. Rotation of the factor axes strengthens the Zr loadings, the other loadings being relatively stable. NICHOLLS and LORING (1962) have indicated that Zr may provide a good indicator of relative proximity to shoreline. The loadings of TiO_2 and Na_2O are thought to indicate that detrital rutile and ?albite are more abundant inshore. The opposed CaO loading is thought to reflect calcium carbonate precipitation in the open sea off shore. The correlations of factor 5 with factors 1 and 3 have been previously discussed and are consistent with the interpretation of the factor as a function of relative proximity to shoreline. The factor loadings of factor 5 are consistent with the palaeontological division into marine and nonmarine strata. Factor 5 shows a significant correlation with factor 6 indicating quartz is more abundant in sediments deposited at some distance from, rather than close to, the shoreline. This fact seems to be inconsistent with finer debris (clay minerals) being carried further out to sea than coarse debris (quartz) before deposition. However, the correlation is thought to be a function of the large number of off-shore sandstones. (e.g. Immediately below the Iron post limestone)which were included in the section.

Factor 6 accounts for most of the total variance of the data. This reflects the very many variables whose variances are dominated by clay variation. SiO_2, CaO, and Zr have positive loadings but B, Rb, K_2O, Al_2O_3, H_2O^-, F, TiO_2, V, Cr, Ni, Ba, Na_2O, Cu, MgO, Fe_2O_3, and C show significant negative loadings. Factor 6 is interesting in that on rotation of the factor axes it is modified from a "clay v quartz" rate of deposition factor to a factor purely dominated by clay. Rotation of the factor axes virtually eliminates all positive loadings except Zr which tends to show an increasing antipathy towards clay. Rotation of the negative loadings eliminated C, and Fe_2O_3. The loadings for Cu and MgO weaken, those for Na_2O, TiO_2, V, Cr, Ni, Ba, F, and H_2O^- are relatively stable, and the loadings for B, Rb, K_2O, Al_2O_3, and H_2O^+ strengthen. The factor scores for factor 6 show a very strong correlation with the total clay contents quoted by HIRST (1968). The trace elements F, B, and Rb appear to be almost exclusively dominated by factor 6 whereas Cu, V, Cr, Ni, and Ba can be seen also associated with factor 2 (rate of deposition).

The foregoing interpretation of the data for Viséan sediments shows marked similarity to that for roof rocks. The siderite and pyrite factors are common to both sets of data and the phosphate factor for the roof rocks is analogous to the calcium carbonate factor for the Viséan rocks. The Eh factor and rate of deposition factor for the roof rocks are in large part alternative expressions of the rate of deposition and clay factors for the Viséan sediments. The variation from marine to non-marine sediments in the Visean sediments is expressed by factor 5 whereas in the roof rocks the variation indicated by the illite factor is probably related to provenance rather than transgression. The trace element variations in roof rocks will be largely controlled by factors similar to those at work in cyclothemic sediments. The data of CURTIS (1969), NICHOLLS and LORING (1962), and that supplied by Dr. D. M. Hirst provide a good guide to the trace element distributions to be expected in cyclothemic sediments. Roof rocks show essentially the same variations as cyclothemic sediments. In order to assess the ways in which seatearths differ from normal cyclothemic sediments it has been necessary to investigate the factors controlling the distributions of elements in these sediments. The limited data obtained for roof rocks indicates that a detailed study of such rocks may reveal details of source area variation throughout the Carboniferous. However, the vast majority of the observed variations in roof rocks are related to the normal variations within cyclothemic sediments.

TABLE 4.1

MINERALOGICAL ANALYSES OF 14 ROOF ROCKS COMPARED WITH 10 CYCLOTHEMIC SEDIMENTS AFTER NICHOLLS AND LORING (1962).

SAMPLE	C	CBT	QZ	CHL	ILL	KAOL	T.C.
LL1	0.4	1.6	62	3	27	6	36
LL2	0.4	1.5	58	4	30	6	40
LL3	0.2	1.3	60	4	28	6	38
LL4	0.5	1.0	66	3	24	6	33
LL5	0.6	6.3	57	3	27	6	36
TB1	0.7	0.1	56	3	25	14	42
TB2	0.4	0.2	31	5	40	24	69
TB3	1.8	0.1	62	3	20	13	36
BS2	0.8	3.1	51	4	20	21	45
BS4	1.3	7.4	44	4	21	23	48
BS12	1.3	4.3	8	6	37	44	87
BS14	0.4	2.8	9	6	38	44	88
BS20	1.0	3.2	20	8	31	37	76
BS22	1.2	0.1	23	8	31	38	77
BC1731	10.6	0.3	2	4	49	26	79
BC1	0.2	0.4	52	4	27	15	46
BC2	0.3	1.9	32	5	42	16	63
BC3	2.6	3.3	29	5	51	6	62
BC4	0.3	3.5	43	6	30	15	51
BC5	0.4	2.8	34	5	42	13	60
BC6	0.4	1.2	34	6	47	8	61
BC7	1.1	0.3	29	4	43	18	65
BC8	1.0	1.3	32	3	41	17	61
BC9	0.7	0.2	29	3	40	21	64

TABLE 4.2

MAJOR ELEMENT ANALYSES OF 28 ROOF ROCKS

SAMPLE	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	K_2O	Na_2O
LL1	77.9	0.61	9.9	4.30	0.44	0.016	0.29	2.30	0.37
LL2	74.7	0.81	12.9	4.15	0.45	0.014	0.34	2.90	0.33
LL3	76.0	0.60	11.8	4.20	0.44	0.014	0.22	2.70	0.38
LL4	80.5	0.64	9.0	3.50	0.35	0.013	0.16	2.20	0.30
LL5	68.3	0.48	10.5	8.60	2.00	0.044	0.30	2.00	0.28
LL13	50.3	0.80	20.2	5.85	1.20	0.020	0.47	4.05	0.39
LL16	48.4	0.75	21.6	7.08	1.06	0.024	0.55	3.85	0.35
BS2	66.1	0.78	17.2	4.86	0.85	0.022	1.24	1.70	0.39
BS4	59.1	0.59	16.4	10.68	3.15	0.060	0.50	1.75	0.36
BS12	48.2	0.95	23.4	8.28	2.86	0.048	0.79	2.60	0.29
BS14	49.0	0.92	27.1	6.06	1.35	0.026	0.59	3.09	0.35
BS20	52.9	1.03	25.0	5.60	1.46	0.020	0.29	2.85	0.29
BS22	55.5	1.15	26.9	2.75	0.60	0.010	0.19	2.95	0.29
TB1	73.5	0.72	14.0	2.61	0.68	0.010	0.22	2.60	1.40
TB2	59.6	0.87	20.5	3.34	1.33	0.022	0.25	4.00	0.92
TB3	77.8	0.88	9.9	1.69	0.44	0.012	0.17	2.10	1.23
ST1	55.7	1.16	21.8	2.94	0.94	0.010	0.30	1.39	0.22
ST2	55.9	1.13	22.9	3.09	1.04	0.012	0.32	1.46	0.23
NP1	54.6	0.97	21.0	7.78	2.18	0.030	0.62	3.19	0.47
NP3	53.6	0.95	21.5	8.20	2.51	0.032	0.65	3.03	0.44
KB2	54.9	1.11	22.1	5.87	1.41	0.024	0.25	2.58	0.21
KB3	57.4	1.17	22.6	2.95	1.01	0.014	0.18	2.69	0.18
KB13	52.9	1.03	23.9	7.45	1.86	0.024	0.25	2.35	0.19
KB15	53.9	1.06	26.7	2.87	0.90	0.010	0.24	2.54	0.19
KB21	53.7	1.17	21.3	7.01	1.57	0.034	0.25	2.15	0.18
KB23	58.1	1.16	21.7	4.09	1.16	0.020	0.19	2.26	0.22
KB37	51.0	1.03	24.3	4.45	1.15	0.016	0.17	2.37	0.21
KB39	50.9	1.01	25.1	3.86	1.03	0.012	0.15	2.34	0.20

TABLE 4.2 (CONTINUED)

MAJOR ELEMENT ANALYSES OF 28 ROOF ROCKS

SAMPLE	S	P_2O_5	C	H_2O^+	H_2O^-	CO_2
LL1	0.20	0.11	0.40	1.80	0.60	0.61
LL2	0.22	0.09	0.43	1.90	0.60	0.59
LL3	0.14	0.12	0.20	1.96	0.60	0.51
LL4	0.25	0.09	0.50	1.90	0.50	0.39
LL5	0.29	0.14	0.57	2.04	0.65	2.41
LL13	1.34	0.11	5.60	5.13	1.50	0.05
LL16	1.46	0.09	4.40	5.93	1.40	0.30
BS2	0.11	0.12	0.75	4.20	0.50	1.20
BS4	0.20	0.09	1.30	3.00	0.53	2.85
BS12	0.15	0.24	1.30	8.39	0.51	2.05
BS14	0.19	0.16	0.38	8.96	0.77	1.10
BS20	0.06	0.07	1.02	8.34	0.64	1.25
BS22	0.15	0.03	1.22	8.67	0.68	0.02
TB1	0.03	0.10	0.70	2.42	0.60	0.05
TB2	0.09	0.06	0.40	2.88	1.50	0.06
TB3	0.03	0.09	1.80	2.24	0.52	0.02
ST1	0.13	0.11	6.40	6.22	0.30	0.03
ST2	0.38	0.09	5.70	6.29	0.32	0.05
NP1	0.03	0.15	2.12	4.00	0.85	2.01
NP3	0.11	0.15	1.48	4.30	0.90	2.21
KB2	1.62	0.11	2.03	7.40	0.65	0.15
KB3	0.42	0.08	2.40	7.53	0.66	0.21
KB13	0.02	0.08	0.10	6.89	0.55	2.01
KB15	0.27	0.04	1.24	9.09	0.53	0.44
KB21	1.13	0.13	3.92	6.29	0.49	0.66
KB23	0.56	0.13	2.00	6.96	0.50	0.38
KB37	0.67	0.04	5.50	8.56	0.48	0.20
KB39	0.16	0.04	5.70	8.67	0.44	0.40

TABLE 4.3

MAJOR ELEMENT CORRELATION COEFFICIENT MATRIX BASED ON LOGARITHMIC TRANSFORMED ANALYTICAL DATA FOR 28 ROOF ROCKS

ELEMENT	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	K_2O
SiO_2	1.00							
TiO_2	-0.60	1.00						
Al_2O_3	-0.92	0.77	1.00					
Fe_2O_3				1.00				
MgO	-0.69		0.53	0.75	1.00			
MnO				0.90	0.79	1.00		
CaO				0.60	0.47	0.59	1.00	
K_2O								1.00
Na_2O	0.46		-0.45					
S								
P_2O_5				0.49		0.57	0.59	
C	-0.48	0.46						
H_2O^+	-0.88	0.79	0.93					
H_2O^-								0.89
CO_2				0.79	0.52	0.70	0.47	

ELEMENT	Na_2O	S	P_2O_5	C	H_2O^+	H_2O^-	CO_2
SiO_2							
TiO_2							
Al_2O_3							
Fe_2O_3							
MgO							
MnO							
CaO							
K_2O							
Na_2O	1.00						
S	-0.51	1.00					
P_2O_5			1.00				
C		0.50		1.00			
H_2O^+	-0.59			0.47	1.00		
H_2O^-						1.00	
CO_2							1.00

TABLE 4.4

EIGENVALUES EXTRACTED FROM ROOF ROCK CORRELATION MATRIX

EIGENVALUE	PERCENTAGE OF VARIANCE	CUMMULATIVE PERCENTAGE
4.769	31.796	31.796
4.101	27.338	59.134
2.101	14.005	73.139
1.314	8.757	81.896
1.078	7.187	89.082
0.580	3.864	92.946
0.426	2.837	
0.228	1.517	
0.135	0.900	
0.103	0.686	
0.065	0.436	
0.051	0.341	
0.025	0.164	
0.016	0.106	
0.010	0.067	

TABLE 4.5

VARIMAX ORTHOGONAL FACTOR MATRIX AND COMMUNALITIES

FACTOR	1	2	3	4	5	6	COMM
SiO_2					-0.37	0.86	0.97
TiO_2					-0.28	-0.88	0.88
Al_2O_3						-0.96	0.97
Fe_2O_3	0.26				0.90		0.96
MgO					0.84	-0.42	0.95
MnO	0.30				0.91		0.93
CaO	0.76				0.44		0.80
K_2O				0.96			0.95
Na_2O		0.24	-0.67	-0.39		0.48	0.96
S		0.30	0.92				0.96
P_2O_5	0.85				0.31		0.87
C		0.80	0.31			-0.39	0.91
H_2O^+						-0.95	0.95
H_2O^-				0.97			0.97
CO_2		-0.52			0.77		0.90

Factor loadings of less than 0.25 have been omitted.

TABLE 4.6

PROMAX OBLIQUE FACTOR MATRIX FOR KMIN = 3

FACTOR	1	2	3	4	5	6
SiO_2					-0.32	0.79
TiO_2					-0.38	-0.96
Al_2O_3						-0.98
Fe_2O_3			(0.15)		0.89	
MgO			(-0.22)		0.92	-0.30
MnO					0.94	
CaO	0.75					
K_2O				1.02		
Na_2O			-0.61	0.29		0.39
S		0.37	0.98			
P_2O_5	0.88					
C		0.85	0.29			
H_2O^+						-0.95
H_2O^-				0.97		
CO_2		-0.51			0.73	

Factor loadings less than 0.25 have been omitted

TABLE 4.7

INTERFACTOR CORRELATIONS FOR PROMAX OBLIQUE FACTOR MATRIX

KMIN = 3

FACTOR	1	2	3	4	5	6
1	1.00					
2	0.00	1.00				
3	-0.14	-0.06	1.00			
4	0.13	0.19	-0.18	1.00		
5	0.44	-0.07	0.16	0.16	1.00	
6	0.22	-0.22	-0.26	0.05	-0.19	1.00

TABLE 4.8

SUMMARY STATISTICS FOR 15 CHEMICAL COMPONENTS IN 28 ROOF ROCKS

	MAX	MIN	MEAN	S.DEV	C.V. %	VAR	EVAR	COMM
SiO_2	80.50	48.17	59.66	10.02	16.8	100.34	3.50	0.96
TiO_2	1.17	0.48	0.91	0.20	22.0	0.041	0.00083	0.98
Al_2O_3	27.07	9.00	19.68	5.54	28.0	30.70	0.38	0.99
Fe_2O_3	10.68	1.69	5.15	2.22	43.0	4.94	0.20	0.96
MgO	3.15	0.35	1.27	0.72	56.6	0.519	0.040	0.92
MnO	0.06	0.01	0.022	0.012	54.4	0.00014	0.000003	0.98
CaO	1.24	0.15	0.36	0.24	66.7	0.057	0.0032	0.94
K_2O	4.05	1.39	2.57	0.66	25.6	0.440	0.0066	0.98
Na_2O	1.40	0.18	0.39	0.29	74.5	0.087	0.0074	0.92
S	1.62	0.02	0.37	0.45	121.9	0.199	0.00055	0.99
P_2O_5	0.24	0.03	0.10	0.043	43.0	0.002	0.0004	0.80
C	6.40	0.10	2.13	1.98	93.0	3.90	0.11	0.97
H_2O^+	9.09	1.80	5.43	2.59	47.6	6.69	0.28	0.96
H_2O^-	1.50	0.30	0.67	0.31	46.4	0.093	0.0046	0.95
CO_2	2.85	0.02	0.79	0.84	106.4	0.713	0.016	0.98

MAX = Maximum percent

MIN = Minimum percent

MEAN = Mean percent

S.DEV = Standard deviation

C.V.% = Coefficient of variation percent

VAR = Variance

EVAR = Error variance estimated from precision

COMM = Estimated communality

TABLE 4.9

FACTOR SCORES FOR 28 ROOF ROCKS COMPUTED FOR THE FACTOR MATRIX GIVEN IN TABLE 4.6

	1	2	3	4	5	6
LL1	0.353	-1.200	0.343	-0.233	-0.612	1.785
LL2	0.299	-1.351	0.384	0.135	-0.817	1.099
LL3	0.159	-1.750	0.161	0.045	-0.760	1.583
LL4	-0.472	-1.268	0.734	-0.665	-1.080	1.809
LL5	0.219	-0.540	0.548	-0.376	1.566	1.726
LL13	0.633	1.899	0.737	2.254	0.194	-0.066
LL16	0.472	1.196	1.078	2.055	0.637	-0.188
BS2	1.807	-0.556	-0.465	-0.821	0.159	0.384
BS4	0.087	0.372	-0.207	-0.623	2.211	0.775
BS12	1.972	-0.040	-0.125	-0.166	1.615	-0.830
BS14	1.299	-0.872	-0.041	0.752	0.606	-0.839
BS20	-0.578	-0.645	-0.496	0.142	0.443	-0.916
BS22	-1.891	0.204	-0.263	0.497	-1.362	-0.992
TB1	0.096	0.652	-2.406	0.410	-1.311	1.279
TB2	-0.676	0.676	-1.777	2.331	-0.234	0.393
TB3	-0.110	1.309	-2.300	-0.282	-1.891	1.504
ST1	0.250	1.203	-0.153	-2.004	-1.030	-0.722
ST2	0.049	1.218	0.339	-1.740	-0.767	-0.692
NP1	1.227	0.262	-1.377	0.789	1.149	-0.264
NP3	1.265	0.221	-0.687	0.856	1.315	-0.270
KB2	0.014	0.482	1.435	0.093	0.220	-0.623
KB3	-0.733	0.001	0.883	-0.083	-0.646	-0.796
KB13	-0.702	-2.430	-0.689	-0.548	0.821	-0.891
KB15	-1.452	-0.685	0.579	-0.318	-0.704	-1.107
KB21	0.201	0.462	1.498	-0.716	0.768	-0.627
KB23	0.022	-0.004	0.936	-0.648	-0.167	-0.583
KB37	-1.817	0.805	0.967	-0.419	-0.058	-0.910
KB39	-1.994	0.335	0.363	-0.716	-0.263	-1.022

TABLE 4.10

COMPARISON OF AVERAGE CYCLOTHEMIC SEDIMENTS WITH THE AVERAGE COMPOSITION OF 28 ROOF ROCKS.

	A	B	C	D
SiO_2	59.66	51.14	62.04	65.35
TiO_2	0.91	0.87	0.89	0.69
Al_2O_3	19.68	21.64	21.26	14.32
Fe_2O_3	5.15	7.43	3.19	5.11
MgO	1.27	1.70	0.95	0.90
MnO	0.024	0.095	0.029	0.19
CaO	0.36	0.33	0.33	1.94
Na_2O	0.39	0.71	0.50	0.31
K_2O	2.57	3.95	3.10	2.92
S	0.37	2.65	0.28	0.51
P_2O_5	0.10	0.12	0.12	n.d.
C	2.13	2.94	1.76	2.09
H_2O^+	5.43	5.09	5.32	2.39
H_2O^-	0.67	1.95	1.11	0.67
CO_2	0.79	0.32	0.61	2.37
B	n.d.	86	60	111
Ba	n.d.	586	396	303
Co	n.d.	23	30	n.d.
Cr	n.d.	118	145	80
Cu	n.d.	108	38	18
F	n.d.	n.d.	n.d.	919
Ga	n.d.	33	25	n.d.
Li	n.d.	n.d.	122	n.d.
Ni	n.d.	69	61	40
Pb	n.d.	54	8	15
Rb	n.d.	n.d.	164	158
Sr	n.d.	111	74	162
V	n.d.	n.d.	167	47
Zr	n.d.	n.d.	247	261

n.d. = not determined.

KEY TO TABLE 4.10

A	Average of 28 roof rocks (This work).
B	Average of 14 cyclothemic sediments from the Mansfield Marine Band cyclothem. Major elements (S687, 3, 6, 9, 11, 15, 19, 21, 23, 24, 27, 29, 32, and S689) after SPEARS (1964). Trace elements (S952, 2, 6, 8, 12, 16, 18, 22, 24, 26, 28, 32, and S970) after CURTIS (1969).
C	Average of 10 cyclothemic sediments from the Bersham cyclothem (BC1731 and BC1-9) after NICHOLLS and LORING (1962).
D	Average of 49 unpublished analyses of Viséan cyclothemic sediments supplied by Dr. D. M. Hirst.

TABLE 4.11

VARIMAX FACTOR MATRIX AND COMMUNALITIES BASED ON 49 VISEAN CYCLOTHEMIC SEDIMENTS ANALYSED FOR 25 CHEMICAL VARIABLES

	1	2	3	4	5	6	COMM
SiO_2		-0.63	-0.29			0.67	0.97
TiO_2		0.36			-0.40	-0.79	0.94
Al_2O_3			0.26			-0.93	0.98
Fe_2O_3		0.25	0.74			-0.53	0.96
MgO		0.51	0.39			-0.70	0.93
MnO			0.91				0.92
CaO	0.44		-0.29		0.71	0.33	0.91
Na_2O		0.33		-0.35	-0.47	-0.56	0.79
K_2O						-0.93	0.99
H_2O^+			0.30			-0.85	0.84
H_2O^-						-0.85	0.87
CO_2	0.91						0.95
C		0.73	0.26			-0.50	0.92
S				0.91			0.81
B						-0.96	0.96
F		0.33		0.32		-0.83	0.93
V		0.54				-0.79	0.94
Cr		0.54				-0.80	0.95
Ni		0.48				-0.80	0.95
Cu		0.61				-0.70	0.91
Rb						-0.97	0.99
Sr	0.37	0.80					0.89
Zr					-0.94		0.92
Ba		0.49				-0.82	0.97
Pb				0.90			0.85

Factor loadings less than 0.25 have been omitted.

TABLE 4.12

CORRELATIONS BETWEEN PROMAX FACTORS KMIN = 5 FOR FACTOR ANALYSIS OF 49 VISEAN SEDIMENTS FOR 25 CHEMICAL VARIABLES

FACTOR	1	2	3	4	5	6
1	1.00					
2	0.01	1.00				
3	-0.12	0.32	1.00			
4	-0.08	0.23	0.18	1.00		
5	0.47	-0.32	-0.41	0.10	1.00	
6	0.23	-0.74	-0.52	-0.24	0.52	1.00

FIG. 4·1 SIX FACTORS EXTRACTED FROM 28 ROOF ROCKS FOR 15 VARIABLES

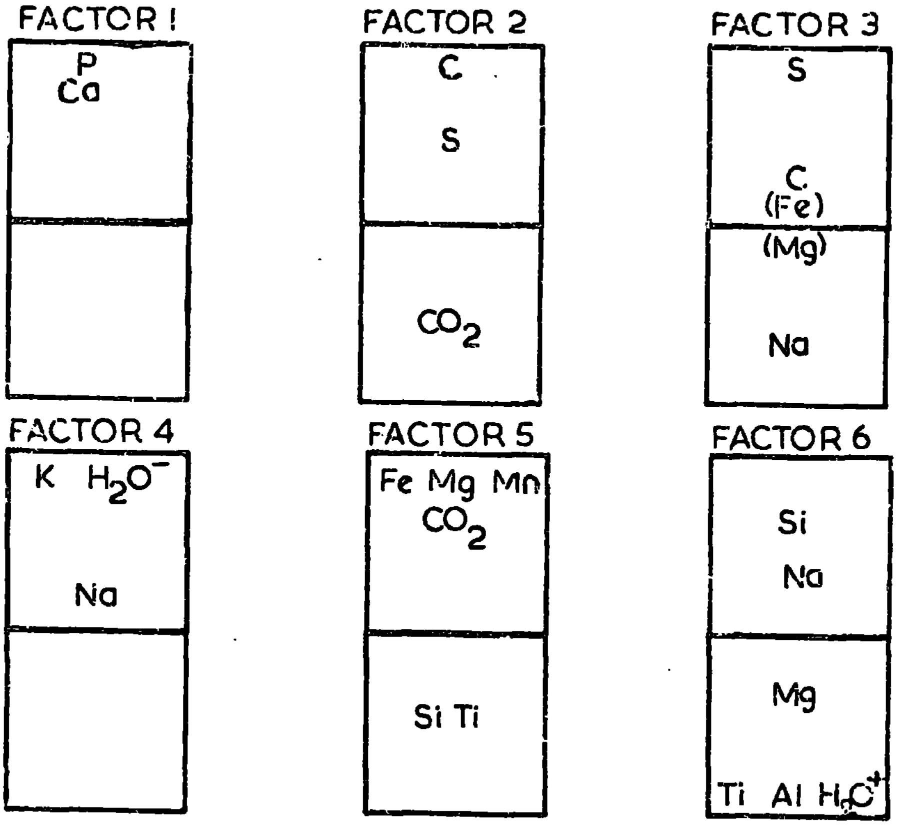


FIG. 4.2 ILLITE CONTENTS FOR 14 ROOF ROCKS v FACTOR SCORES FOR FACTOR 4.

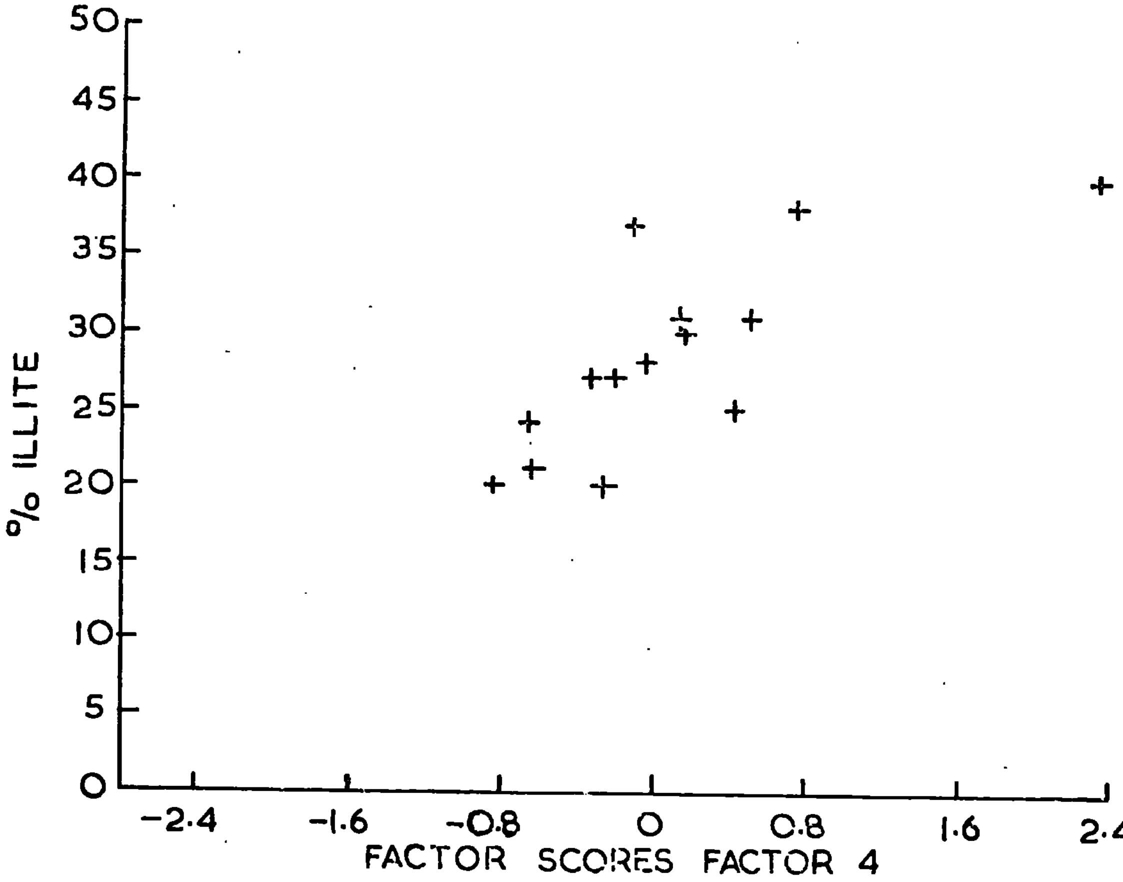


FIG. 4·3 SIDERITE CONTENT FOR 14 ROOF ROCKS v FACTOR SCORES FOR FACTOR 5.

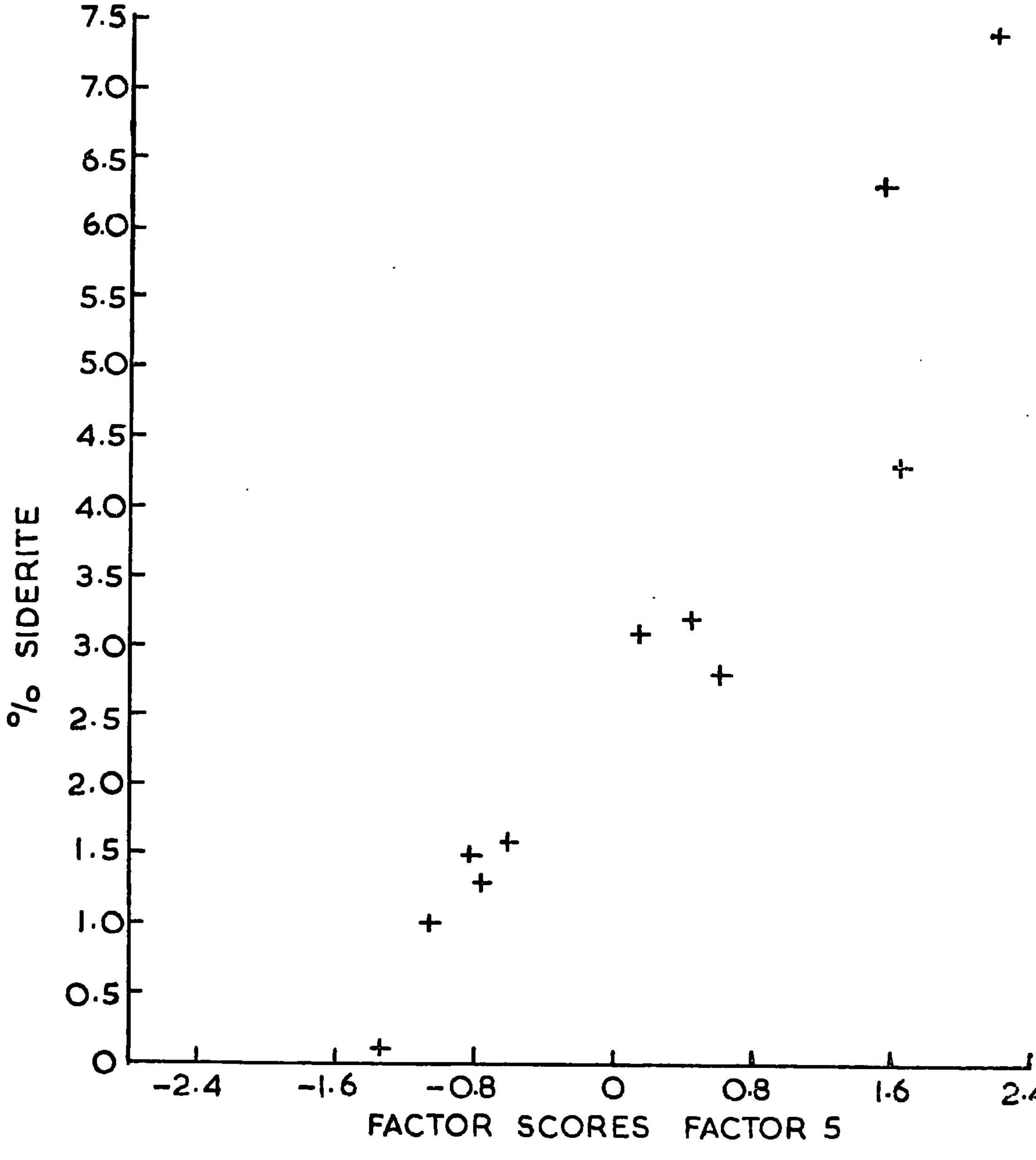


FIG. 4·4 QUARTZ CONTENT FOR 14 ROOF ROCKS v FACTOR SCORES FOR FACTOR 6

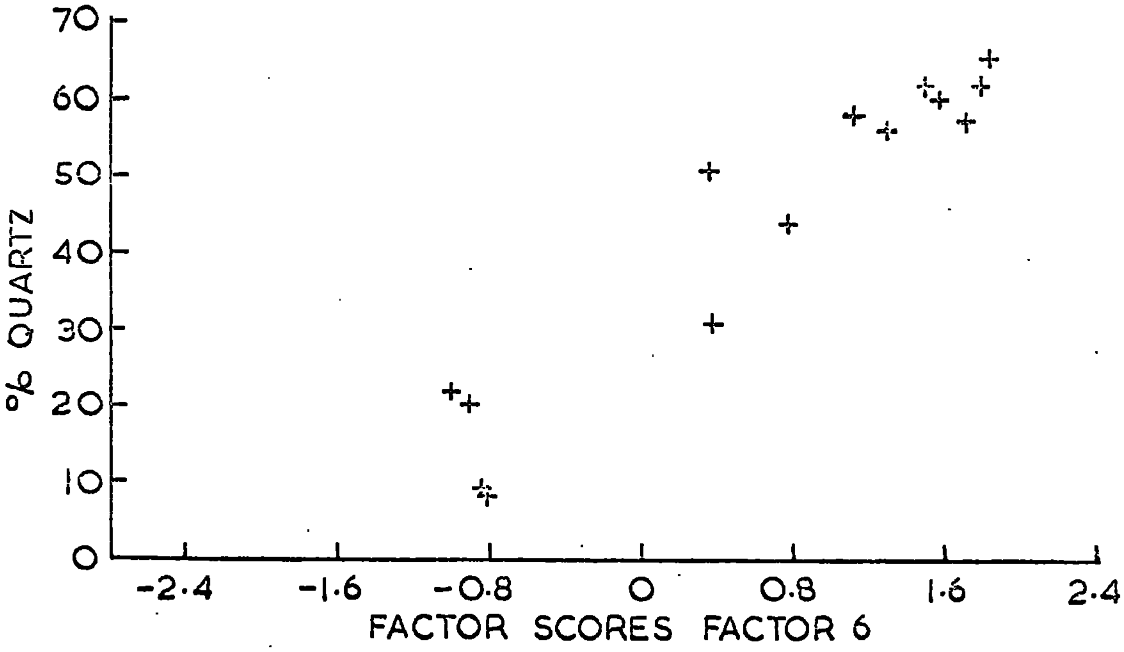


FIG. 4·5 TOTAL CLAY CONTENT FOR 14 ROOF ROCKS v FACTOR SCORES FOR FACTOR 6

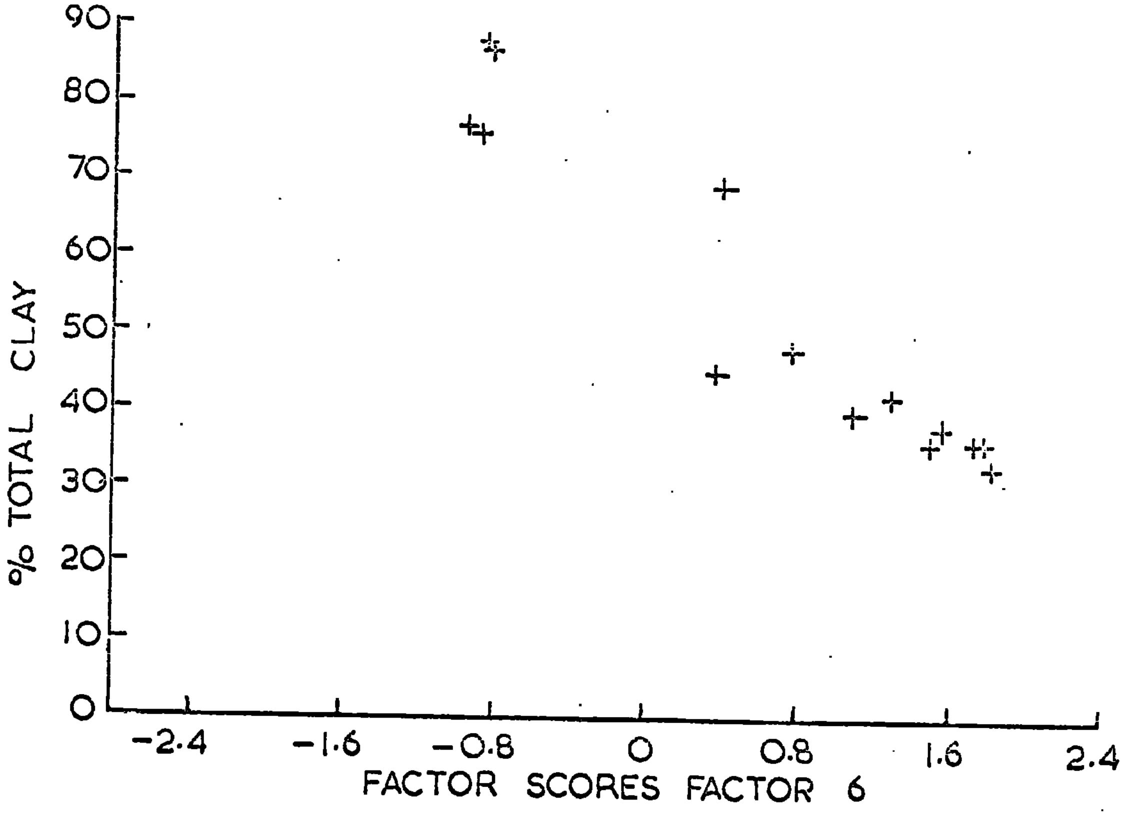
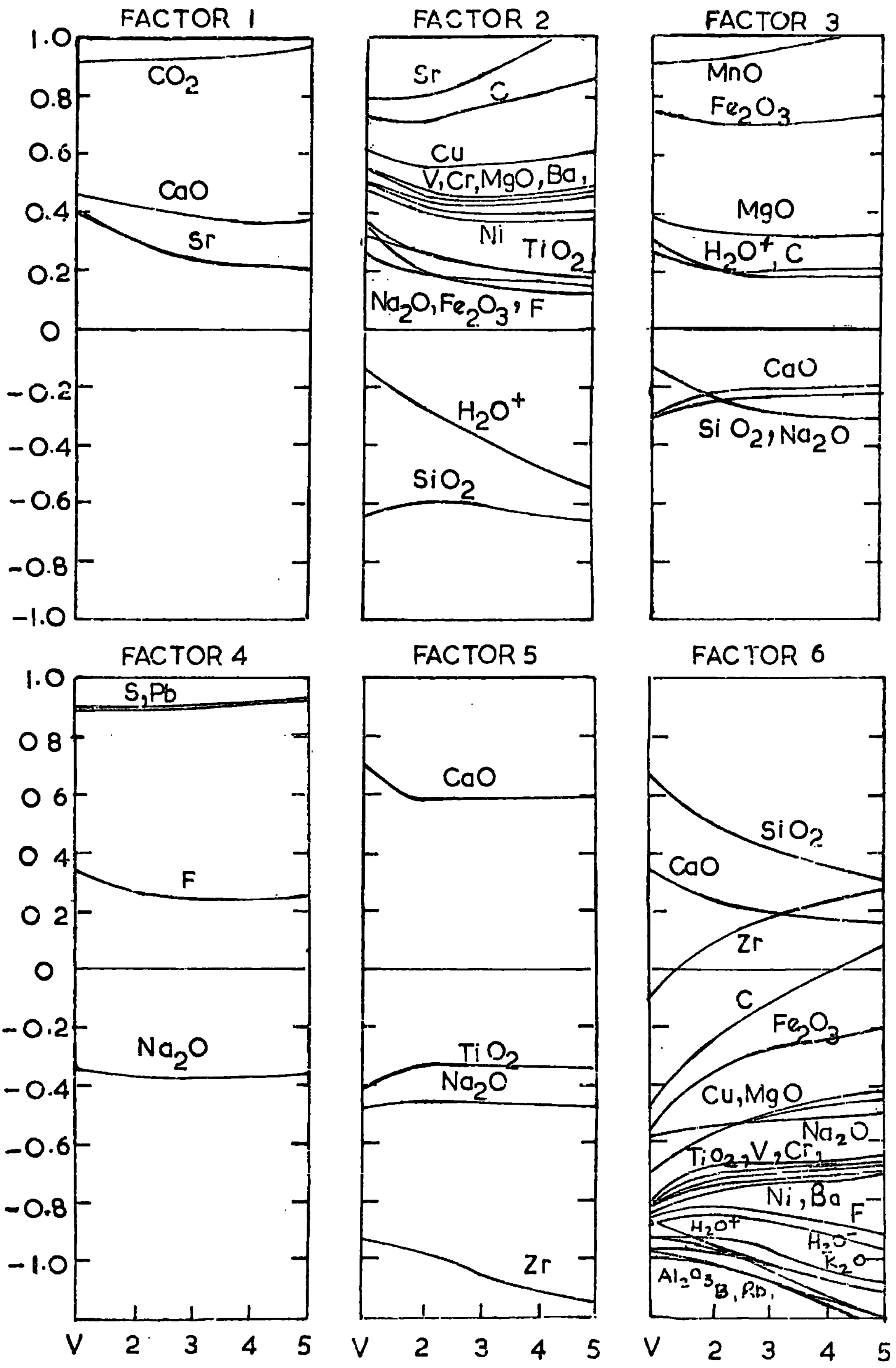


FIG. 4·6 VARIATION OF FACTOR LOADINGS ON ROTATION OF FACTOR AXES



4.5 REFERENCES TO CHAPTER FOUR

CARROLL, D., (1958), The rôle of clay minerals in the transportation of iron, Geochim. Cosmochim. Acta, 14, 1-27.

CURTIS, C. D., (1969), Trace element distribution in some British Carboniferous sediments, Geochim. Cosmochim, 33, 519 - 523.

CURTIS, C. D., and SPEARS, D. A., (1968), The formation of sedimentary iron minerals, Econ. Geol., 63, 257 -270.

DUNHAM, K. C., DUNHAM, A. C., HODGE, B. L., and JOHNSON, G. A. L., (1965), Granite beneath Viséan sediments with mineralization at Rookhope, Northern pennines, Quart, J. Geol. Soc. Lond., 121, 383 - 417.

GOLDSCHMIDT, V. M., (1954), Geochemistry, Clarendon Press, Oxford.

HENDRICKSON, A. E., and WHITE, P. O., (1964), Promax: a quick method for rotation to oblique simple structure, Brit. J. Statis. Psychol., 17, 65 - 70.

HIRST, D. M., (1968), Relationships between minor elements, mineralogy, and depositional environment in Carboniferous sedimentary rocks from a borehole at Rookhope (Northern pennines), Sediment. Geol., 2, 5 - 12.

KAYE, M. J., DUNHAM, A. C., and HIRST, D. M., (1968), A comparison of two methods of quantitative mineralogical analysis of sedimentary rocks, J. Sed. Pet., 38, 675 - 679.

KRUMBEIN, W. C., and GARRELS, R. M., (1952), Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials, J. Geol., 60, 1 - 33.

LOVE, L. G., (1967), Sulphides of metals in recent sediments, In, Proc. 15th Inter-Univ. Geol. Cong., Dept. Geol. Leicester, 1969.

NICHOLLS, G. D., and LORING, D. H., (1960, Some chemical data on British Carboniferous sediments and their relationship to the clay mineralogy of these rocks, Clay Min. Bull., Min. Soc. Lond., 4, 196 - 207.

NICHOLLS, G. D., and LORING D. H., (1962), The geochemistry of some British Carboniferous sediments, Geochim. Cosmochim. Acta, 26, 181 - 223.

SPEARS, D. A., (1964), The major element geochemistry of the Mansfield Marine Band in the Westphalian of Yorkshire, Geochim. Cosmochim. Acta, 28, 1679 - 1696.

SPEARS, D. A., (1965), Boron in some British Carboniferous sedimentary rocks, Geochim. Cosmochim. Acta, 29, 315 - 328.

SPENCER, D. W., DEGENS, E. T., and KULBICKI, G., (1968), Factors affecting element distributions in sediments, In, Origin and distribution of the elements, Ed. L. H. Arhens.

CHAPTER FIVE

THE SIGNIFICANCE OF CHEMICAL AND MINERALOGICAL DIFFERENCES BETWEEN SEATEARTHS AND ROOF ROCKS

5.1 INTRODUCTION

The data for seatearths and roof rocks has been discussed in isolation in Chapters three and four respectively. The purpose of this Chapter is to point out the chemical and mineralogical differences between seatearths and roof rocks which may be significant in the genesis of the former. In addition to the samples discussed in previous Chapters several sections were examined in detail. Theyare:-

(a) The Top Busty Coal section from the Modiolaris Zone of the Middle Coal Measures of the Durham - Northumberland Coalfield.

(b) The Upper, Middle, and Lower Brockwell Coal sections from the Communis Zone of the Lower Coal Measures of the Durham - Northumberland Coalfield.

(c) The Upper Little Limestone Coal section from near the base of the Namurian in the Yoredale type facies of Cumberland.

Full details of the samples involved were given in Chapter one. Since only five horizons were examined in detail and because the nature of roof measures varies so considerably (as indicated in Chapter four) it is virtually impossible to find a section typical of the Upper Carboniferous. Instead, sections (a) and (c) were chosen because the sandy nature of the roof measures in these samples may indicate fast deposition and thus may provide a fairly accurate reflection of the source rocks. The section listed under (b) were chosen to illustrate the variation in roof measures through a relatively short period of time.

5.2 MINERALOGICAL DIFFERENCES BETWEEN SEATEARTHS AND ROOF ROCKS

Mineralogical analyses (using the methods outlined in Appendix I) were carried out on 14 roof rocks and 15 seatearths from the detailed sections previously described. The results are shown in Table 5.1. These data are compared with those of other authors in Table 5.2.

5.21 QUARTZ

Microscopic examination of roof rocks and seatearths showed that the quartz grains in the latter were, on average, considerably smaller than those of the former. Grain size distribution curves (determined by wet pipette analysis) shown in Fig. 5.1 demonstrate the fine grain size of these seatearths. The macro-quartz in roof rocks, even in the argillaceous sediments, is relatively coarse and angular. In the seatearths some angular relatively fresh grains are present but much of the quartz occurs as rounded and abraded grains of a grain size approaching that of the clay minerals. The average analyses for this work indicate that roof rocks are richer in quartz and this fact is contrary to the data of DIXON et al. (1970). It is thought that the contradictions may be explained by the following factors :-

(a) There is a distinct difference in provenance.

(b) There is a distinct difference in stratigraphic range of the material analysed.

(c) The roof measures analysed in this work were deliberately chosen to be sandy.

Although factor (c) may be responsible for the relatively high mean quartz content for roof rocks in this work it is thought that the figure for seatearths is fairly typical. Perhaps the greatest difference between the quartz contents of seatearths and roof rocks is the greater variability of the quartz contents of the roof rocks. In 14 roof rocks quartz ranges from 8 to 66 percent, while in 15 seatearths quartz varies from 14 to 35 percent and in the total of 42 seatearths from 2 to 44 percent. The data in Table 5.1 show that there is no consistent relationship between the quartz content of roof measures to that of the corresponding seatearth and this is particularly well illustrated in the sequence which includes the three Brockwell coals. The variations in quartz content between seatearths and roof rocks leads to the following conclusions :-

(a) The quartz in seatearths is finer grained, more rounded, and more abraded than that of roof rocks and this is thought to provide evidence of churning and reworking of <u>in situ</u> seatearths.

(b) The variation of quartz content in seatearth profiles shows a slight but consistent increase towards the base of the unit. This fact has been noted by many other workers e.g. MOORE (1968).

(c) The variation of quartz content in seatearths is restricted when compared with the variation observed in roof rocks. This restricted compositional range may imply similar depositional conditions for seatearths when considered together with other evidence.

(d) There is no consistent relationship between the quartz content of roof rocks and that of the preceding seatearth. This fact is related to the variability of roof rocks discussed in Chapter four.

5.22 CARBONACEOUS MATTER

The carbonaceous matter in both seatearths and roof rocks consists of coaly partings, coaly fragments, fossil wood, spores and other carbonaceous film derived from planty material. Calamites is commonly found in the roof rocks and Stigmaria rootlets are typical of almost every seatearth examined. The amount of carbon present in the samples is largely a function of the frequency of coaly partings which are commonly found in the sediments in the proximity of coal seams.

5.23 CARBONATE (SIDERITE)

Both seatearths and roof rocks contain carbonate usually in the form of siderite nodules. The occurrence of such nodules in Upper Carboniferous sediments is well known and ironstone bands developed as a result of concentration of such nodules have in the past been worked for iron. Such bands commonly occur above coal seams rather than below them and in the present work although the concentration of nodules is relatively small they are significantly more abundant in roof rocks. The data of DIXON et al. (1970) substantiates this tendency and the roof rocks analysed by these workers contained considerable amounts of siderite.

X-ray diffraction analysis of siderite nodules separated from both roof rocks and seatearths showed that they consist of siderite together with coarse, well crystalline kaolinite and often a little pyrite. GRIM and ALLEN (1938), SCHULTZ (1958), HUDDLE and PATTERSON (1961), WILSON (1965), and MOORE (1968) all remark on a concentration of siderite nodules towards the base of seatearths and the Upper Little Limestone section in Table 5.1 shows such a trend. CURTIS (1967) indicated that the development of siderite nodules needs a relatively high partial pressure of CO_2 and that such pressures are generated during diagenesis. ATTWELL et al. (1969) show that siderite nodules are deformed in a manner consistent with overburden pressure in diagenesis and that on a microscopic scale the siderite crystallites are oriented with the c-axis vertical. Thus, the evidence that siderite nodules are formed during diagenesis is considerable. CURTIS and SPEARS (1968) indicate that a reaction of the form :-

$$4Fe(OH)_3 + 3C_{org} \xrightarrow{-4e} 3CO_2 + 4Fe^{2+} + 6H_2O$$

may occur in the diagenetic environment. Such a reaction requires that sulphide ion activity be low and pyrite may form prior to the reaction to remove sulphide ions. This would explain the association of pyrite with siderite nodules. Samples LL5 and BS4 show carbonate enrichment adjacent to coal seams and the Upper Little Limestone seatearth is rich in both carbon and carbonate. Thus, there is evidence that carbon provided a source for diagenetic carbonate. KELLER (1957) stated that root respiration and decay of vegetation may generate relatively high CO_2 concentrations near the surface in modern soils. Leaching of CO_2 as the bicarbonate ion has been put forward by KELLER (1957) as a theory for the formation of carbonate concentrations in soils. Such processes were probably active in seatearth formation but calcite rather than siderite would be formed. The process was probably responsible for the removal of Ca^{2+} from seatearths by leaching.

The reaction is :-

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$

This reaction releases hydrogen ions and therefore tends to lower the pH of the environment and favours leaching of metal ions. Leaching of Fe in this way may be responsible for the distribution of siderite nodules developed in some seatearths. Three factors are thought to be important in the formation of siderite nodules.

(a) Fe must be available. Siderite nodules are absent from the Top Busty section probably due to the leaching of readily available iron. (See Table 5.4)

(b) Carbon in a readily oxidisable form, or CO_2 must be available. Absence of this component may explain the excess Fe oxides present in samples LL1 - 4, although recent weathering is a more likely explanation.

(c) Sulphide must be removed as pyrite.

5.24 CLAY MINERALS

Table 5.3 shows the clay mineral fraction compositions of the detailed sections together with the average roof and floor of DIXON et al. (1970). The clay mineralogy of seatearths and roof rocks consists essentially of three minerals; chlorite, illite (as defined in Chapter two), and kaolinite. From Table 5.3 the following points are apparent :-

(a) Seatearths are in general more kaolinitic than roof rocks.

(b) From the relative mean depletions of clay minerals from roof rocks to seatearth the order of clay mineral stability in seatearths may be deduced as kaolinite > illite > chlorite.

(c) Over the restricted stratigraphic range of the Brockwell coals the composition of the clay mineral fraction of roof rocks is virtually constant.

(a) is consistent with seatearths being leached of mobile elements. (b) implies that chlorite and illite are destroyed at the expense of, and to form kaolinite and that chlorite is the more rapidly altered mineral. (c) shows that change of source material does not explain the roof to floor variations unless rapid fluctuations in source corresponding to roof and floor are envisaged. Since the Upper Brockwell roof is sandy and the Middle and Lower Brockwell roof rocks relatively argillaceous it is likely that rate of deposition also has little effect on the composition of the clay mineral fraction. Sample TB2 represents a silty band in the sandy roof of the Top Busty section. With the exception of a slight decrease in chlorite content no significant changes in composition are observed. This evidence again indicates that rate of deposition has little effect on the compsotion of the clay mineral fraction of the sediments. RAYNER (1968) considers the time for the deposition of seatearth to be greater than that for the whole of the other sediments making up a cyclothem, thus, it is important to exclude the immediate effects of slow deposition as significant modifiers of clay mineralogy.

X-ray diffraction shows that the chlorite is Mg-rich. Chlorite is thought to be the least stable mineral in seatearths and its depletion bears this out in all but one case; the Lower Brockwell seatearth is enriched in chlorite. Unlike the other clay minerals chlorite occurs predominantly as large flakes, especially in the roof rocks. Thus the breakdown of chlorite requires mechanical as well as chemical action since the rate of chemical alteration will be proportional to surface area. The chlorite in the Lower Brockwell seatearth is unusually coarse and this may explain its anomalous stability. Many chlorite flakes show overgrowths characteristic of partial diagenetic recrystallisation.

Table 5.3 shows the "illites" classified according to the scheme outlined in Chapter two. In general, the illite in seatearths is less well crystalline than that of the corresponding roof rock. The Upper Little Limestone section contains an unusual mixed-layer mineral thought to be a K-bentonite/illite, such minerals are characteristically of volcanic origin (See Chapter two). The Upper Little Limestone section is thought to be the result of a mixture of airborn volcanic ash and detrital sediment. Such an origin would explain the extremely complex clay mineralogy of the section and is consistent with the chemistry. Vulcanism can be demonstrated locally at the approximate stratigraphic horizon and it is interesting that an almost identical mixed-layer mineral occurs in the Dunfermline

Splint seatearth of very similar age. Seatearths often contain a few coarse micaceous grains which have survived mechanical breakdown. Illite is depleted in seatearths relative to roof rocks but to a lesser extent than chlorite. Primary mechanical breakdown of the mineral probably determines the rate of chemical degradation.

Kaolinite is thought to be the final stable product of the seatearth formation process. It is strongly enriched in seatearth relative to roof rocks. Leaching was stated by KELLER (1956) to be one of the environmental factors favouring kaolinite formation and low pH also promotes kaolinite formation.

All the clay minerals contain numerous inclusions of which rutile, zircon, and apatite are the most common. Examination of the clay mineralogy of roof rocks and seatearths shows that :-

(a) All seatearths examined are relatively rich in clay minerals.

(b) The clay mineral fraction of seatearths is modified, often strongly, relative to that of roof rocks.

(c) The clay mineralogy of seatearths shows little or no vertical profile.

(d) The relative stabilities of the clay minerals in seatearths are kaolinite > illite > chlorite.

(e) The modification of the clay mineral fraction of seatearths is not significantly affected by rate of deposition.

(f) Source material is of relatively constant composition over several cyclothems. Thus, it is not a significant factor in explaining the modification of seatearths.

(g) Primary mechanical breakdown of clay minerals probably controls the rate of chemical degradation.

5.3 CHEMICAL DIFFERENCES BETWEEN SEATEARTHS AND ROOF ROCKS

The geochemistry of seatearths and roof rocks has already been discussed in Chapters three and four where various factors were deduced which control the chemistry. These factors indicate that to a very large extent the chemistry of the sediments is controlled by their mineralogy and in Chapter three it was shown how accurately the chemistry could be deduced from mineralogical analysis. Chemical variations from seatearth to roof rock reflect the mineralogical variations previously discussed. The major element analyses include 15 chemical components; SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, MnO, CaO, Na_2O, K_2O, S, P_2O_5, C, H_2O^+, H_2O^-, and CO_2; and are given in Table 5.4. The Top Busty and Upper Little Limestone sections were analysed for 6 trace elements; Ba, Nb, Rb, Sr, Y, and Zr; and the analyses are given in Table 5.5.

5.31 CHEMICAL COMPONENTS RELATED TO THE QUARTZ DISTRIBUTION

Total SiO_2 shows a strong positive correlation with quartz in the 29 rocks of detailed sections for which mineralogical determinations were made. Although such a correlation is to be expected its presence indicates the quartz determinations are consistent with the chemistry. Qualitative evaluation of the grain size distributions of the rocks in the detailed sections indicates that quartz content increases with the increase of median grain size.

Since median grain size is commonly accepted as a function of rate of deposition, PETTIJOHN (1956) it is thought that SiO_2 and quartz contents are reasonable indicators of rate of deposition. This conclusion can only be drawn for the roof rocks and the grain size of the seatearths appears to be finer than the quartz content would imply.

Detrital feldspar is one of the minerals expected to be covarient with quartz. Only in the Top Busty roof was there any evidence for feldspar by X-ray diffraction and the anomalously high Na_2O content of these sediments may reflect detrital albite preserved by relatively fast deposition. Na_2O showed a positive correlation with SiO_2 in seatearths and this fact could also indicate that at least part of the variance of Na may be related to detrital feldspar in these rocks. However, in view of the theory of origin for seatearths to be presented in Chapter six preservation of albite in seatearths is thought to be unlikely and ion exchange of K for Na favoured by slow deposition as explained by NICHOLLS and LORING (1960) may account for the distribution of Na_2O in seatearths.

Zircon is another common detrital mineral and a covariance of Zr with quartz is to be expected if this were the case. In both roof sections the Zr-quartz covariance is observed in the roof rocks. In seatearths in general (See Chapter three) Zr also appears to be covarient with quartz. However, the geochemistry of Zr in sediments cannot be explained solely in terms of free detrital zircon since Zr is very strongly enriched in the seatearths where the detrital quartz content is relatively low.

NICHOLLS and LORING (1962) suggested that Zr may substitute for Al in clay minerals and a secondary covariance with total clay would explain the observed distribution of Zr in the sections. Zr substitution is not thought to be an important process and to explain the observed data pure clays would have to contain several hundred ppm Zr. Microscopic examination of the clay minerals shows that they contain numerous inclusions of detrital minerals of which zircon, rutile, and apatite are common and inclusion of detrital zircon in clay minerals is thought to explain the observed distribution. Y appears to be covarient with Zr in the sections and high Y contents are characteristic of igneous zircons. Unlike Zr it is thought that Y may be absorbed on clay minerals and such a process may dominate the variance of this element in the more argillaceous sediments.

Rutile, like zircon, is a common detrital mineral and the variance of TiO_2 is thought to be controlled by the same processes as that of Zr. TiO_2 is dominantly covarient with clay minerals as shown in Fig. 5.2 and free detrital rutile is not common. Nb is strongly covarient with TiO_2 and its subsitution in rutile has been discussed in Chapter three. Both Zr and TiO_2 are strongly enriched in seatearths and inclusion in clay minerals is thought to account for this fact.

The third detrital mineral commonly found as inclusions in clay minerals is apatite, however, the concentration of P_2O_5 is reduced rather than increased in seatearths. The rather indeterminate variation of P_2O_5 is thought to result from several interacting processes :-

(a) Free detrital apatite covarient with quartz.

(b) Detrital apatite included in clay minerals.

(c) Authigenic apatite formed in situ.

(d) Organic phosphatic debris.

The complexity of these processes and the low concentration of P_2O_5 in the sediments is thought to account for the difficulties in isolating particular processes relating to phosphorus. The very low content of P_2O_5 in seatearths may however, be almost totally detrital and reflect a fairly low pH during seatearth formation preventing the precipitation of calcite and apatite.

To summarise, quartz variation is in part responsible for the variance of Na_2O, Zr, Y, TiO_2, Nb, and P_2O_5. The control of quartz is strongest for Zr but can certainly be demonstrated for the other elements when the process is dominant in quartzose sediments.

5.32 CHEMICAL COMPONENTS RELATED TO DIAGENETIC MINERALS

The diagenetic origin of siderite and pyrite has been discussed previously in this chapter and by CURTIS and SPEARS (1968). It is also possible that at least part of the chlorite present may be diagenetic although it is difficult to assess the relative strengths of various processes in the formation of minor mineral phases because analytical error is at its greatest for these components. SPEARS (1964) demonstrated the covariance of Fe with S and CO_2 by subtraction of Fe involved in each diagenetic mineral and then plotting the remainder against the chemical component not recalculated. Similar plots can be made for the present data but do not show strong trends. The variance of Fe and the other ferromagnesian elements (Mg and Mn) in the sections investigated is thought to be the result of several interacting processes all of which are active in particular parts of the sections. These processes are :-

(a) Accumulation of ferromagnesian elements, especially Mg, substituted in clay minerals, especially chlorite.

(b) Accumulation of ferromagnesian elements as ferric oxide/hydroxide either precipitated or carried into the basin of deposition on clay minerals as suggested by CARROLL (1958).

(c) Incorporation of ferromagnesian elements, which accumulated as a result of (a) and (b) at least partly, into diagenetic pyrite (mainly Fe), and siderite. The importance of (c) in Coal Measures sediments has been stressed by NICHOLLS and LORING (1962), and SPEARS (1964), CURTIS (1967), CURTIS and SPEARS (1968), and CURTIS (1969) and has been shown to be a strong factor in roof rocks (Chapter four) and certainly present as a factor in seat-earths (Chapter three). The relationship between organic carbon and diagenetic siderite and pyrite has been previously discussed and organic material is thought to provide a source of S by promoting bacterial activity during accumulation & as a source of CO_2 during diagenesis. Much organic matter is probably destroyed prior to diagenesis but bacterial reduction of SO_4^{2-} to S^{2-} is probably associated with organic matter. Althought a general covariance of diagenetic minerals and carbon can be demonstrated in detail an antipathy may exist since the amount of C is fixed after burial and prior to diagenesis and if this is fairly constant in a sequence of sediments C - C converted to CO_2 will be correlated negatively with CO_2. Oxide and hydroxide grain coatings were observed in the Upper Little Limestone section roof together with siderite. These samples form a highly permeable sandstone, secondary weathering is probably the significant factor here. The concentration of ferromagnesian elements immediately above the coal in this section may be a function of relatively recent secondary mobilisation. Ferromagnesian elements in clay minerals will be discussed later but there is a marked chlorite-Mg relationship and diagenetic chlorite cannot be ruled out as a possibility.

To summarise, diagenetic minerals in the sections are at least partially responsible for the variance of Fe_2O_3, MgO, MnO, S, C, and CO_2. Diagenetic minerals are notably more important in roof rocks.

5.33 CHEMICAL COMPONENTS RELATED TO THE CLAY MINERALS

Almost every element determined has at least part of its variance controlled by the clay mineral variation. Three processes are involved :-

(a) Inclusion of detrital minerals (zircon, rutile, apatite) accounts for the majority of the variation of Zr, Y, TiO_2, Nb, and probably part of that of P_2O_5 in the detailed sections examined.

(b) Many elements may be present to a very large extent in clay mineral lattices. K, Al, Si, and H_2O^+ are very largely distributed in this way. Fe may replace Al as the ferric ion in clays or occur as the ferrous ion in some illites. Mg and Mn will behave in a similar way to ferrous iron. Na occurs in the same site as K.

(c) Sorption processes are particularly active in holding elements about clay minerals. Elements like Rb, Ba, K, Na, Sr, and Ca may be significantly affected by such processes as adsorption, and cation exchange. H_2O^- is extremely important in such processes since most ions are hydrated to a greater or lesser extent in aqueous solution and H_2O^- is retained at clay mineral surfaces, and in inter-sheet lattice positions especially in the expandable numerals. Almost all minor elements and many major elements are enriched in seatearths relative to roof rocks owing to their presence in clay minerals. Al_2O_3 is strongly covarient with total clay as shown in Fig. 5.3. In order to eliminate the effect of increasing clay content on the alkali and alkaline earth metals, element/Al ratios were computed and are shown in Table 5.6. In the Top Busty section all 6 elements are significantly depleted relative to Al, in the seatearths. The depletion of Na is anomalously high due to albite present in the roof measures. The order of depletion of alkali and alkaline earth metals may be deduced as $Rb < Ba < K < Na < Sr < Ca$ with a significant break ocurring between K and Na. In the Upper Little limestone section Rb and Ba are actuallly enriched relative to Al in the seatearths but K, Na, Sr, and Ca are all depleted. The order of depletion (assuming enrichment is negative depletion) is the same as that deduced for the Top Busty section. The enrichment of Rb and Ba appears to provide strong evidence against leaching, however, more than one process is at work. HIRST (1958) and NICHOLLS and LORING (1960) have discussed the possibility of using Na/K as an indicator of rate of deposition. Slow deposition is said to favour the exchange of K for Na in clay minerals under favourable salinity and pH conditions. HIRST (1962) indicates that alkalis may be preferentially absorbed in the order Cs> Rb>K>Na and SPENCER (1966) found that K, Cs, Rb and Ba were exchanged for Ca, Na, and Sr in argillaceous Silurian sediments. Both adsorption and cation exchange are favoured by slow deposition thus the order of depletion of elements in seatearths is consistent with very slow deposition. Sample TB2, a silty band in the sandy roof of the Top Busty section also indicates that slow deposition favours exchange of Rb, Ba, and K for Na, Sr, and Ca. Table 5.7 shows alkali and alkaline earth : K ratios and clearly indicates the points discussed. The order of depletion of alkalies and alkaline earths in seatearths can be explained in terms of slow deposition and cation exchange. The fact that all elements are depleted in the Top Busty section and most in the Upper Little Limestone section has not been explained, however, two processes are thought to be active in modelling the alkali and alkaline earth distributions in seatearths.

(a) Slow deposition and cation exchange tending to remove Ca, Sr, and Na but adding K, Ba, and Rb.

(b) Leaching which tends to remove all ions. This process may also be selective.

The enrichment of Rb and Ba in the Upper Little Limestone seatearth is thought to be a function of slow deposition but the depletion of K indicates leaching has also occurred. The Top Busty seatearth has been leached. It has been suggested that illite is the major mineral fixing alkaline earth ions by NICHOLLS and LORING (1962). The present data for the two detailed sections indicated that these elements are much more strongly related to total clay. In the sections examined very few components can be related to particular clay minerals. The Mg-chlorite relationship is fairly strong and is illustrated in Fig. 5.4. H_2O^+ is particularly related to kaolinite and H_2O^- is strongly covarient with illite. The covariance of absorbed ions with total clay is thought to reflect the dominance of surface area in controlling the process. In seatearths as shown in Chapter three many elements can be related to particular clay minerals and the absence of the very strong Rb-illite correlation in the two detailed sections is explained as follows :-

(a) Ions are incorporated into all sediments by adsorption processes related to total clay content and mineral surface area.

(b) In unleached sediments much adsorbed material is retained and perhaps more strongly incorporated during diagenesis by absorption into the lattice.

(c) In seatearths many adsorbed ions and chlorite and illite are removed or broken down by leaching but illite is the most successful mineral in retaining trace elements, probably in intersheet positions as opposed to surface adsorption.

In summary, many elements are enriched in clay minerals. Inclusion, lattice substitution, and sorption processes are active in explaining the covariance of elements with clay minerals. Depletion of many elements relative to Al, which bears a strong relationship to total clay, indicates that leaching of seatearths relative to roof rocks has occurred. Leaching may have been pre or post depositional and the evidence for each alternative will be discussed in Chapter six.

TABLE 5.1

MINERALOGICAL ANALYSES OF DETAILED SECTIONS

SAMPLE	C	CBT	QZ	CHL	ILL	KAOL	T.C.	TYPE
LL1	0.4	1.6	62	3	27	6	36	R
LL2	0.4	1.5	58	4	30	6	40	R
LL3	0.2	1.3	60	4	28	6	38	R
LL4	0.5	1.0	66	3	24	6	33	R
LL5	0.6	6.3	57	3	27	6	36	R
LL6	4.4	0.4	21	1	45	28	75	S
LL7	5.1	1.1	20	1	45	28	75	S
LL8	6.4	1.2	21	1	45	26	73	S
LL9	6.6	1.7	35	1	37	20	58	S
LL10	4.6	2.2	26	1	43	24	68	S
TB1	0.7	0.1	56	3	25	14	42	R
TB2	0.4	0.2	31	5	40	24	69	R
TB3	1.8	0.1	62	3	20	13	36	R
TB4	1.7	0.6	15	n.d.	17	66	83	S
TB5	0.3	0.3	14	n.d.	18	67	85	S
TB6	0.2	0.3	14	n.d.	19	66	85	S
TB7	0.1	0.3	15	n.d.	22	63	85	S
BS2	0.8	3.1	51	4	20	21	45	R
BS4	1.3	7.4	44	4	21	23	48	R
BS6	2.4	0.3	15	1	28	53	82	S
BS8	2.4	0.4	20	2	24	52	78	S
BS12	1.3	4.3	8	6	37	44	87	R
BS14	0.4	2.8	9	6	38	44	88	R
BS16	2.4	0.5	22	3	16	56	75	S
BS18	0.7	0.3	22	3	20	54	77	S
BS20	1.0	3.2	20	8	31	37	76	R
BS22	1.2	0.1	23	8	31	38	77	R
BS25	0.6	0.7	22	10	22	45	77	S
BS27	0.5	0.5	22	9	25	43	77	S

R = ROOF ROCK
S = SEATEARTH
LL = UPPER LITTLE LIMESTONE COAL SECTION
TB = TOP BUSTY COAL SECTION
BS = UPPER, MIDDLE, AND LOWER BROCKWELL COAL SECTION

TABLE 5.2

COMPARISON OF AVERAGE MINERALOGICAL DATA FOR SEATEARTHS AND ROOF ROCKS

MINERAL	A	B	C	D	E
CHLORITE	3	5	4	2	4
ILLITE	41	40	29	38	30
KAOLINITE	18	14	21	25	44
TOTAL CLAY	62	59	54	65	78
QUARTZ	27	35	43	33	19
SIDERITE	9	2	3	1	2
FELDSPAR	1	-	1	2	1

A = Average roof rock, DIXON et al. (1970)

B = Average of 9 mudstones, from NICHOLLS and LORING (1962).

C = Average of 14 roof rocks, this work.

D = Average seatearth, DIXON et al. (1970).

E = Average seatearth of 42, this work.

TABLE 5.3

COMPOSITION OF CLAY MINERAL FRACTIONS FOR SEATEARTHS AND ROOF ROCKS

SEDIMENT	NO. SAMPLES	CHL	ILL	KAOL
Upper little Lst. roof	5	8	74g	18
Upper Little Lst. floor	5	1	37g	62
Top Busty roof	3	7	58a-b	35
Top Busty floor	4	n.d.	23b	77
Upper Brockwell roof	2	8	44a-b	48
Upper Brockwell floor	2	2	34d	64
Middle Brockwell roof	2	7	43b-c	50
Middle Brockwell floor	2	4	23d	73
Lower Brockwell roof	2	10	40c-d	50
Lower Brockwell floor	2	12	30d-e	58
Mean roof for 5 seams	14	7	54	39
Mean floor for 5 seams	15	4	40	56
Mean East Midlands roof*	-	5	66	29
Mean East Midlands floor*	-	3	58	39

*After DIXON et al. (1970).

TABLE 5.4

MAJOR ELEMENT ANALYSES OF THE UPPER LITTLE LIMESTONE, TOP BUSTY, AND BROCKWELL SECTIONS

SAMPLE	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	S	P_2O_5
LL1	77.9	0.61	9.9	4.30	0.44	0.29	0.37	2.30	0.20	0.11
LL2	74.7	0.81	12.9	4.15	0.45	0.34	0.33	2.90	0.22	0.09
LL3	76.0	0.80	11.8	4.20	0.44	0.22	0.38	2.70	0.14	0.12
LL4	80.5	0.64	9.0	3.50	0.35	0.16	0.30	2.20	0.25	0.09
LL5	68.3	0.48	10.5	8.60	2.00	0.30	0.28	2.00	0.29	0.14
LL6	54.2	1.16	23.5	1.86	0.70	0.33	0.43	3.77	1.47	0.05
LL7	53.3	1.15	23.1	1.83	0.72	0.37	0.44	3.84	2.05	0.04
LL8	52.4	1.07	22.2	1.98	0.70	0.38	0.45	3.69	0.68	0.06
LL9	59.8	0.72	18.1	1.57	0.59	0.30	0.40	3.09	0.90	0.01
LL10	55.1	0.87	21.9	1.51	0.65	0.40	0.48	3.79	1.17	0.02
TB1	73.5	0.72	14.0	2.61	0.68	0.22	1.40	2.60	0.03	0.10
TB2	59.6	0.87	20.5	3.34	1.33	0.25	0.92	4.00	0.09	0.06
TB3	77.8	0.88	9.9	1.69	0.44	0.17	1.23	2.10	0.03	0.09
TB4	52.8	1.33	28.0	1.30	0.52	0.15	0.19	2.10	0.51	0.02
TB5	53.7	1.12	28.9	1.32	0.57	0.10	0.22	2.29	0.12	0.01
TB6	53.7	1.16	28.9	1.44	0.59	0.11	0.23	2.55	0.11	0.02
TB7	53.3	1.13	28.5	1.54	0.66	0.12	0.27	2.87	0.13	0.02
BS2	66.1	0.78	17.2	4.86	0.85	1.24	0.39	1.70	0.11	0.12
BS4	59.1	0.59	16.4	10.68	3.15	0.50	0.36	1.75	0.20	0.09
BS6	51.8	1.10	27.9	1.80	0.79	0.18	0.28	2.84	0.06	0.02
BS8	52.4	1.17	28.1	1.62	0.77	0.17	0.28	2.59	0.14	0.02
BS12	48.2	0.95	23.4	8.28	2.86	0.79	0.29	2.60	0.15	0.24
BS14	49.0	0.92	27.1	6.06	1.35	0.59	0.35	3.09	0.19	0.16
BS16	53.3	1.83	27.5	1.80	0.72	0.13	0.24	2.11	0.06	0.02
BS18	53.4	1.28	28.9	1.65	0.63	0.13	0.26	2.38	0.05	0.02
BS20	52.9	1.03	25.0	5.60	1.46	0.29	0.29	2.85	0.06	0.07
BS22	55.5	1.15	26.9	2.75	0.60	0.19	0.29	2.95	0.15	0.03
BS25	56.5	1.06	22.3	4.38	1.79	0.17	0.31	2.66	0.09	0.03
BS27	55.9	1.14	23.4	4.62	1.84	0.24	0.31	2.44	0.07	0.03

TABLE 5.4 (CONTINUED)

MAJOR ELEMENT ANALYSES OF THE UPPER LITTLE LIMESTONE, TOP BUSTY, AND BROCKWELL SECTIONS.

SAMPLE	MnO	CO_2	C	H_2O^+	H_2O^-
LL1	0.016	0.61	0.40	1.80	0.60
LL2	0.014	0.59	0.43	1.90	0.60
LL3	0.014	0.51	0.20	1.96	0.60
LL4	0.013	0.39	0.50	1.90	0.50
LL5	0.044	2.41	0.57	2.04	0.65
LL6	0.007	0.15	4.37	6.54	1.67
LL7	0.006	0.40	5.10	6.00	1.25
LL8	0.005	0.45	6.37	7.23	1.34
LL9	0.005	0.65	6.50	6.20	1.20
LL10	0.005	0.84	4.55	6.81	1.40
TB1	0.010	1.47	0.20	1.45	0.56
TB2	0.022	0.46	0.53	5.75	1.90
TB3	0.012	0.99	0.22	1.55	0.60
TB4	0.010	0.20	1.68	10.30	0.74
TB5	0.012	0.10	0.29	10.53	0.69
TB6	0.011	0.10	0.23	10.46	0.70
TB7	0.009	0.10	0.11	10.48	0.73
BS2	0.022	1.20	0.75	4.20	0.50
BS4	0.060	2.85	1.30	3.00	0.53
BS6	0.011	0.10	2.41	10.02	0.71
BS8	0.007	0.15	2.42	9.38	0.76
BS12	0.048	2.05	1.30	8.39	0.51
BS14	0.026	1.10	0.38	8.96	0.77
BS16	0.006	0.21	2.38	9.22	0.47
BS18	0.006	0.12	0.71	9.99	0.44
BS20	0.020	1.25	1.02	8.34	0.64
BS22	0.010	0.02	1.22	8.67	0.68
BS25	0.023	0.27	0.59	9.37	0.50
BS27	0.022	0.21	0.51	8.72	0.60

TABLE 5.5

TRACE ELEMENT DATA FOR THE UPPER LITTLE LIMESTONE AND TOP BUSTY SECTIONS

SAMPLE	Ba	Nb	Rb	Sr	Y	Zr
LL1	119	6	35	59	5	190
LL2	160	5	44	52	5	181
LL3	191	4	44	52	4	173
LL4	159	2	33	62	6	230
LL5	102	4	31	65	3	130
LL6	662	15	140	79	19	322
LL7	674	14	139	72	17	326
LL8	804	14	138	76	14	307
LL9	745	10	102	57	10	276
LL10	651	14	134	70	8	201
TB1	154	14	84	84	28	407
TB2	485	23	176	132	39	264
TB3	177	15	66	73	26	577
TB4	296	23	90	46	26	513
TB5	284	16	87	38	25	292
TB6	260	16	100	38	20	336
TB7	425	18	125	45	22	304

TABLE 5.6

ALKALI AND ALKALINE EARTH ELEMENTS : ALUMINA RATIOS FOR THE UPPER LITTLE LIMESTONE AND TOP BUSTY SECTIONS

SAMPLE	Rb/Al	K/Al	Na/Al	Ba/Al	Sr/Al	Ca/Al
LL1	0.67	3.68	0.45	2.27	1.12	3.94
LL2	0.64	3.70	0.33	2.34	0.76	3.55
LL3	0.75	3.75	0.47	3.24	0.88	2.59
LL4	0.69	3.75	0.47	3.33	1.30	2.40
LL5	0.69	3.62	0.41	2.26	1.44	3.16
LL6	1.12	2.51	0.26	5.31	0.64	1.90
LL7	1.13	2.60	0.27	5.48	0.59	2.07
LL8	1.17	2.51	0.29	6.83	0.65	2.29
LL9	1.13	2.55	0.30	7.40	0.57	2.13
LL10	1.15	2.62	0.31	5.61	0.60	2.46
TB1	1.13	2.92	1.87	2.08	1.13	2.13
TB2	1.62	3.05	0.63	4.43	1.31	1.64
TB3	1.65	3.34	1.71	3.36	1.39	2.35
TB4	0.61	1.17	0.10	2.00	0.31	0.65
TB5	0.57	1.24	0.11	1.92	0.25	0.47
TB6	0.65	1.38	0.11	1.79	0.25	0.52
TB7	0.83	1.58	0.13	2.81	0.29	0.57
	$x10^{-3}$	$x10^{-1}$	$x10^{-1}$	$x10^{-3}$	$x10^{-3}$	$x10^{-2}$

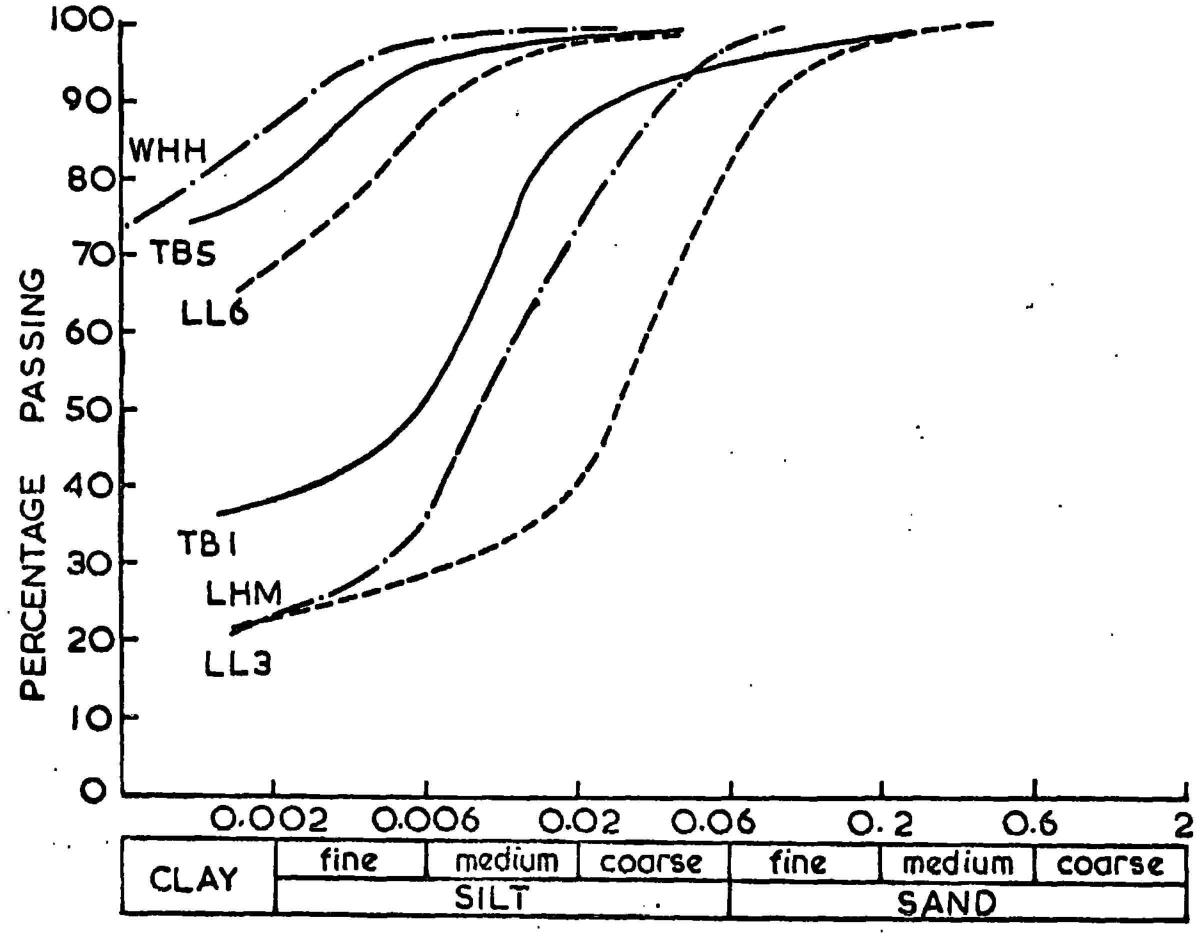
TABLE 5.7

ALKALI AND ALKALINE EARTH ELEMENTS : POTASSIUM RATIOS FOR THE UPPER LITTLE LIMESTONE AND TOP BUSTY SECTIONS

SAMPLE	Rb/K	Na/K	Ba/K	Sr/K	Ca/K
LL1	1.80	1.22	0.61	3.04	1.07
LL2	1.77	0.88	0.63	2.06	0.96
LL3	1.85	1.27	0.86	2.37	0.69
LL4	1.85	1.25	0.89	3.47	0.64
LL5	1.90	1.13	0.60	3.98	1.40
LL6	4.48	1.02	2.13	2.55	0.76
LL7	4.35	1.02	2.11	2.27	0.80
LL8	4.65	1.16	2.28	2.18	0.78
LL9	4.43	1.16	2.90	2.24	0.84
LL10	4.38	1.14	2.14	2.29	0.94
TB1	3.89	6.40	0.71	3.87	0.73
TB2	5.31	2.58	1.45	4.29	0.54
TB3	4.92	5.11	1.01	4.16	0.70
TB4	5.18	0.81	1.71	2.65	0.56
TB5	4.58	0.86	1.55	2.02	0.38
TB6	4.73	0.80	1.23	1.80	0.38
TB7	5.23	0.84	1.72	1.82	0.36
	$x10^{-3}$	$x10^{-1}$	$x10^{-2}$	$x10^{-3}$	$x10^{-1}$
BC1 *	7.1	1.9	1.78	2.1	1.5
BC2	5.3	1.7	1.99	4.3	0.7
BC3	5.8	2.3	1.36	2.2	0.6
BC4	7.3	3.6	1.36	2.7	0.9
BC5	4.7	2.8	1.37	3.2	0.9
BC6	5.6	2.7	1.19	2.8	1.2
BC7	4.8	2.4	1.32	3.2	1.0
BC8	6.0	2.1	4.43	2.3	1.4
BC9	5.6	2.6	3.33	2.8	1.0

* Bersham cyclothem data of NICHOLLS and LORING (1962) For comparison.

FIG. 5.1 GRAIN SIZE DISTRIBUTION FOR SOME SEATEARTHS AND ROOF ROCKS



W.H.H.	Warsop High Hazels roof (After TAYLOR and SPEARS (1970))
TB5	Top Busty seatearth
LL6	Upper Little Limestone seatearth
TB1	Top Busty roof (siltstone)
LHM	Lumley High Main roof (After TAYLOR and SPEARS (1970))
LL3	Upper Little Limestone roof (siltstone/sandstone)

WHH and LHM are included to illustrate the wide variation in roof rocks.

FIG. 5.2 TiO_2 v TOTAL CLAY FOR DETAILED SECTIONS

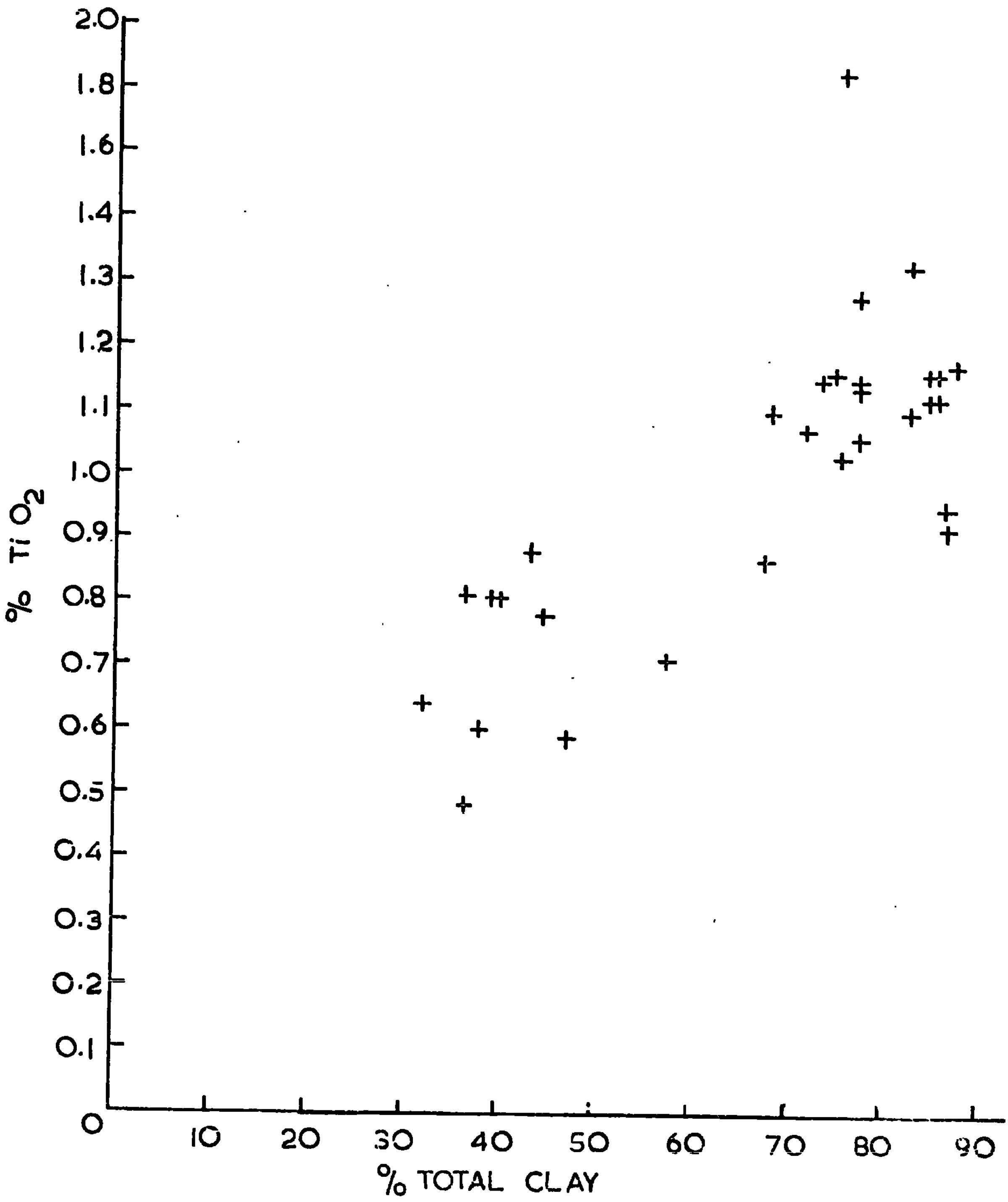


FIG.5·3 Al_2O_3 v TOTAL CLAY FOR DETAILED SECTIONS

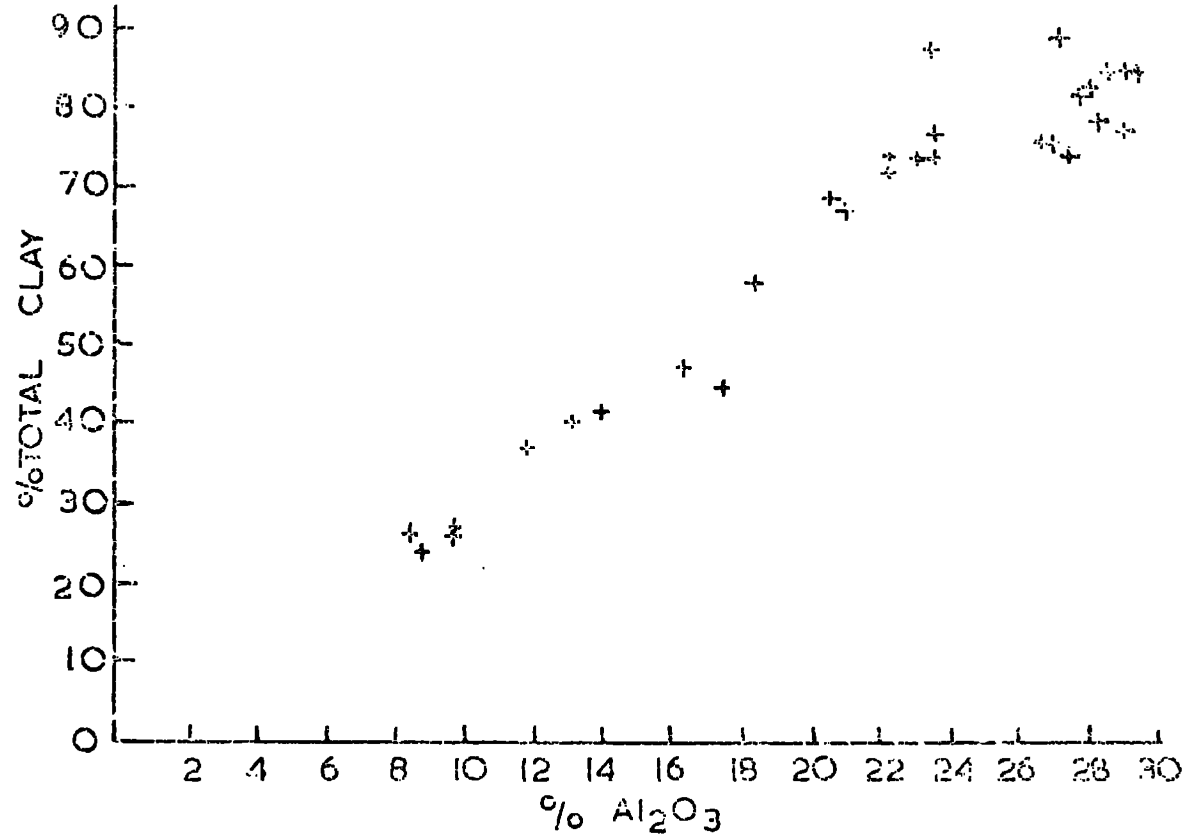
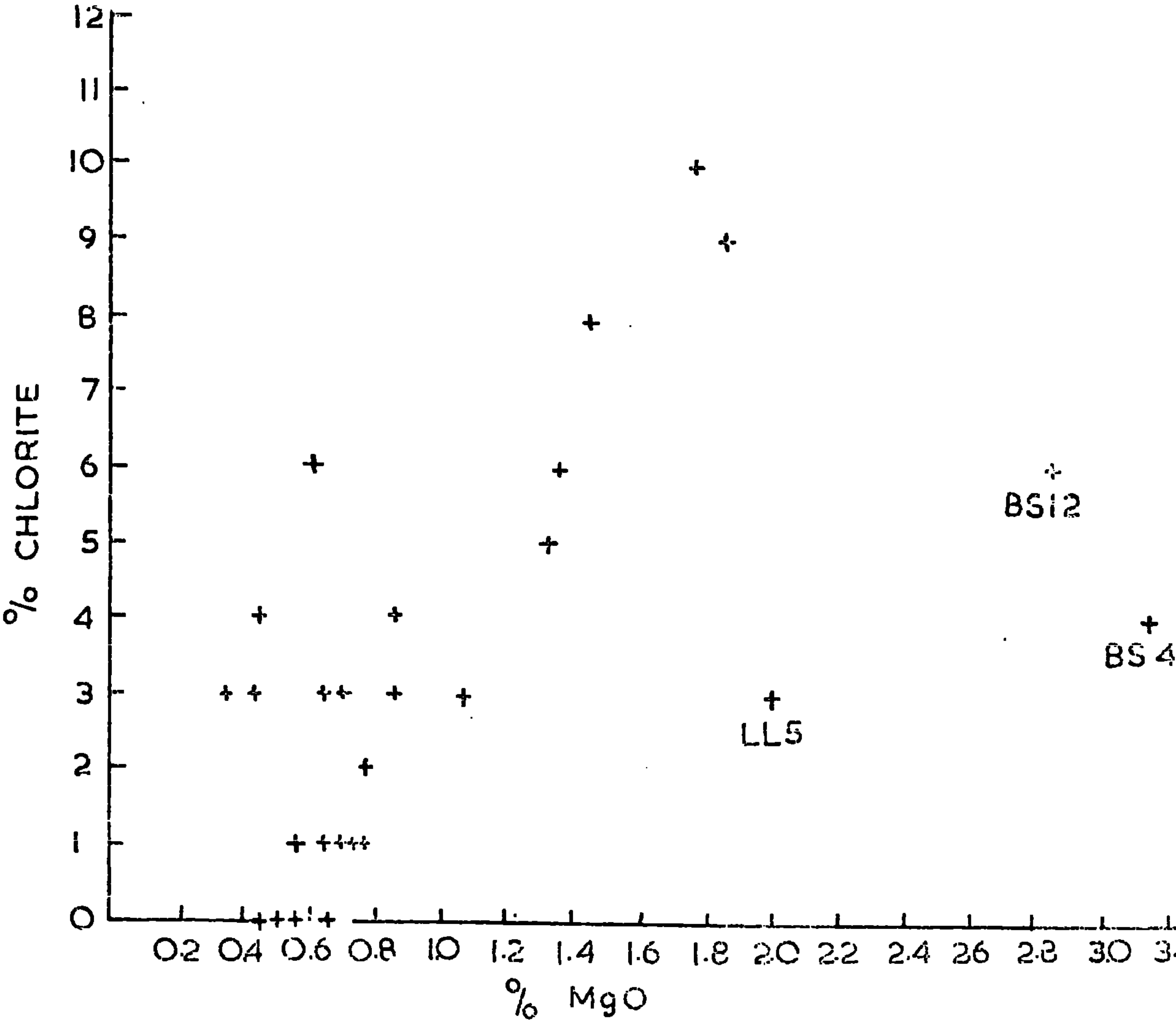


FIG.5·4 MGO v CHLORITE FOR DETAILED SECTIONS



5.4 REFERENCES TO CHAPTER FIVE

ATTWELL, P. B., HIRST, D. M., and TAYLOR, R. K., (1968), Diagenetic recrystalization and orientation of two carbonate species, Sedimentology, 11, 237 - 247.

CARROLL, D., (1958), The role of clay minerals in the transportation of iron, Geochim. Cosmochim. Acta, 14, 1 - 27.

CURTIS, C. D., (1967), Diagenetic iron minerals in some British Carboniferous sediments, Geochim. Cosmochim. Acta, 31, 2109 - 2123.

CURTIS, C. D., (1969), Trace element distribution some British Carboniferous sediments, Geochim. Cosmochim. Acta, 33, 519 - 523.

CURTIS, C. D., and SPEARS, D. A., (1968), The formation of sedimentary iron minerals, Econ. Geol., 63, 257 - 270.

DIXON, K., SKIPSEY, E., and WATTS, J. T., (1970), The distribution and compsosition of inorganic matter in British coals. Part 2 : Aluminosilicate minerals in the coal seams of the East Midlands Coal fields., J. Inst. Fuel, 43, 124 - 128.

GRIM, R. E., and ALLEN, V. T., (1938), Petrology of the Pennsylvanian underclays of Illinois., Bull. Geol. Soc. Am., 49, 1483 - 1513.

HIRST, D. M., (1958), Ph.D. Thesis, University of Manchester.

HIRST, D. M., (1962), The geochemistry of modern sediments from the Gulf of Paria - 1, The relationship between the mineralogy and the distribution of the major elements., Geochim. Cosmochim. Acta, 26, 309 - 334.

HIRST, D. M. (1962), The geochemistry of modern sediments from the Gulf of Paria - 11. The location and distribution of the trace elements., Geochim. Cosmochim. Acta, 26, 1147 - 1187.

HUDDLE, J. W., and PATTERSON, S. M., (1961), Origin of Pennsylvanian underclay and related seat rocks., Bull. Geol. Soc. Am., 72, 1643 - 1660.

KELLER, W. D., (1956), Clay minerals as influenced by their environment of formation, Bull. Am. Ass. Petrol. Geol., 40, 2689 - 2710 .

KELLER, W. D., (1957), The principles of chemical weathering., Lucas Bros., Columbia, Missouri.

MOORE, L. R., (1968), Some sediments closely associated with Coal Seams, In, Coal and Coal-Bearing Strata, Eds. Murchison and Westoll, Oliver and Boyd, Edin.

NICHOLLS, G. D., and LORING, D. H., (1960), Some chemical data on British Carboniferous sediments and their relationship to the clay mineralogy of these rocks, Clay. Min. Bull., Min. Soc., Lond., 4, 196 - 207.

NICHOLLS, G. D., and LORING, D. H., (1962), The geochemistry of some British Carboniferous sediments, Geochim. Acta, 26, 181 - 223.

PETTIJOHN, F. J., (1956), Sedimentary rocks, Harper, New York.

RAYNER, D. H., (1967), The Stratigraphy of the British Isles, Cambridge University Press.

SCHULTZ, L. G., (1958), The petrology of underclays, Bull. Geol. Soc. Am., 69, 363 - 402

SPEARS, D. A., (1964), The major element geochemistry of the Mansfield Marine Band in the Westphalian of

Yorkshire, Geochim. Cosmochim. Acta, 28, 1679 - 1696.

SPENCER, D. W., (1966), Factors affecting element distributions in a Silurian graptolite band, Chem. Geol., 1, 221 - 249.

TAYLOR, R. K., and SPEARS, D. A., (1970), The breakdown of British Coal Measure rocks, Int. J. Rock Mech. Min. Sci., 7, 481 - 501.

WILSON, M. J., (1965), The origin and geological significance of South Wales underclay, J. Sed. Pet., 35, 91 - 99.

CHAPTER SIX

SUMMARY AND CONCLUSIONS

6.1 SUMMARY OF PALAEOGEOGRAPHICAL BIOLOGICAL AND PALAEOCLIMATIC CONDITIONS

In Chapter one the palaeogeographic conditions of seatearth deposition were discussed. The general conditions may be summarised as follows :-

(a) Broad flat lying delta/swamp conditions.

(b) Broad expanses of shallow, brackish to fresh water.

(c) Low surrounding topography.

(d) Very low detrital supply with reworking of the sediments.

(e) Hydrophytic flora sporadically encroaching on slowly built mudbanks.

(f) Low pH, 4.5 - 5.5 and falling.

(g) Eh, oxidising but falling.

(h) Humid, tropical to subtropical.

MOORE (1964) suggests that a high level of organic activity would occur at the quoted pH and this combined with the Eh would tend to prevent organic debris accumulating.

6.2 SUMMARY OF QUALITATIVE MINERALOGICAL EVIDENCE

Seatearths are essentially quartz-illite-kaolinite assemblages with minor amounts of chlorite, siderite, and carbonaceous matter. The quartz is relatively fine grained (usually less than medium silt grade) and shows signs of rounding and abrasion. The illites present in seatearths vary considerably from well ordered micaceous minerals to strongly disordered and/or interlayered minerals. The kaolinites are essentially well ordered. Chlorite is often preserved as coarse flakes and is Mg-rich. Siderite almost invariably occurs as discrete nodules associated with minor pyrite and recrystallised kaolinite laths. The carbonaceous matter occurs either as films or as coaly partings and particles. Roof rocks show essentially the same mineralogy as seatearths in a qualitative sense though the clay minerals are often better ordered and the quartz more coarse grained, angular,and fresh.

6.3 SUMMARY OF QUANTIATIVE MINERALOGICAL AND CHEMICAL VARIATIONS WITHIN SEATEARTHS

The major chemical components of seatearths show a very restricted variation and the results of this work agree well with those of previous workers. The mineralogy is much more variable but mineralogy and major element composition are very closely linked. Trace element composition is only partially controlled by mineralogy. Of the minor elements only Zr, Cr, and V are concentrated and even the concentrations of these elements is not excessive. Factor analysis of the data for seatearths yeilds eight factors, of these a leaching factor, a proximity to shoreline factor, a sorting factor, and a chlorite/diagenesis factor are most important. A ? sulphide diagenesis factor, ? mineralisation factor, and two factors related to stratigraphy and provenance were also found. The clay mineral fraction composition of seatearths appears to vary systematically with stratigraphy and the variation is parallelled by work in the South Wales Coalfield.

6.4 SUMMARY OF QUANTITATIVE MINERALOGICAL AND CHEMICAL VARIATION WITHIN ROOF ROCKS

In both mineralogical and a chemical sense roof rocks were found to show variations very similar to those shown by sequences of cyclothemic sediments. Factor analysis of data for roof rocks and cyclothemic sediments revealed essentially the same factor pattern. It is concluded that roof rocks accumulated under a variety of conditions and any stratigraphical variation in these sediments would be extremely difficult to detect. The data compares well with previous data on similar sediments.

6.5 SUMMARY OF MINERALOGICAL AND CHEMICAL DIFFERENCES BETWEEN SEATEARTHS AND ROOF ROCKS

The most striking differences between seatearths and roof rocks is in their quantitative mineralogy. Roof rocks are usually more arenaceous than seatearths and their quartz is normally fresher, coarser, less abraded and more angular. The quartz content variation in seatearths is very much less than that of roof rocks. Seatearths often show a slight but significant increase in quartz content towards the base of the unit. There is no consistent relationship between quartz content or lithology of roof rock and seatearth. Both roof rocks and seatearths contain carbonaceous matter, largely as coaly fragements and partings. Carbonates in both seatearths and roof rocks are normally siderite and usually occur as concretions or nodules. Such concretions are sometimes concentrated in ironstone bands though care was taken not to sample such bands. Seatearths are often enriched in siderite nodules towards the base, however, roof rocks generally contain more carbonate than seatearths. The clay mineral fraction of seatearths is often strongly modified relative to that of the roof rocks and the deduced order of stability of minerals in seatearths is kaolinite > illite > chlorite . Rate of deposition does not appear to account for the modification of the clay mineralogy and large fluctuations in the degree of weathering at source are not thought to occur. It was found that grain-size exerts a strong influence over the rate of chemical breakdown. The clay mineralogy of seatearths was found to be constant and shows no "profile".

The chemical differences between seatearths and roof rocks, especially for major chemical components, was found to be directly related to the mineralogy. Quartz variation accounts for part of the variances of Na, Zr, Y, Ti, Nb, and P. Fe, Mg, Mn, S, C, and CO_2 are strongly related to the diagenetic minerals. Clay minerals are responsible for the variation of almost all chemical components to some degree. Three processes are important in the control of chemistry by the clay mineralogy; inclusion, lattice substitution, and sorption. Inclusion effects Zr, Y, Ti, Nb, and P. Lattice substitution effects K, Al, Si, and H_2O^+. Sorption processes tend to control Rb, Ba, K, Na, Sr, and Ca. Ions affected by sorption processes are depleted in seatearths due to leaching.

6.6 ORIGIN AND GENESIS OF SEATEARTHS

Lithologically seatearths have been divided by various workers (HUDDLE and PATTERSON, 1961; SCHULTZ, 1958;

WILSON, 1965a; MOORE, 1968) into three or four units :-

(a) An upper plastic clay unit immediately below the coal.

(b) A carbonaceous unit, sometimes shaly, somtimes unbedded.

(c) A clay rich unit commonly with siderite nodules towards the base.

(d) A lower transition zone grading into normal detrital sediment.

Chemically the division between units is impossible to detect but mineralogically the upper units commonly contain a degraded illite. This feature was also found by NICHOLLS and LORING (1962, Sample BC1731). The upper carbonaceous unit is thought to be transitional into coal and the plastic unit, which is often absent, may be the result of dewatering of the coal. Such units occur when the coal is a good aquifer and when the roof rocks are highly argillaceous.

The palaeogeographic evidence summarised in Chapter one and section one indicates that seatearths accumulated in broad expanses of shallow, brackish to fresh water. As seatearth formation begins the low topography provides only a very slow detrital supply. In the shallows, sediment was reworked and redistributed, and mudbanks slowly rose above the surface and were colonised by hydrophytic vegetation. Humic acids resulting from plant decay would slowly reduce the pH of the virtually stagnant waters to 4.5 - 5.5, and the Eh of the environment would begin to fall. MOORE (1964) suggested that at this pH microbiological activity would be high and prevent accumulation of plant debris. Under such acid conditions relatively minor fluctuations of the water table would result in leaching and reworking of the silty muds. Slow addition of more muddy sediment and continual churning and leaching of the sediments results in the middle unit of the seatearth. A relatively large fluctuation in the water table at this time may result in complete or partial reworking of the whole unit. The amount of leaching and reworking of a particular seatearth depends on :-

(a) The original sediment/source rock.
(b) The rate of deposition
(c) The amount of fluctuation of the water table.
(d) The amount of root action.

Seatearth deposition is envisaged as :-

(a) Slow, sporadic influx of muddy sediment.

(b) Continual churning by root action and leaching by minor fluctuations of the water table.

(c) Wholesale reworking when relatively large water table fluctuations occur.

The transition from normal sediment to seatearth can be explained in terms of such a process. As conditions stabalise and detrital supply almost ceases, pH falls still further, together with Eh. At pH 3.5 - 4.5 microbiological activity is inhibited and organic matter begins to accumulate together with the last detrital sediment. This represents the transition into coal. Coal accumulates as organic debris in stagnant waters of low pH and Eh. Roots never seem to extend into seatearths which may imply movement of organic debris and continuing minor fluctuations of the water table. The upper unit of seatearths has been reported by MOORE (1968) to sometimes contain marine microfossils. When coal accumulates, conditions are probably finely balanced between regression and transgression, the seatearth having accumulated under slightly regressive conditions. The theory of seatearth formation is essentially that envisaged by MOORE (1968) though more emphasis is placed on reworking and leaching within the basin of deposition. The constant reworking of seatearth material explains the near absence of any profile. The question of whether the material is weathered at source or at the site of deposition does not arise if seatearths form the source material for re-deposited seatearth to which some extra detrital material is being slowly admixed. MOORE (1968) indicates that a series of vegetations are preserved in seatearths, these must be envisaged as the last series of colonisations. Lateral variation in seatearths is thought to be mainly quartz variation and can be explained in terms of winnowing and the occurrence of channels through the low lying shallow delta/ swamp.

6.7. STRATIGRAPHICAL VARIATIONS IN SEATEARTHS AND THEIR IMPLICATIONS FOR UPPER CARBONIFEROUS SEDIMENTATION

Two factors emerging from the factor analysis of seatearths were interpreted in terms of source rock variations. These interpretations were rather tentative, but the factor scores suggest that later seatearths incorporate more fresh sediment than the earlier deposits. Factor two in the factor analysis of seatearths also showed a systematic stratigraphic variation indicating that the later seatearths are less leached and reworked than the earlier ones. Two factors are thought to be responsible for the chlorite and illite rich nature of the uppermost seatearths.

(a) The later seatearths were subject to more rapid addition of fresh sediment and consequently appear less leached.

(b) The later seatearths were less leached and reworked at source, or at the site of deposition.

The same variation was observed by WILSON (1965) and interpreted as a change in palaeoclimatic conditions which led to a hotter climate and less leaching. SPEARS (1965) indicated that in the Lower Carboniferous chemical weathering was more important than in the Upper Carboniferous where mechanical weathering becomes important. The data for seatearths suggests that a similar trend exists within the Upper Carboniferous. The addition of fresh material to later seatearths implies a stronger mechanical contribution to these sediments.

6.8 ECONOMIC APPLICATIONS

The main economic use of seatearths is as a source material for refractories. The refractoriness of a material largely depends on the clay : quartz ratio; the higher the ratio the higher the refractoriness, in general. Another general conclusion is that Mg, Fe, Ca, K, and Na tend to lower refractoriness though it is mineralogy rather than chemistry which controls this property. GRIM (1962) indicates that kaolinitic clays are most satisfactory as refractories, however, small amounts of illite and quartz are often desirable in order to provide reheat expansion and aid moulding. WILSON (1965b) indicated that chlorite tends to have an adverse effect on refractoriness.

From the above discussion it is apparent that Scottish seatearths and seatearths earlier than the Middle Carboniferous provide the best potential refractory clays. Certain exceptions, where volcanic addition is expected, may be made but such additions are extremely unlikely in the Lower Coal Measure seatearths of Durham and Northumberland and it is here that the Tilley seam seatearth is an extensively worked refractory clay.

In addition to their use as refractory materials seatearth constitute the floor measures in coal workings. Seatearths containing volcanic interlayer clay may be sensitive to "wetting" and present difficulties because of their tendency to expand. TAYLOR and SPEARS (1970) have pointed to the potential instability of such material in spoil heaps and in the past coal washery practice was greatly affected by these minerals.

6.9 REFERENCES TO CHAPTER SIX

GRIM, R. E., (1962), Applied clay mineralogy., McGraw-Hill Co. Inc. New York.

HUDDLE, J. W., and PATTERSON, S. H., (1961), Origin of Pennsylvanian underclay and related seat rocks., Bull. Geol. Soc. Am., 72, 1643 - 1660.

MOORE, L. R., (1964), Microbiology, mineralogy and genesis of a tonstein, Proc. Yorks. Geol. Soc., 34, 235 - .

MOORE, L. R., (1968), Some sediments closely associated with Coal seams., In, Coal and Coal bearing strata, Ed. Murchison and Westoll, Oliver and Boyd, Edin.

NICHOLLS, G. D., and LORING, D. H., (1962), The geochemistry of some British Carboniferous sediments., Geochim. Cosmochim. Acta, 26, 181 - 223.

SCHULTZ, L. G., (1958), The petrology of underclays., Bull. Geol. Soc. Am., 69, 363 - 402.

SPEARS, D. A., (1965), Boron in some British Carboniferous sedimentary rocks., Geochim. Cosmochim. Acta, 29, 315 - 328.

TAYLOR, R. K., and SPEARS, D. A., (1970), The breakdown of British Coal Measure rocks., Int. J. Rock Mech. Min. Sci. ,7, 481 - 501.

WILSON, M. J., (1965a), The origin and significance of South Wales underclays., J. Sed. Pet., 35, 91 - 99.

WILSON, M. J., (1965b), The underclays of the South Wales Coalfield east of the Vale of Neath., Trans. Inst. Mining Engineers, 124, 389 - 404.

APPENDIX I

ANALYTICAL PROCEDURES

1.1 MINERALOGICAL ANALYSIS

Two complimentary methods of mineralogical analysis, X-ray diffraction and differential thermal analysis, were employed. HOFMANN (1956) indicated that X-ray diffraction is perhaps the best method of analysis and the differential thermal method was used as a check on the accuracy of the diffraction method.

Artificial mixtures of standard minerals, described in Table A1.1, were prepared to cover the expected range in composition of the rocks to be analysed. The mixtures were ground to a maximum grain size of less than 5μ in order to eliminate any grain size effects inherent in the analytical methods. Mixing was carried out in a mechanical mixer for 60 minutes, the powders being mixed in plastic bottles with plastic mixing balls to avoid contamination. Table A1.2 shows the compositions of the fifteen standard mixtures prepared. About 2 grammes of each mixture was prepared and to half of this 10 percent of boehemite was added and thoroughly mixed. Boehemite was the internal standard used in the X-ray diffraction technique.

1.11 DIFFERENTIAL THERMAL ANALYSIS

The basic theory and technique of the method have been described and discussed by SEWELL and HONEYBORNE (1957) and MACKENZIE and MITCHELL (1957). For the quantitative work undertaken a Standata 5 - 50 apparatus was used. The details were as follows :-

Furnace : Platinum wound capable of a maximum temperature of 1500°C.

Crucibles : Two balanced platinum crucibles with an approximate capacity of 0.25 cc.

Holder : Ceramic crucible holder which makes base line drift negligible below 1000°C

Thermocouples : Pt/Rh thermocouples inset into the base of the crucibles.

Sheath : A mullite sheath protects the block, crucibles, and thermocouples during heating.

Heating rate : 10°C per minute from 38°C to 1000°C.

Atmosphere : Nitrogen for quantitative work.

Inert reference : Alumina.

Fig. A1.1 shows the apparatus diagramatically and Fig. A1.2. shows differential thermal curves, for minerals of interest in this investigation, obtained on the apparatus.

MACKENZIE and MITCHELL (1957) indicate that the following factors may influence the size and shape of peaks on differential thermal curves :-

(a) The inert reference material. Alumina was used as an inert reference material since its thermal properties are similar to those of calcined clay minerals. The grain size of the alumina was of the same order as that of the standards and samples. For quantitative work 0.12 grammes of alumina were weighed into one of the crucibles using a standard packing procedure.

(b) The positioning of the thermocouples. The Standata 5 - 50 is designed so that the thermocouples fit into impressions in the bases of the crucibles and are thus as near as possible to the centre of the sample for each run.

(c) The heating rate. A heating rate as close as possible to 10°C per minute was used throughout the quantitative work. Slight departures from linearity were noted in the first 100°C of heating. MACKENZIE and MITCHELL (1957) indicate this factor affects peak shape rather than the quantitative measurement of peak area.

(d) The packing of the sample. A strictly standard procedure was used in the packing of samples and the inert reference material. The crucible was filled to the brim and tapped lightly five times. This was repeated three times when it was found that the crucible usually contained about 0.12 grammes of material. Where this figure was not approached the sample was repacked. This procedure produced a relatively constant sample weight and the alumina crucible was always made up to exactly 0.12 grammes.

(e) The weight of the sample. It was found that corrections for variations in sample weight, over a small range, were more easily made and lead to greater precision than the use of a less rigorous packing technique to give constant weight.

(f) The grain size of the sample. Sample and standard preparation involved the grinding of all powders to a grain size less than 5μ.

(g) The pretreatment of the sample. All samples and standards were preheated to 60°C for 60 minutes and then allowed to equilibrate to constant relative humidity over a period of 24 hours. Conditions of constant R.H. were provided by a saturated solution of $Mg(NO_3)_2.6H_2O$ which gives an R.H. of 55 percent at 18°C and is only slightly affected by slight temperature fluctuations.

It has been shown by SPELL et al., (1945) that for mixtures of clay minerals, except when montmorillonite is present, that the reaction peak areas are directly proportional to the amount of clay species reacting. SEWELL and HONEYBORNE (1957) show that this assumption, made on the basis of empirical evidence, is only valid theoretically if the thermal conductivities of the mixtures are similar. This fact has induced GRIMSHAW and ROBERTS (1953) and SABATIER (1954) to suggest dilution procedures. SEWELL and HONEYBORNE (1957) suggest the use of a controlled atmosphere since gases released during heating may affect the thermal conductivity of the reacting mixture. The analytical method adopted did not include dilution since there is an inherent loss in sensitivity involved that could not be sacrificed. The use of a controlled nitrogen atmosphere was adopted, however, for two reasons. First to reduce the effects of the possible conductivity variation and second to prevent the exothermic oxidation of carbonaceous matter. This second factor was seen to virtually obliterate the clay mineral reactions when the experiments were carried out in air since the oxidation of carbon is a very strong exothermic reaction. From the thermal curves obtained the following peak areas were measured:-

The 970°C kaolinite exotherm.
The 600°C kaolinite - illite - chlorite endotherm.
The 100 - 200°C 'loosely bound water' endotherm.

The 573°C quartz inversion on the cooling curve.

The 970°C exotherm was used to calibrate kaolinite after BADGER (1955) despite the objections raised by GRIM (1947) that disorder and crystallinity variations affect the peak area. Fig. A1.3 shows the calibration curve obtained and the calibration data is given in Table A1.3. It is thought that the similar degrees of disorder and crystallinity in the sample and standard kaolinites permitted the application of this calibration. Five standards were prepared containing kaolinite, diluted with inert alumina, and from them the relationship between the 600°C endotherm and 970°C exotherm for kaolinite was obtained. The relationship is shown in Fig. A1.4. In clay mineral - quartz mixtures the 600°C endotherm represents the dehydroxylation of illite, kaolinite, and chlorite. This peak area was used to calibrate H_2O^+ and is shown in Fig. A1.5. and the data is given in Table A1.3. Chlorite was not calibrated by differential thermal analysis owing to its low concentration and is therefore a source of error. Illite was calibrated by subtraction of the kaolinite contribution to the 600°C endotherm and the calibration curve and data are given in Fig. A1.6. and Table A1.3. respectively. Quartz was calibrated from the 573°C inversion peak area on the cooling curve and H_2O^- from the 100 - 200°C endotherm peak area. The calibration curves are shown in Figs. A1.7. and A1.8. respectively and the data is given in Table A1.3. Empirical precision data for differential thermal analysis are given in Table A1.4. Comparisons of H_2O^+ and H_2O^- determinations by gravimetric and differential thermal methods are given in

Table A1.5. Recently DAVIS and HOLDRIDGE (1969) have obtained results of a similar precision using a similar differential thermal technique. Only selected samples were analysed by the differential thermal method to provide an independent check on the accuracy of the more rapid, sensitive and precise X-ray diffraction method.

1.12 X-RAY DIFFRACTION ANALYSIS

This was the major method employed for quantitative mineralogical analysis. In developing the X-ray diffraction technique the following factors were taken into consideration :-

(a) Rapidity. Since it was proposed to carry out a large number of mineralogical analyses, a rapid method was considered essential.

(b) Simplicity of technique. In order to obtain a reproduceable technique the sample preparation and running technique must be simple.

(c) Precision. A method with a precision of less than 5 percent relative was required.

(d) Accuracy. Compatibility with analytical data from independent methods was required.

(e) Scope for extension to a wider range of samples. A method which could be applied to a wide range of ancient sediments was required.

Conditions (a) and (b) made it desirable for all minerals to be determined on one mount and in order to increase the sensitivity for clay minerals a smear mount was used. Precision of the level required was only attainable by use of an internal standard. GRIFFIN (1954) first suggested the use of boehemite as an internal standard for the analysis of clay minerals from powder photographs and GIBBS (1967) used the mineral as internal standard for diffractometer work. Boehemite is suitable as an internal standard for the following reasons :-

(a) Mass absorption coefficient. Boehemite has a mass absorption coefficient at the Cu Kα wavelength of the same order as those of clay minerals and quartz. This fact means that for absorption purposes the samples and standards may be considered effectively homogeneous.

(b) Diffracted intensities. The medium to high diffracted intensities of boehemite allowed the addition of a relatively small percentage of internal standard. Thus, little loss in sensitivity was incurred.

(c) Interferences. Boehemite interferes with none of the proposed analytical peaks. The proximity of the 6.18Å boehemite peak to the 14Å chlorite, 10Å illite, 7Å kaolinite, and 4.26Å quartz peaks gives the added advantage of only one internal standard peak measurement to determine four minerals.

The analytical method employed, using boehemite as an internal standard, was as follows :- Two water smear mounts of each sample and standard were prepared. Each mount was run twice from 4 - 22° two theta at a scanning speed of ½° per minute using Cu Kα radiation. Pulse height selection was used to increase peak to background ratios. The Philips 1 KW diffractometer generator was set at 40 Kv and 20 ma. Three methods of recording and measurement were tried, they were :-

(a) Measurement of peak height from traces.

(b) Measurement of peak height x peak width at half height as an estimate of peak area from traces.

(c) Measurement of peak area by counting.

It was found that method (a) gave good results for quartz and adequate results for kaolinite and chlorite. The results for illite were hopelessly inadequate. Method (b) gave good results for the four minerals but the method is highly subjective in the selection of the background level and occasional "bad" results are obtained by error in peak width measurement. The accurate measurement of peak width was the main difficulty and source of error in method (b). Method (c) was found to be objective and gave the highest precision and was therefore adopted. Details of the counting positions are given in Table A1.6 and the data used for calibration is shown in Table A1.7. The precision was determined empirically for each mineral at three different scanning speeds. The results of the precision tests are shown in Table A1.8. Figs. A1.9 and A1.10 illustrate the variation of precision with scanning speed and concentration respectively. It can be seen from Table A1.8 and Fig. A1.9 that little gain in precision is observed if the scanning speed is reduced from ½ to ¼° two theta per minute. Consequently samples were run at ½° two theta per minute. Calibration curves for the minerals chlorite, quartz, kaolinite and illite are shown in Figs. A1.11, A1.12, A1.13, and A1.14 respectively. Table A1.9 shows comparative data for the X-ray diffraction and differential thermal determinations of quantitative mineralogy. The agreement is good for quartz and the results for clay minerals are within the limits of precision for the two methods.

1.2 CHEMICAL ANALYSIS

Three methods of chemical analysis were used :-

(a) Gravimetry.

(b) Flame photometry.

(c) X-ray fluorescence spectrometry.

Table A1.10 shows the chemical variables determined and the analytical technique employed. X-ray fluorescence analysis was by far the most important technique, 24 out of 29 variables being determined in this way.

1.21 GRAVIMETRY

Four chemical variables were determined by gravimetric methods. Carbon and carbon dioxide were determined on a carbon train after GROVES (1951). CO_2 was freed by addition of orthophosphoric acid and absorbed on soda lime, carbon was oxidised to CO_2 by addition of chromium trioxide to the flask after the CO_2 determination and absorbed in the same way. H_2O^- was determined as weight loss below 110°C after equilibration under conditions of constant relative humidity. H_2O^+ was determined immediately after H_2O^- by the method of RILEY (1958).

The weight of sample used in the carbon dioxide and carbon determinations was chosen to give a precision of 5 percent relative at 1 percent concentration. The precision at lower concentrations tends to fall and very low carbon and carbon dioxide contents are subject to considerable error. The precision of the H_2O^- determinations was found empirically to be 3.2 percent relative at 0.5 percent concentration and similar precision for the H_2O^+ determinations was observed at 8 percent concentration.

1.22 FLAME PHOTOMETRY

Only one element, sodium, was determined in this way. The use of the method was necessary because the X-ray fluorescence determinations of the element were very close to the detection limit of the method. The empirical precision was approximately 3 percent relative over the range of concentration encountered. The method used was essentially that of SHAPIRO and BRANNOCK (1952).

1.23 X-RAY FLUORESCENCE SPECTROMETRY

For the purpose of analysis elements were split into two groups. The groups were :-

(a) Major elements. Those elements present in sufficient quantity to be significant in any matrix correction for another major element. This group comproses fourteen variables, Si, Al, Fe, Mg, Ca, Na, K, Ti, S, P, C, CO_2, H_2O^+, and H_2O^-. The determination of five of these variables; Na, C, CO_2, H_2O^+, and H_2O^-, was carried out prior to the processing of the X-ray data. Table A1.11 gives details of the determination of the 9 remaining elements using a Philips 1212 automatic spectrometer.

(b) Trace elements. Those elements present in low concentrations and negligible in the calculation of matrix effects. This group comprises fifteen elements; Ba, Cr, Cu, La, Mn, Nb, Ni, Pb, Rb, Sc, Sr, V, Y, Zn, and Zr. Table. A1.12 gives details of the conditions for their determination.

Major elements and some trace elements are determined by relating peak counts over and above the background to concentration.

Let, p be the counts obtained on the peak,

b be the counts obtained for the background,

And, e_p be the error in the peak counts,

e_b be the error in the background counts,

Then, the percentage error in the p-b is given by :-

$$e_{p-b} = \frac{(e_p + e_b) \times 100}{(p - b)} \qquad (1)$$

Now, for some trace elements the ratio (p-b)/b is used as a function of concentration.

Let, $P = p - b$ and $e_P = e_p + e_b$, thus the percentage error in the ratio $r = (p-b)/b$ is given by :-

$$e_r = \frac{(P + e_P)}{(b - e_b)} - \frac{(P - e_P)}{(b + e_b)} \cdot \frac{b}{P} \times 100 \qquad (2)$$

Simplification of (2) gives :-

$$e_r = \frac{2b(Pe_b + be_P) \times 100}{P(b^2 - e_b^2)} \qquad (3)$$

Making the substitutions assumed prior to (1) gives :-

$$e_r = \frac{2b(pe_b + be_p) \times 100}{(p - b)(b^2 - e_b^2)} \qquad (4)$$

Now making the assumption $e_p = p^{\frac{1}{2}}$ and $e_b = b^{\frac{1}{2}}$ gives :-

$$e_r = \frac{2b(pb^{-1} + p^{\frac{1}{2}}b^{-\frac{1}{2}}) \times 100}{b^{-\frac{1}{2}}(p - b)(b - 1)} \qquad (5)$$

or

$$e_r = \frac{2((r + 1) + (r + 1)^{\frac{1}{2}}) \times 100}{r(b^{\frac{1}{2}} - b^{-\frac{1}{2}})} \qquad (6)$$

Thus the precision of trace and major element determinations may be estimated theoretically and empirically. The detection limit as used in Tables A1.11 and A1.12 is defined as the concentration equivalent to $3b^{\frac{1}{2}}$. The assumptions of the square root of the counts for the errors in both peak and background counts is common practice in electronic counting statistics.

X-ray fluorescence analysis involves the measurement of observed intensities of fluorescent radiation and the subsequent deduction of the concentration of the element fluorescing present in the sample. Intuitively it is expected that strict proportionality between fluorescent intensity and concentration will apply. This is not the case in practice and LIEBHAFSKY and WINSLOW (1958) list three main causes of deviations from proportionality.

(a) Effects due to heterogeneity of the sample.

(b) Effects due to electronic instability.

(c) Effects due to the chemical composition of the sample undergoing analysis.

In practice (a) and (b) can be effectively eliminated and (c) the so called matrix effects remain as the only major source of analytical error.

If it is accepted that matrix effects are a function of chemical differences between samples and standards then three methods are available for their reduction or elimination :-

(a) Fuse or mix the sample with a diluent. This has the effect of reducing the chemical variability between sample and standard and therefore reduces matrix effects. ROSE et al. (1963) suggest the use of lanthanum oxide as a heavy absorber in silicate fusions and the use of this leads to a strong reduction in the variation of absorption coefficients for whole samples at the wavelengths of light elements. Although all fusion and dilution techniques appreciably reduce matrix effects they do not eliminate them and fusion methods suffer three disadvantages over neat briquette methods :-

(1) Sensitivity is lost due to dilution.

(2) The sample is effectively destroyed.

(3) The methods are generally more time consuming than neat briquette techniques.

(b) Employ a method of close range calibration. This method involves the preparation of or availability of a large number of standards and the plotting of numerous calibration curves for elements in various matrices. Chemical variability between sample and standards is minimised by choice of a calibration in a similar matrix to the sample and matrix effects are effectively eliminated. This method is ideal if the samples to be analysed are of restricted compositional range.

(c) Employ some empirical or theoretical matrix correction procedure. Unlike methods (a) and (b) the use of mathematical and statistical correction procedures should be capable of producing accuracy of the same order as precision since the perfect correction procedure will remove all errors except statistical counting errors. In practice all correction procedures involve assumptions and rigorous theoretical correction is extremely complex. Most correction procedures depend on the knowledge of certain coefficients which have been determined empirically and the empirical data contains significant error. It is considered that each element should be calibrated individually and only those for which matrix correction significantly reduces the standard error of estimate for the calibration curve should be corrected.

In theory matrix effects result from the interaction of four factors :-

(a) Absorption, by the sample, of primary X-rays generated by bombardment of the tube target with electrons.

(b) Enhancement, by the sample, of primary X-rays.

(c) Absorption, by the sample, of secondary X-rays generated by bombardment of the sample with primary X-rays.

(d) Enhancement, by the sample, of secondary X-rays.

Of these factors (b) is trivial and (a) and (d) rarely exceed 10 percent of the total effect. Thus, (c), secondary absorption is responsible for the bulk of any observed matrix effects. Several assumptions are now made which were listed by LUCAS-TOOTH and PYNE (1964) :-

(a) Enhancement may be treated as negative absorption.

(b) The absorption by each element is a linear function of its concentration.

(c) Absorption for each element is additive to give a whole sample absorption.

Thus, for the ith sample at the anlytical wavelength of the jth element we may compute a whole sample absorption factor :-

$$M_{ij} = \sum_{k=1}^{r} m_{kj} p_{ik} = \sum_{k=1}^{r} (PA_{kj} - PE_{kj} + SA_{kj} - SE_{kj}) p_{ik} \qquad (7)$$

Where PA_{kj}, PE_{kj}, SA_{kj}, SE_{kj} are theoretical coefficients of primary absorption, primary enhancement, secondary absorption and secondary enhancement respectively; and m_{kj} is the total elemental matrix coefficient; for the kth element at the analytical wavelength of the jth element.

p_{ik} is the concentration of the kth element in the ith sample and M_{ij} represents a total matrix factor summed over r elements. The parameter M_{ij} will transform the observed intensity I_{ij}^{obs} into a corrected intensity I_{ij}^{cor} free from matrix effects. Thus :-

$$I_{ij}^{cor} = M_{ij} I_{ij}^{obs} = f(p_{ij}) \qquad (8)$$

ANDERMANN and KEMP (1958) suggested that the intensity of scattered radiation at a particular wavelength was an approximate function of the theoretical matrix effects and KALMAN and HELLER (1962) found that the parameter peak/background is largely free from matrix effects.

$$X_{ij} = (I_{ij}^{obs} - BG_{ij}^{obs})/BG_{ij} \simeq f(I_{ij}^{cor}) = f(p_{ij}) \qquad (9)$$

The function of p_{ij} in equation (9) can be deduced from peak/background measurements on standards by simple linear regression methods. The adequacy of this procedure tends to break down at concentrations which give an "X" value greater than about 30 but has been successfully used to eliminate matrix effects from trace element data. Table A1.13 shows 10 trace elements determined on G1 and W1 using "spiked" standards in a matrix similar to G1. The results for Nb, V, and Y have been corrected for line interferences. Only Zn shows significant difference from the accepted value. All determinations are the mean value of greater than five observations and the empirical (rather than theoretical) precision is quoted.

Matrix corrections for elements present in trace amounts are relatively simple, however, much more complex methods have been found to be necessary in the correction of major element data. As previously mentioned, all correction procedures are approximate and should only be applied when absolutely necessary. Thus, the first step in correction of major element data is to discover which elements require correction. Table A1.14 shows an idealised set of data typical of that encountered in the calibration of silicate data by simple linear regression relating concentration to X-ray intensity. The first problem is one of precision and arises for the elements Na and Mg for which low count rates are observed. Increased counting times can improve precision and the precision is the limit of possible accuracy. Although the correlation coefficient and standard error of estimate parameters indicate fairly low accuracy for these elements and the observed intercepts are high, these parameters are accepted because of the relatively low precision for Na and Mg. High intercepts are observed for Si and Al, however, these may be a function of the range of the data used in the calibration and between 40 and 75 percent silica, for example, the linear relationship may accurately calibrate Si and the intercept is irrelevant. Correlation coefficient is a deceptive parameter and significance tables for this assume the two variables plotted are normally distributed and this is often far from the case in practice. The standard error of estimate has been found to be the best parameter for assessment of calibration data and Si, Al, and Fe were selected for matrix corrections because this parameter was too high for acceptance. To summarise, when assessing the adequacy of a simple linear regression line as calibration the following points should be noted :-

(a) Are the results as accurate as could be expected in view of the precision?

(b) Is the intercept significant in view of the range of the calibration attempted?

(c) Is the data approximately normally distributed and if so is the correlation coefficient high enough to account for most of the variance of the intensity in terms of concentration? Precision must be considered here.

(d) Is the standard error of estimate low enough for the accuracy required, remembering the figure given is only strictly applicable at the mean?

Having decided that Si, Al, and Fe require correction, some sort of procedure must be derived. From equation (7) it can be seen that :-

$$M_{ij} = f(p_{ik}) \quad (k = 1, 2, \ldots r) \tag{10}$$

Substituting into equation (8) gives :-

$$I^{cor}_{ij} = f(p_{ik}) I^{obs}_{ij} = f(p_{ij}) \quad (k = 1, 2, \ldots r) \tag{11}$$

This equation may be simplified to :-

$$1/I^{obs}_{ij} = f(p_{ik}/p_{ij}) \quad (k = 1, 2, \ldots r) \tag{12}$$

Equation (11) is a generalised form of the more specific equations given by LUCAS-TOOTH and PYNE (1964), HOLLAND and BRINDLE (1966), KODAMA et al. (1967) and NORRISH and HUTTON (1969). Equation (12) demonstrates the ratio inherent in equation (11) and explains why this equation has no unique solution. Complete solution of equation (12) can be made under the assumption :-

$$\sum_{k=1}^{r} p_{ik} = 100\% \quad (k = 1, 2, \ldots r) \tag{13}$$

if p_{jk} is expressed as a percentage. This assumption implies that even though, in our example, only three elements required correction all elements are involved in that correction. It is as well to note that all elements means C, CO_2, H_2O etc. in silicates, and, in sediments this is very important. Solution of equation (11) can be made in two ways once the function $f(p_{ik})$ in this equation has been determined. This function merely consists of r factors of the form of m_{kj} in equation (7) and thus an estimate of the function may be made from data presented by authors such as HEINRICH (1966). HOLLAND and BRINDLE (1966) use an estimate of this kind. NORRISH and HUTTON (1969) obtained an empirical function using simple oxide mixtures. Equation (11) can readily be used to determine this function by a multiple regression procedure from even normal standards, however, the values obtained from simple mixtures for the coefficients are probably most reliable. As was previously stated equation (11) may be solved in two ways once $f(p_{ik})$ is known :-

(a) An iterative procedure similar to that of HOLLAND and BRINDLE (1966). This method is shown in the form of a flowchart on the left hand side of Fig. A.1.15. The steps are :-

(A) Establish a preliminary calibration for each element by simple linear regression.

(B) Determine correction factors using either empirical or theoretical coefficients and establish a corrected calibration for each element using simple linear regression.

(C) Use the function derived in step (A) to arrive at an initial analysis for an unknown. Either normalise directly to 100% or assume any excess or defficiency is oxygen.

(D) Use the initial estimate of the analysis to derive a set of approximate correction factors M'_{ij} and estimate a set of corrected intensities $I_{ij}^{cor'}$.

(E) Use the estimates of corrected intensity to deduce a new analysis from the corrected calibration derived in step (B). Either normalise to 100% or assume any excess or defficiency is oxygen.

(F) Compare the old and new analyses. If agreement is unsatisfactory return to step (B) using the new analysis an initial estimate.

(G) If agreement is satisfactory then continue to make any secondary corrections.

(b) An interative procedure similar to that indicated by NORRISH and HUTTON (1969). This method is illustrated on the right hand side of Fig. A1.15 and only differs from the preceeding method in steps (D) and (E) :-

(D) Use initial analysis to deduce corrected intensity from the function determined in step (B).

(E) Obtain a new estimate of all concentrations by solving r simultaneous equations of the form :-

$$I_{ij}^{cor}/I_{ij}^{obs} = \sum_{k=1}^{r} m_{kj} P_{ik}^{new}$$

Under the assumption made in equation (13).
The flowchart assumes that all elements are to be corrected but those not to be corrected can be reset in step (B) of each iteration.

Line overlap is often a problem in X-ray fluorescence analysis, for example, the Ti K_β interference with V K_α. In order to determine V the effects of Ti must be eliminated. Assuming background corrections have been made two intensities are determined; the V K_α line and the Ti K_β line.

Multiple regression techniques are particularly useful in deducing a function of the form :-
V conc. = a x V K_α intensity - b x Ti K_β intensity. Multiple regression allows a and b to be determined without the necessity of a standard containing no V. Many elements require correction in this way and the poor precision for Nb in Table A1.13 is largely due to the large number of corrections that have been applied since Rb interferes with Y which in turn interferes with Nb.

In order to test calibrations a second set of independent standards may be run. In such cases two types errors may be found :-

(a) Random errors may result because of two factors. First, the analytical values accepted for the standards may be in error, and, second, the correction procedures may not remove all random errors. It is advisable to plot out all calibration curves in order to spot any 'bad' standards.

(b) Consistent errors may also arise from two sources:- first, due to the set of test standards being of different origin to the calibration standards. Synthetic standards often show consistent errors when tested with natural samples and various factors possibly related to grain size and mineralogy may explain this observation in silicates. The second type of consistent error is revealed by plotting the composition of the calibration standards derived from the calibration against their true composition. This may reveal inadequacies in the correction procedure. Consistent errors may be reduced by application of a secondary correction. HOLLAND and BRINDLE (1966) use a second order polynomial as a secondary correction and whilst it is difficult to find theoretical justification for this its practical effect in improving accuracy can be demonstrated in some cases. Since such a procedure is likely to reduce consistent errors of type 2 its application can be justified practically.

TABLE A1.1

STANDARD MINERALS

MINERAL	SOURCE	IMPURITIES+
Kaolinite	English China Clays, Cornwall.	None detected.
Kaolinite	Separated from sample TB 5.	5 % Quartz.
Illite	Morris Illite, U.S.A. (A.P.I.)	3 % Quartz, 2 % Carbon.
Illite	Separated from sample FB 2.	2 % Quartz.
Chlorite	Penninite (single crystal*).	None detected.
Quartz	Madagascar (single crystal*).	None detected.
Siderite	Weardale (single crystal*).	None detected.
Ankerite	Boltsburn (single crystal*).	None detected.
Carbon	Anthracite, South Wales.	4 % Ash content

* Mineral obtained from Durham University Geology Department Collection.

\+ Samples were examined microscopically and by X-Ray Diffraction for impurities. Quartz impurity was determined by the method of TROSTEL and WYNNE (1940). Carbon impurity was determined by the method described in the text.

TABLE A1.2

COMPOSITION OF STANDARD MIXTURES

STANDARD	%KAOL	%ILL	%CHL	%TCL	%QTZ	%ANK	%SID	%CAR
SES 1	39.9	10.1	5.0	60.0	30.0	2.0	8.0	-
SES 2	20.0	40.0	-	60.0	29.8	5.2	2.0	3.0
SES 3	42.8	19.9	2.0	64.7	25.2	5.8	4.3	-
SES 4	15.0	50.0	-	65.0	25.2	4.4	5.4	-
SES 5	40.0	20.1	5.0	65.1	30.2	3.0	1.6	-
SES 6	30.0	30.0	7.2	67.2	20.7	2.7	5.5	3.9
SES 7	25.0	35.1	10.1	70.2	25.2	-	3.1	1.5
SES 8	45.0	22.9	2.0	69.9	30.1	-	-	-
SES 9	14.9	60.1	-	75.0	20.0	2.2	2.8	-
SES 10	49.9	24.7	-	74.6	25.4	-	-	-
SES 11	5.1	70.0	5.0	80.1	14.9	2.2	2.8	-
SES 12	59.8	15.0	5.0	79.8	20.2	-	-	-
SES 13	3.3	80.5	1.5	85.3	10.0	2.9	1.8	-
SES 14	68.7	14.5	2.3	85.5	14.5	-	-	-
SES 15	84.8	5.1	-	89.9	10.1	-	-	-

KAOL = Kaolinite. ILL = Illite. CHL = Chlorite. TCL = Total Clay. QTZ = Quartz. ANK = Ankerite. SID = Siderite. CAR = Carbon.

TABLE A1.3

DIFFERENTIAL THERMAL ANALYSIS CALIBRATION DATA

SAMPLE	SES 1	SES 6	SES 8	SES 9	SES10	SES12	SES14	SES15	
QUARTZ %	30.0	20.7	30.1	20.0	25.4	20.2	14.5	10.1	
P.A.units	254	171	259	188	214	196	124	94	inv
KAOL %	39.9	30.0	45.0	14.9	49.9	59.8	68.7	84.8	
P.A.units	3360	2500	3750	980	4850	6820	8920	12700	exo
P.A.units*	4600	3500	5200	1300	6500	8800	10900	14200	end
H_2O^+ %	7.31	6.77	7.89	5.69	8.47	9.83	10.71	12.28	
P.A.units	5550	5210	6850	4360	8850	9800	11850	14600	end
ILLITE %	10.1	30.0	23.0	60.1	24.7	15.0	14.5	5.1	
P.A.units$^+$	950	1710	1650	3060	2350	1000	900	400	end
H_2O^- %	0.52	1.08	0.98	1.87	0.99	0.77	0.78	0.57	
P.A.units	422	870	740	1450	850	710	655	560	end

* = determined from Fig. A1.4. inv = inversion peak. exo = exothermic peak. end = endothermic peak. P.A.units = arbitary peak area units. + = determined by subtraction of kaolinite contribution from H_2O^+ endotherm.

TABLE A1.4

DIFFERENTIAL THERMAL ANALYSIS PRECISION DATA						
SAMPLE	NO. DETS.	PEAK	MEAN	SDEV	C.V.%	% MIN.
TB 5	5	H_2O^-	472	35	7.4	0.54 ± 0.04
TB 5	5	H_2O^+	10508	215	2.1	10.00 ± 0.21
TB 5	5	KAOL	7838	167	2.1	63.3 ± 1.3
TB 5	5	ILL	698	85	12.2	8.8 ± 1.1
TB 5	5	QTZ	116	24	20.6	12.5 ± 2.6
FB 1	5	H_2O^-	767	38	4.9	0.94 ± 0.05
FB 1	5	H_2O^+	6504	299	4.6	7.60 ± 0.30
FB 1	5	KAOL	1898	99	5.2	29.0 ± 1.5
FB 1	5	ILL	3706	395	10.7	73.5 ± 7.5
FB 1	5	QTZ	99	31	31.2	10.6 ± 3.2

SDEV = standard deviation. C.V.% = coefficient of variation. NO. DETS. = number of determinations. % MIN. = percent of component determined ± standard deviation. KAOL = kaolinite ILL = illite. QTZ = quartz

TABLE A1.5

COMPARISON OF H_2O^+ AND H_2O^- DETERMINED BY DIFFERENTIAL THERMAL ANALYSIS AND BY GRAVIMETRIC METHODS

SAMPLE	H_2O^+ G.	H_2O^+ T.	H_2O^- G.	H_2O^- T.
TB 5	10.30	10.00	0.69	0.54
TB 7	10.25	10.50	0.71	0.59
FB 1	7.43	7.60	1.82	0.94
FB 2	6.32	6.40	1.96	1.10
LL 6	7.11	7.20	1.51	1.40
LL 8	6.46	6.50	1.65	1.40
BS 6	9.80	9.50	0.69	0.70
BS 8	9.12	8.90	0.71	0.79

G. = gravimetric determination. (See Appendix 1.22)

T. = differential thermal analysis determination.

TABLE A1.6

CALIBRATION DATA FOR QUANTIATIVE X-RAY DIFFRACTION ANALYSIS

MIN.	QUARTZ			CHLORITE		
STD.	1	2	3	1	2	3
SES 1	0.99	0.97	0.97	0.14	0.26	0.26
SES 2	0.90	0.98	0.93	-	-	-
SES 3	0.84	0.83	0.87	0.08	0.13	0.11
SES 4	0.87	0.83	0.91	-	-	-
SES 5	0.951	1.00	1.02	0.24	0.29	0.26
SES 6	0.70	0.77	0.74	0.23	0.30	0.34
SES 7	0.79	0.82	0.88	0.53	0.57	0.57
SES 8	0.97	0.99	1.03	0.06	0.09	0.10
SES 9	0.69	0.68	0.73	-	-	-
SES10	0.88	0.91	0.89	-	-	-
SES11	0.70	0.72	0.67	0.16	0.25	0.29
SES12	0.72	0.71	0.71	0.29	0.30	0.29
SES13	0.37	0.40	0.42	0.10	0.09	0.11
SES14	0.70	0.70	0.68	0.08	0.15	0.19
SES15	0.42	0.40	0.40	-	-	-

MIN.	KAOLINITE			ILLITE		
STD.	1	2	3	1	2	3
SES 1	1.45	1.66	1.63	0.30	0.35	0.34
SES 2	0.67	0.92	0.90	0.34	1.22	1.43
SES 3	1.37	1.76	1.71	0.29	0.73	0.66
SES 4	0.39	0.79	0.79	0.20	1.53	1.60
SES 5	1.34	1.62	1.60	0.90	0.82	0.78
SES 6	1.66	1.49	1.40	0.24	1.12	1.24
SES 7	1.50	1.35	1.33	0.53	1.10	1.27
SES 8	1.70	1.90	1.90	0.33	0.89	0.70
SES 9	0.62	0.78	0.75	0.34	2.07	1.96
SES10	2.01	2.08	2.14	0.88	0.88	0.94
SES11	0.70	0.40	0.30	0.27	2.12	2.03
SES12	2.05	2.44	2.37	0.54	0.53	0.54
SES13	0.27	0.27	0.31	0.38	2.70	2.62
SES14	2.73	3.34	2.80	0.69	0.68	0.82
SES15	4.34	4.31	3.62	0.25	0.39	0.35

MIN. = mineral. STD. = standard identification.

1 = peak height mineral/peak height boehemite.

2 = peak height mineral x half width/peak height boehemite x half width.

3 = counts over peak - background for mineral/counts over peak - background boehemite.

TABLE A1.7

VARIATION OF PRECISION WITH SCANNING SPEED FOR THE X-RAY DIFFRACTION METHOD OF QUANTITATIVE MINERALOGICAL ANALYSIS

SAMPLE		NP 4				TB 5			
SPEED	NO. DET.	%CHL	%ILL	%KAOL	%QTZ	%CHL	%ILL	%KAOL	%QTZ
$\frac{1}{4}^{\circ}$/min	5	11.2	56.8	-	27.0	-	15.8	70.2	13.1
		11.7	53.1	-	27.0	-	15.0	70.5	14.9
		12.4	53.5	-	24.8	-	14.6	69.2	14.4
		11.4	57.2	-	24.5	-	15.5	66.9	14.2
		11.8	55.9	-	26.7	-	14.6	67.2	12.9
MEAN		11.7	55.3	-	26.0	-	15.4	68.8	13.9
SDEV		0.5	1.8	-	1.2	-	0.5	1.7	0.8
C.V.%		3.9	3.3	-	4.8	-	3.6	2.5	6.0
$\frac{1}{2}^{\circ}$/min	5	11.6	55.3	-	27.8	-	15.8	71.0	13.1
		11.6	54.4	-	26.2	-	15.0	69.0	14.8
		12.3	52.2	-	27.4	-	14.6	67.2	15.1
		11.1	56.0	-	24.8	-	16.0	72.4	13.1
		12.0	58.6	-	24.3	-	14.1	67.4	14.4
MEAN		11.7	55.3	-	26.1	-	15.1	69.4	14.1
SDEV		0.5	2.3	-	1.5	-	0.8	2.3	1.0
C.V.%		4.2	4.2	-	5.9	-	5.3	3.3	6.7
1°/min	5	10.8	53.3	-	27.0	-	16.6	74.2	14.5
		11.7	56.4	-	28.0	-	16.2	65.5	13.5
		12.8	50.2	-	28.9	-	15.4	70.0	16.3
		10.9	60.6	-	21.8	-	13.7	68.8	12.0
		12.5	56.2	-	24.3	-	13.1	69.5	13.0
MEAN		11.7	55.2	-	26.2	-	15.0	69.6	13.9
SDEV		0.9	3.9	-	3.5	-	1.5	3.1	1.9
C.V.%		7.8	7.0	-	13.3	-	9.6	4.6	13.8

(CONTINUED OVERLEAF)

(CONTINUED FROM PREVIOUS PAGE, TABLE A1.7)

SPEED = scanning speed. CHL = chlorite. ILL = illitte.

KAOL = kaolinite. QTZ = quartz. SDEV = standard deviation.

C.V.% = coef. of variation = standard deviation x 100/mean.

MEAN = arithmetic mean (average).

N.B.. All figures are rounded to the first place of decimal.

TABLE A1.8

X-RAY PROCEDURE FOR THE DETERMINATION OF QUANTITATIVE MINERALOGY FOR (CHOLRITE) - ILLITE-KAOLINITE-QUARTZ ASSEMBLAGES

MINERAL	PEAK SCANNING LIMITS (IN DEGREES TWO THETA)	FCBG1	FCBG2	PEAK	SPACING
CHLORITE	6.0 - 7.0°	6.0°	7.0°	001	14 Å
ILLITE	7.0 -10.0°	7.0°	10.0°	001	10 Å
KAOLINITE	12.0 -13.0°	11.5°	13.5°	001	7 Å
BOEHEMITE	14.0 -15.0°	13.5°	15.0°	101	6.18 Å
QUARTZ	20.5 -21.5°	20.5°	21.5°	100	4.26 Å

FCBG1 and FCBG2 = fixed count background positions counting for 64 seconds.

TABLE A1.9

COMPARISON OF MINERALOGICAL ANALYSES BY X-RAY DIFFRACTION AND BY DIFFERENTIAL THERMAL ANALYSIS

SAMPLE		TB 5	TB 7	FB 1	FB 2	LL 6	LL 8	BS 6	BS 8
MIN.	METHOD								
CHL	XRD	-	-	2.8	3.5	1.0	0.9	1.2	1.6
	DTA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	DIFF	-	-	+2.8	+3.5	+1.0	+0.9	+1.2	+1.6
ILL	XRD	18.3	21.9	67.7	66.3	47.4	49.0	29.1	24.8
	DTA	10.4	12.8	66.0	63.0	49.4	50.1	23.5	21.5
	DIFF	+7.9	+9.1	+1.7	+3.3	-2.0	-1.1	+5.6	+3.3
KAOL	XRD	67.4	63.3	16.8	15.1	29.9	27.9	54.4	53.1
	DTA	74.8	71.4	25.0	23.7	29.8	29.7	58.6	59.3
	DIFF	-7.4	-8.1	-8.2	-8.6	+0.1	-1.8	-4.2	-6.2
QTZ	XRD	14.3	14.8	12.7	15.1	21.7	22.2	15.3	20.6
	DTA	14.8	15.8	9.0	13.2	20.8	20.2	17.9	19.3
	DIFF	-0.5	-1.0	+3.7	+1.9	+0.9	+2.0	-2.6	+1.3

CHL = chlorite. ILL = illite. KAOL = kaolinite. QTZ = quartz. XRD = x-ray diffraction. DTA = differential thermal analysis. DIFF = difference. n.d. = not determined.

TABLE A1.10

METHODS OF ANALYTICAL DETERMINATION FOR 29 CHEMICAL VARIABLES

VARIABLE	METHOD	EXPRESSION	NO. OF ANALYSES
Aluminium	XRF Maj	% Al_2O_3	75
Barium	XRF Tra	ppm Ba	55
Calcium	XRF Maj	% CaO	75
Carbon	GRAV	% C	55
Carbon dioxide	GRAV	% CO_2	55
Chromium	XRF Tra	ppm Cr	42
Copper	XRF Tra	ppm Cu	42
Iron	XRF Maj	% Fe_2O_3	75
Lanthanum	XRF Tra	ppm La	42
Lead	XRF Tra	ppm Pb	42
Magnesium	XRF Maj	% MgO	75
Manganese	XRF Tra	% MnO	75
Nickel	XRF Tra	ppm Ni	42
Niobium	XRF Tra	ppm Nb	55
Phosphorus	XRF Maj	% P_2O_5	75
Potassium	XRF Maj	% K_2O	75
Rubidium	XRF Tra	ppm Rb	55
Scandium	XRF Tra	ppm Sc	42
Silicon	XRF Maj	% SiO_2	75
Sodium	FP	% Na_2O	75
Strontium	XRF Tra	ppm Sr	55
Sulphur	XRF Maj	% S	75
Titanium	XRF Maj	% TiO_2	75
Vanadium	XRF Tra	ppm V	42
Water +	GRAV	% H_2O^+	55
Water -	GRAV	% H_2O^-	55
Yttrium	XRF Tra	ppm Y	55
Zinc	XRF Tra	ppm Zn	42
Zirconium	XRF Tra	ppm Zr	55

XRF = X-ray fluorescence spectrometry. FP = flame photometry. GRAV = Gravimetry. Maj = Major element. Tra = Trace element.

TABLE A1.11

OPERATING CONDITIONS, PRECISIONS AND DETECTION LIMITS FOR X-RAY FLUORESCENCE DETERMINATION OF MAJOR ELEMENTS USING A PHILIPS 1212 AUTOMATIC SPECTROMETER.

Element		Si	Al	Fe	Mg	Ca
Wavelength (Å)		7.08	8.34	1.93	9.89	3.29
Background (2θ)		-	-	-	-	-
Peak (2θ)		109.07	144.95	85.72	81.33	45.07
Background (2θ)		-	-	-	79.05	-
Tube		Cr	Cr	Cr	Cr	Cr
Generator	KV	60	60	60	50	60
	mA	8	24	8	40	20
Crystal		PET	PET	LiF	GYPSUM	PET
Counter		F	F	F+S	F	F
Collimator		CC	CC	CC	CC	CC
Counts		10^5	10^5	10^5	3×10^4	10^5
Times (secs)		-	-	-	-	-
Line		$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$
Interference		-	-	-	-	-
Precision (%) [*]		1	1	3	5	5
Detection limit[+]		-	-	-	-	2000

TABLE A1.11 (CONTINUED)

OPERATING CONDIONS, PRECISIONS AND DETECTION LIMITS FOR X-RAY FLUORESCENCE DETERMINATION OF MAJOR ELEMENTS USING A PHILIPS 1212 AUTOMATIC SPECTROMETER.

Element		Na	K	Ti	S	P
Wavelength (Å)		11.9	3.74	2.76	5.18	6.07
Background(2θ)		105.05	-	-	-	-
Peak (2θ)		103.12	50.05	36.58	75.65	89.45
Background(2θ)		-	-	-	73.5	87.50
Tube		Cr	Cr	Cr	Cr	Cr
Generator	KV	50	40	40	50	50
	mA	40	8	8	40	40
Crystal		GYPSUM	PET	PET	PET	PET
Counter		$3x10^4$	10^5	10^5	10^4	10^4
Collimator		CC	CC	CC	CC	FC
Time (secs)		-	-	-	-	-
Line		$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$
Interference		-	-	-	-	-
Precision(%) *		7	1	1	2	2
Detection limit+		2000	-	-	1000	1000

* Precision in percent determined from duplicate runs of 75 sedimentary rocks. The precisions are a function of both concentration and counting rates.

\+ Detection limit in parts per million quoted only for major elements of low concentration in seatearth.

TABLE A1.12

OPERATING CONDITIONS, PRECISIONS AND DETECTION LIMITS FOR X-RAY FLUORESCENCE DETERMINATION OF TRACE ELEMENTS USING A PHILIPS 1212 AUTOMATIC SPECTROMETER.

Element		Ba	Cr	Cu	La	Mn
Wavelength (Å)		0.385	2.290	1.541	2.674	2.102
Background (2θ)		-	-	64.80	136.70	93.40
Peak (2θ)		15.53	107.11	65.53	138.70	95.25
Background (2θ)		16.50	109.20	66.50	-	97.10
Tube		W	W	W	Cr	W
Generator	KV	80	60	60	60	50
	mA	24	32	32	32	40
Crystal		LiF	LiF	LiF	LiF	LiF
Counter		S	F	F+S	F	F
Collimator		CC	CC	CC	CC	CC
Counts		-	-	-	-	-
Time (secs)		40	40	100	100	100
Line		$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$
Interference		-	$V\ K_\beta$	-	-	CrK_β
Precision (%)*		8.7	1.7	3.2	4.7	2.3
Detection limit+		5	2	1	5	1

* Precision in percent determined from mean background counts from equation (6). The figures quoted are at the 100 ppm level of concentration. More detailed information is given in Fig. A1.15.

\+ Detection limit in parts per million (rounded up to the nearest one). Estimated from mean background.

TABLE A1.12 (CONTINUED)

OPERATING CONDITIONS, PRECISION AND DETECTION LIMITS FOR X-RAY FLUORESCENCE DETERMINATION OF TRACE ELEMENTS USING A PHILIPS 1212 AUTOMATIC SPECTROMETER.

Element		Nb	Ni	Pb	Rb	Sc
Wavelength (Å)		0.746	1.658	0.982	0.926	3.031
Background (2θ)		29.30	70.00	39.23	36.85	39.50
Peak (2θ)		30.32	71.25	40.34	37.96	40.57
Background (2θ)		30.95	73.20	41.81	39.23	43.50
Tube		W	W	W	W	Cr
Generator	KV	60	60	60	60	60
	mA	32	32	32	32	32
Crystal		LiF	LiF	LiF	LiF	PET
Counter		S	F+S	S	S	F
Collimator		CC	CC	CC	CC	FC
Counts		-	-	-	-	-
Time (secs)		40	100	100	40	100
Line		$K\alpha_1$	$K\alpha_1$	$L\beta_1$	$K\alpha_1$	$K\alpha_1$
Interference		$Y\ K\beta$	-	$AsK\alpha$	-	$CaK\beta$
Precision (%)		4.9	2.4	14.5	7.1	1.0
Detection limit$^+$		3	1	12	3	1

TABLE A1.12 (CONTINUED)

OPERATING CONDITIONS, PRECISIONS AND DETECTION LIMITS FOR X-RAY FLUORESCENCE DETERMINATION OF TRACE ELEMENTS USING A PHILIPS 1212 AUTOMATIC SPECTROMETER.

Element		Sr	V	Y	Zn	Zr
Wavelength (Å)		0.875	2.503	0.829	1.435	0.786
Background (2θ)		34.85	120.00	33.00	59.40	30.95
Peak (20)		35.82	123.28	33.85	60.56	32.06
Background (20)		36.85	126.00	34.85	61.60	33.00
Tube		W	W	W	W	W
Generator	KV	60	60	60	60	60
	mA	32	32	32	32	32
Crystal		LiF	LiF	LiF	LiF	LiF
Counter		S	F	S	F+S	S
Collimator		CC	FC	CC	CC	CC
Counts		-	-	-	-	-
Time (secs)		40	100	40	100	40
Line		$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$	$K\alpha_1$
Interference		-	TiK_β	RbK_β	-	$SrK\beta$
Precision (%)*		6.1	2.3	5.6	3.6	5.5
Detection limit+		3	3	3	2	3

The following abreviations are used in Tables A1.11 and A1.12

S = Scintilation counter. F = Flow counter.

F+S = Flow and Scint. counters CC = Coarse collimator.

FC = Fine collimator.

TABLE A1.13

TRACE ELEMENT DETERMINATIONS ON G1 and W1 USING "SPIKED" STANDARDS WITH AN ARGILLACEOUS SEDIMENT MATRIX.

ELEMENT	G1		W1	
	This work	U.S.G.S.*	This work	U.S.G.S.*
Ba	1100 ± 87	1200	200 ± 18	180
Cu	12 ± 1	13	117 ± 4	110
La	107 ± 5	100	10 ± 2	12
Nb	17 ± 5	20	9 ± 6	10
Rb	225 ± 15	220	21 ± 2	22
V	11 ± 3	16	236 ± 10	240
Y	15 ± 2	13	25 ± 1	25
Zn	55 ± 3	45	95 ± 4	82
Zr	188 ± 11	210	97 ± 5	100

* After FLEISCHER (1968)

TABLE A1.14

TYPICAL DATA OBTAINED AS PRELIMINARY CALIBRATION OF MAJOR ELEMENTS IN X-RAY FLUORESCENCE BY SIMPLE LINEAR REGRESSION

ELEMENT OXIDE	PREC. %	SLOPE cps/%	INT. abs %	CORR. COEF.	STD. ERR. OF EST.abs %	RANGE
SiO_2	1.0	260	8.0	0.97	2.5	40 - 75
Al_2O_3	1.0	390	2.0	0.94	3.5	10 - 35
Fe_2O_3	0.5	1300	-0.1	0.92	1.5	0 - 15
MgO	5.0	70	0.4	0.99	0.3	0. - 50
CaO	0.5	1280	-0.1	0.99	0.4	0 - 15
Na_2O	7.0	15	0.3	0.96	0.3	0 - 10
K_2O	0.2	3200	0.1	0.99	0.1	0 - 5
TiO_2	0.2	7500	0.05	0.99	0.05	0 - 3
S	2.5	120	-0.05	0.98	0.1	0 - 5
P_2O_5	2.0	440	0.05	0.98	0.05	0 - 1

FIG. A1·1 DTA APPARATUS

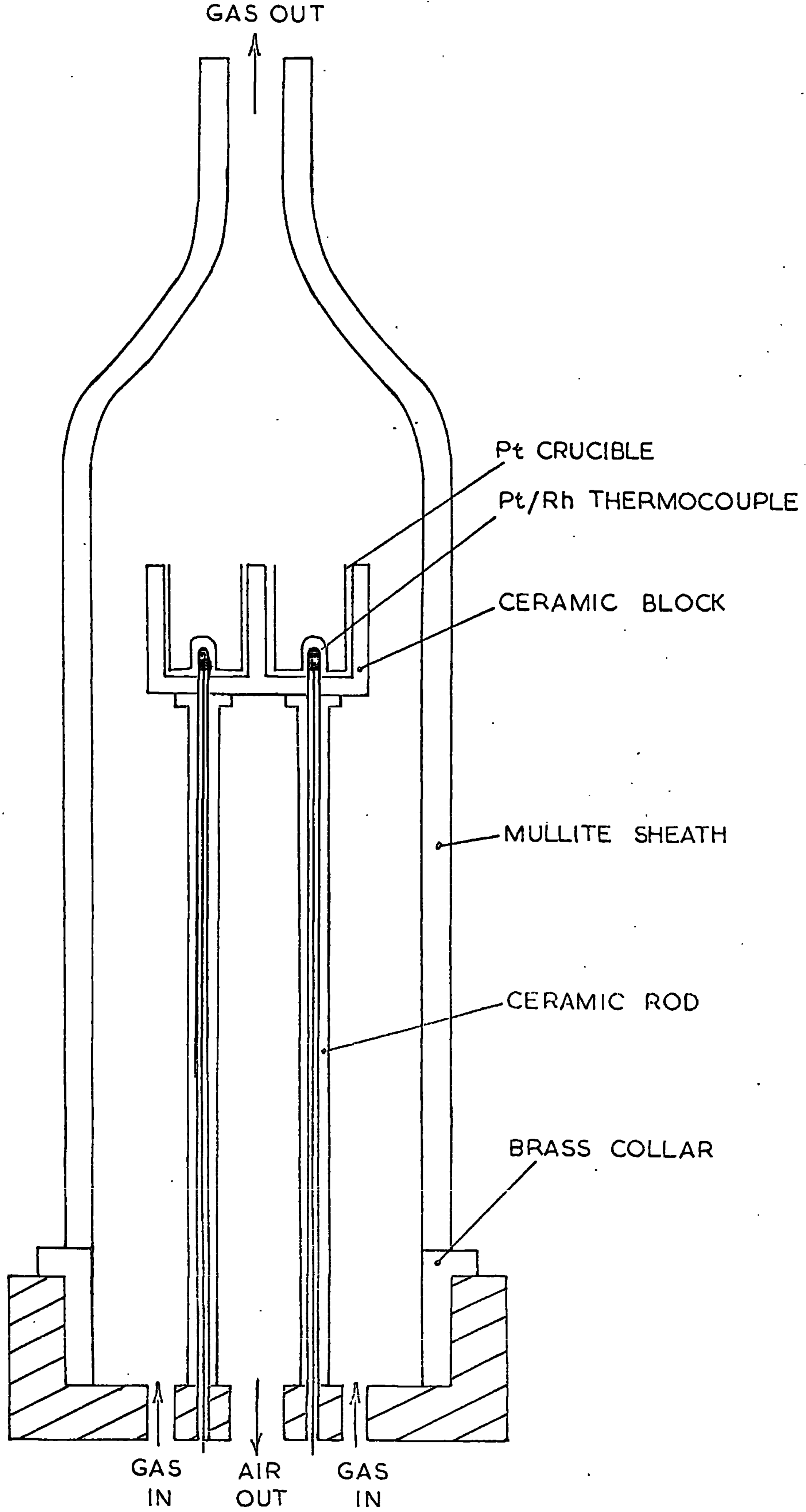
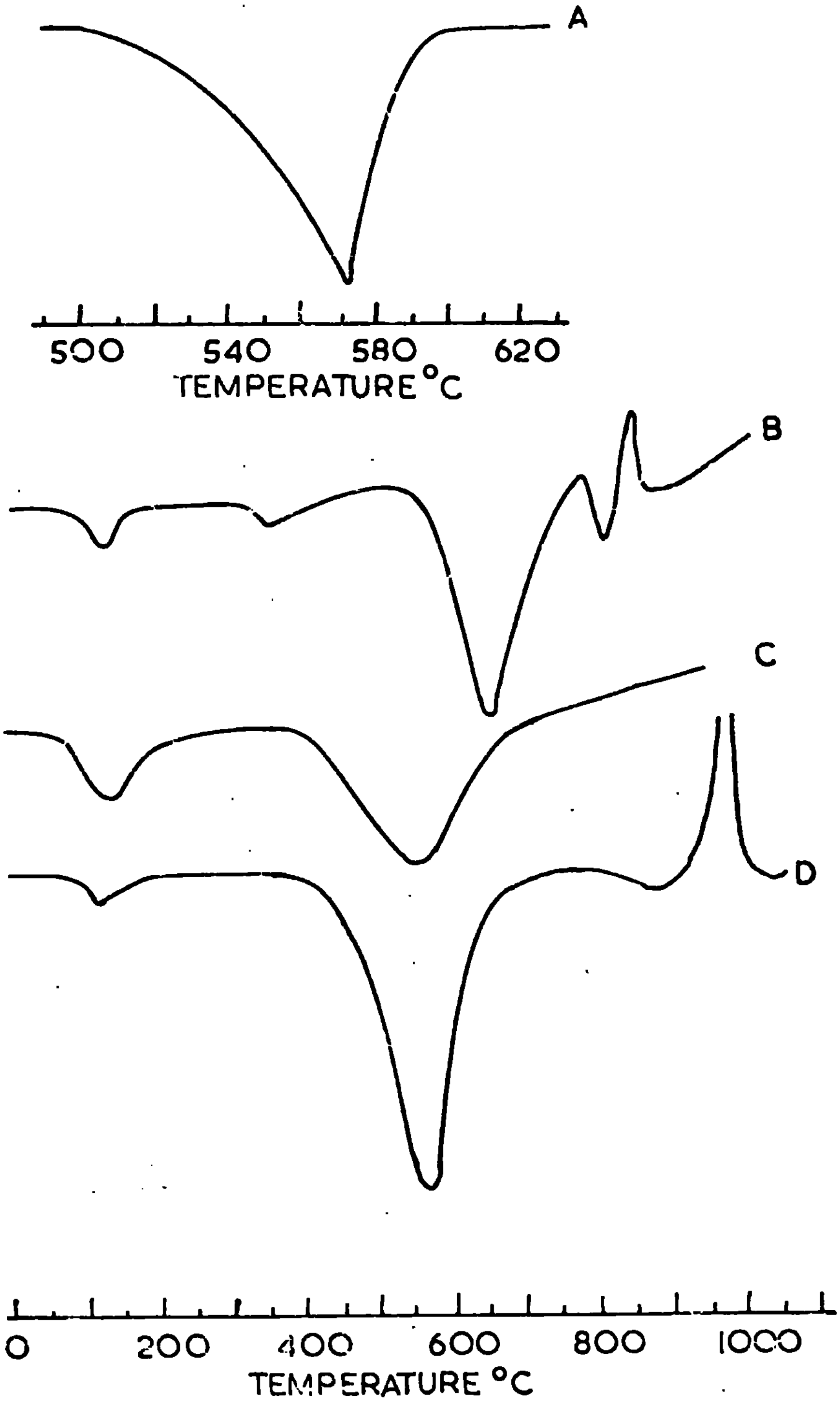


FIG. A1·2 DIFFERENTIAL THERMAL ANALYSIS CURVES (GENERALISED) OF STANDARD MINERALS.



A QUARTZ (scale expanded both horizontally and vertically ×~10)
B PENNINITE
C ILLITE } scales are identical approximately
D KAOLINITE

FIG. A1.3 DIFFERENTIAL THERMAL ANALYSIS KAOLINITE CALIBRATION CURVE.

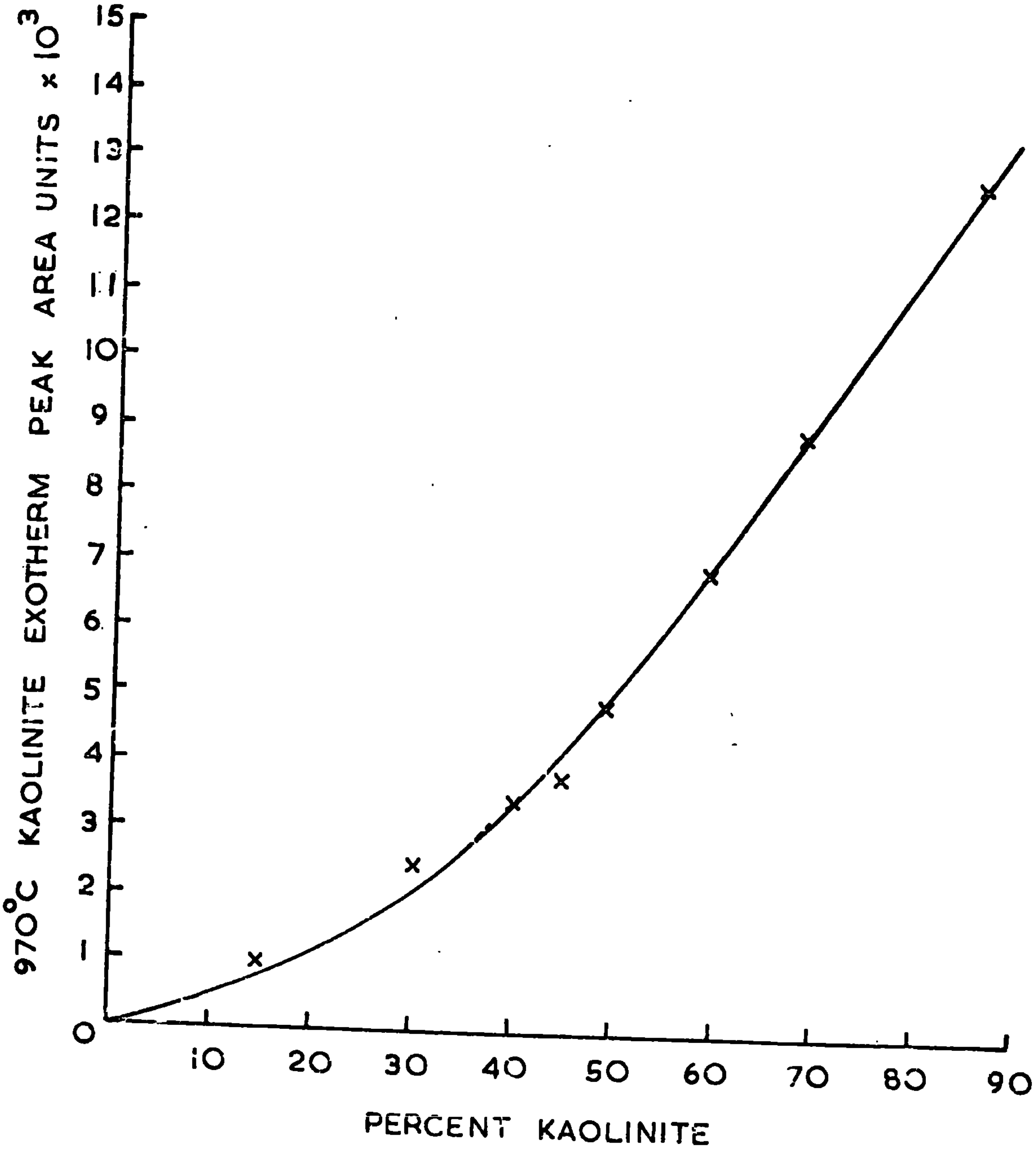
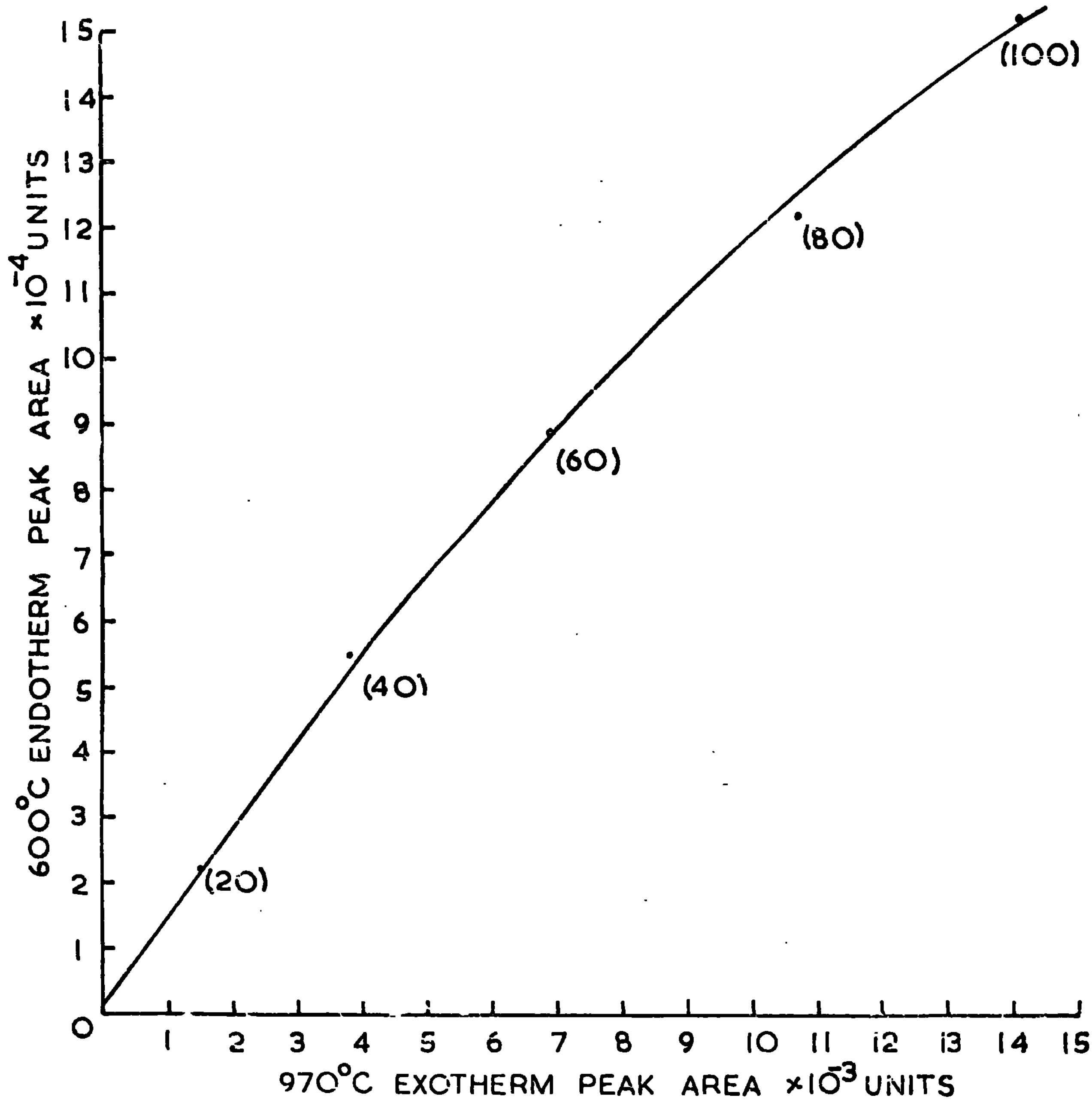


FIG. A1.4 KAOLINITE 970°C EXOTHERM PEAK AREA v 600°C ENDOTHERM PEAK AREA.



Figures in parentheses are % Kaolinite for determination

FIG. A1.5 DIFFERENTIAL THERMAL ANALYSIS H_2O^+ CALIBRATION CURVE.

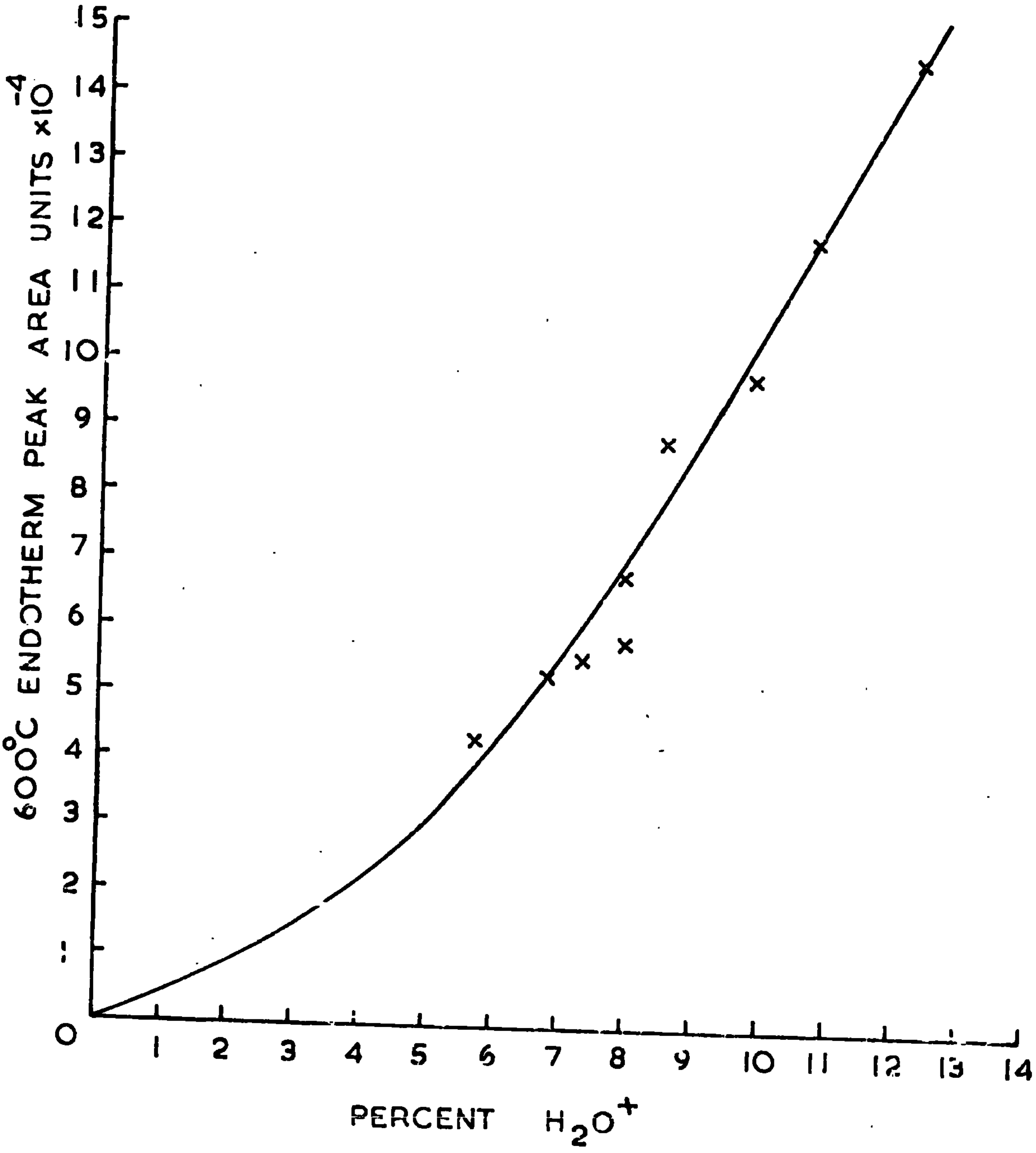


FIG. A1.6 DIFFERENTIAL THERMAL ANALYSIS ILLITE CALIBRATION CURVE.

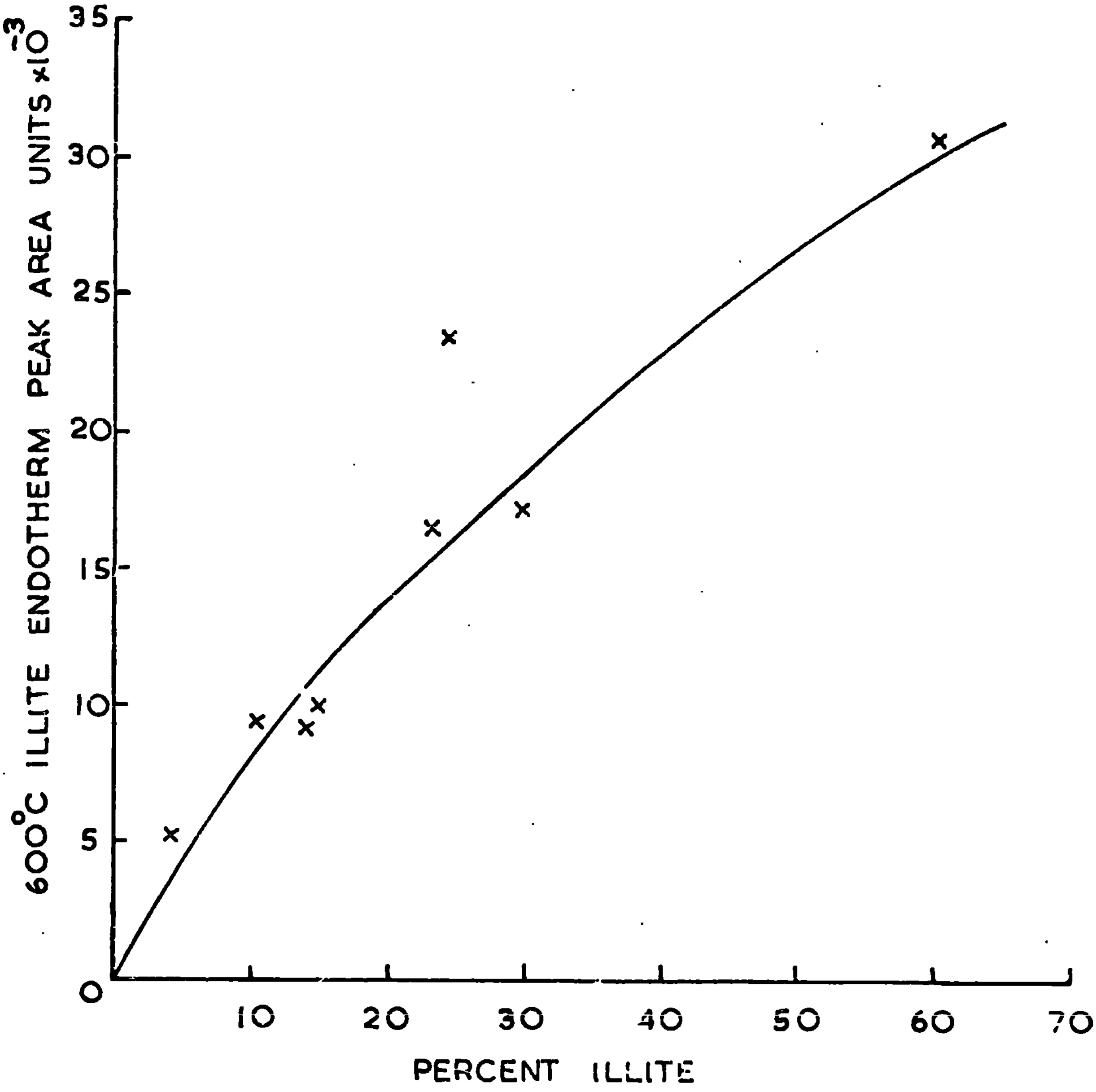


FIG. A1.7 DIFFERENTIAL THERMAL ANALYSIS QUARTZ CALIBRATION CURVE.

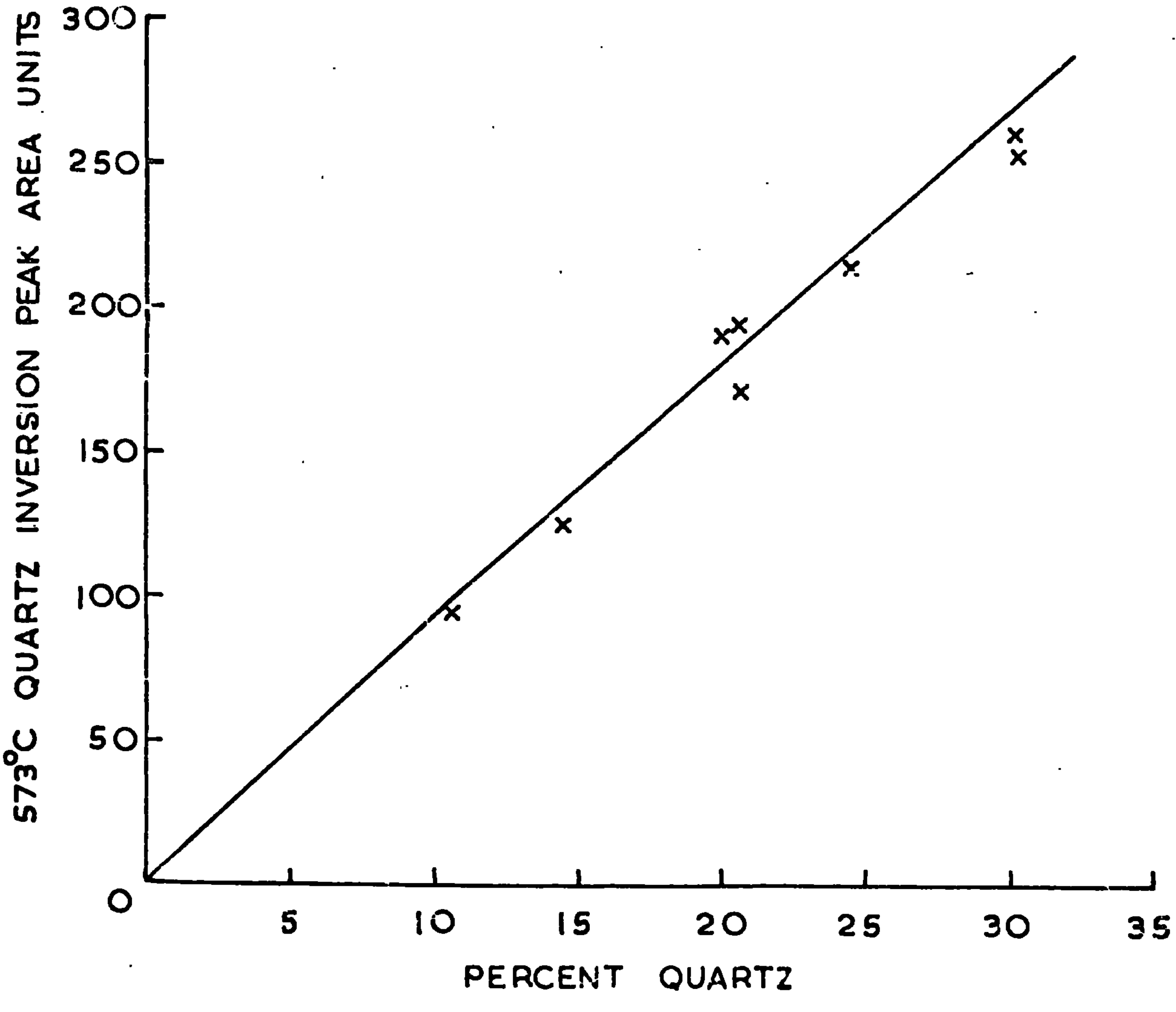


FIG. A1·8 DIFFERENTIAL THERMAL ANALYSIS H_2O^- CALIBRATION CURVE.

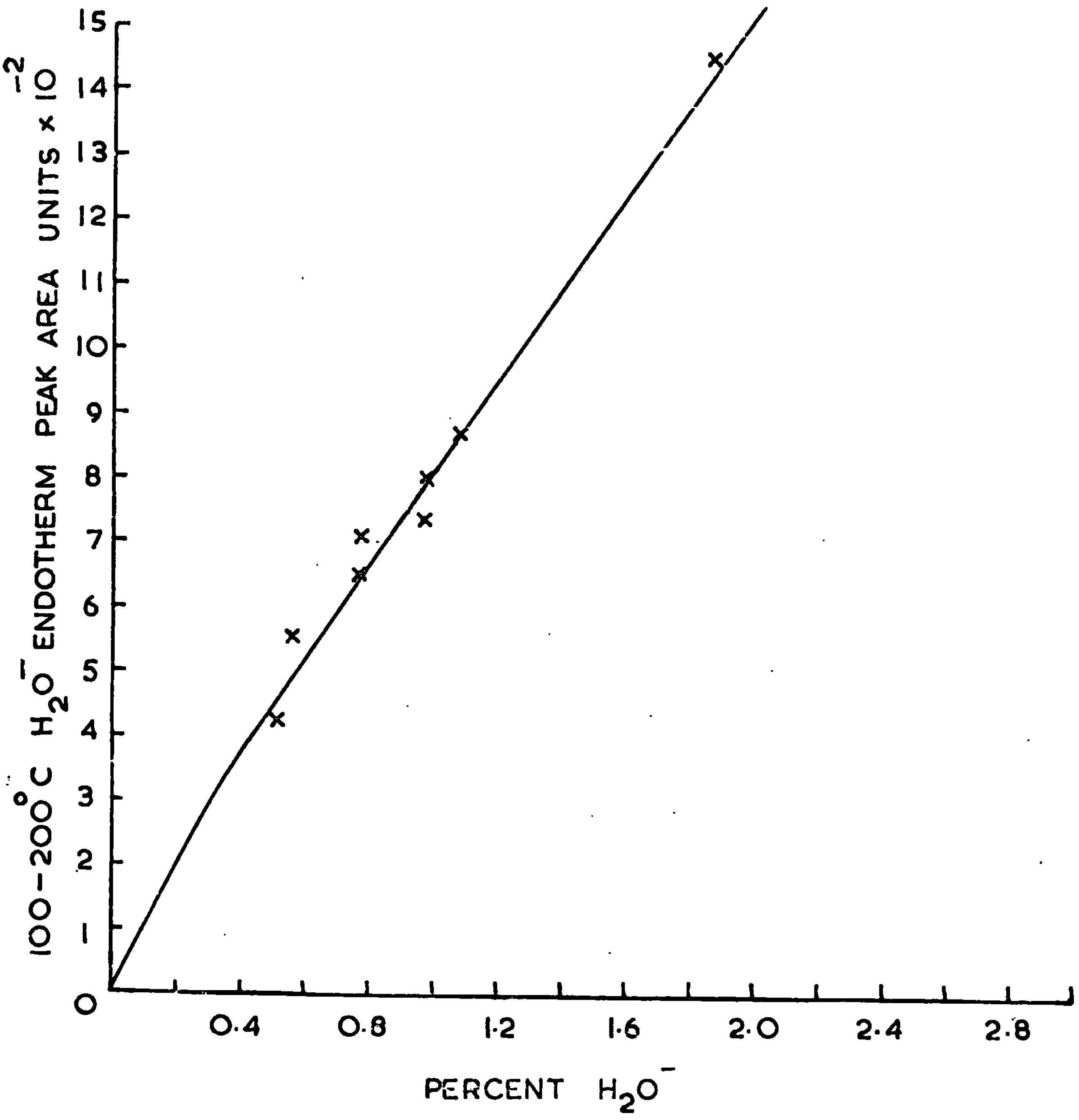


FIG. A1.9 VARIATION OF PRECISION WITH SCANNING SPEED.

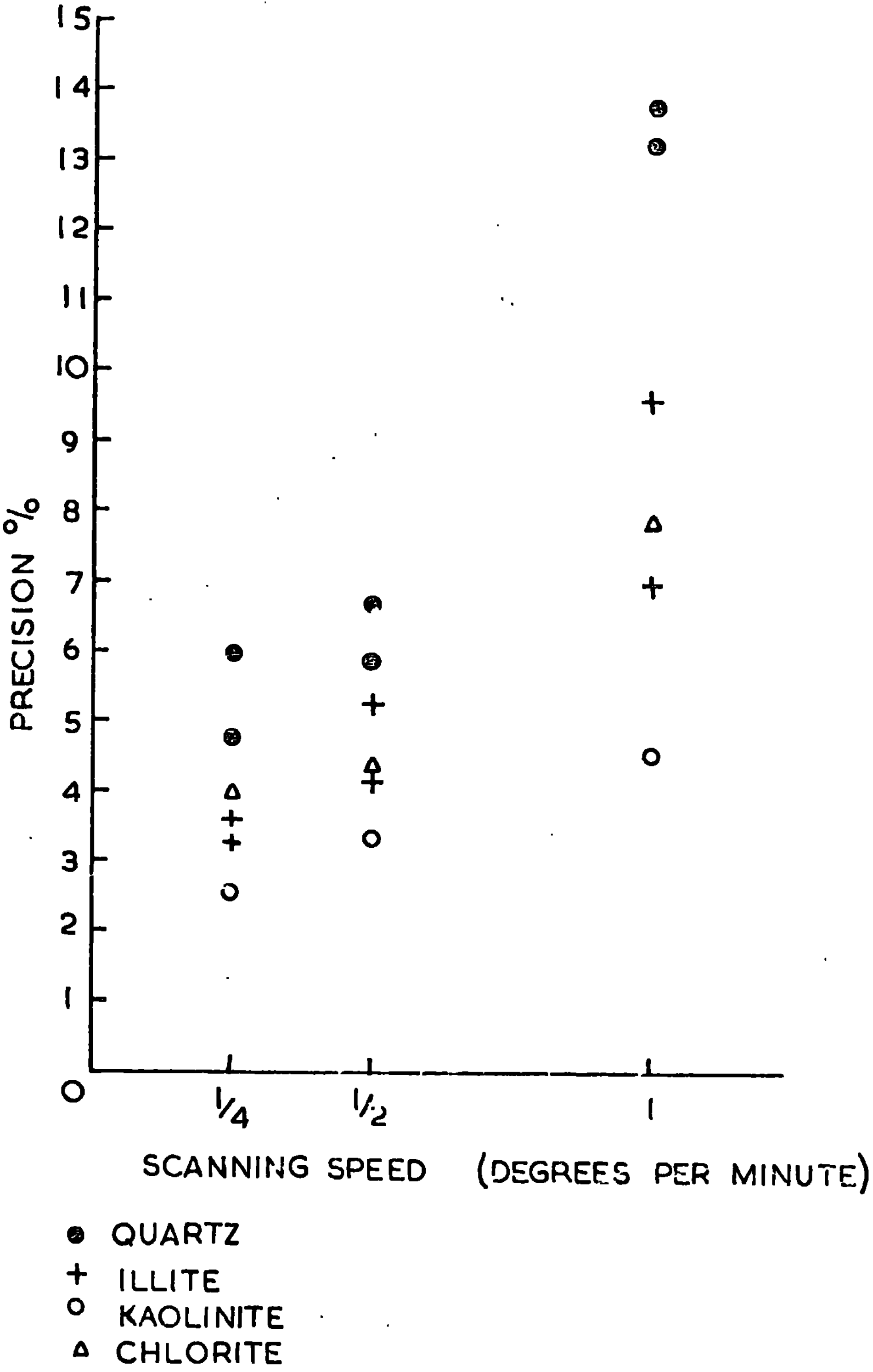


FIG. AI.IO. VARIATION OF PRECISION WITH MINERAL CONCENTRATION.

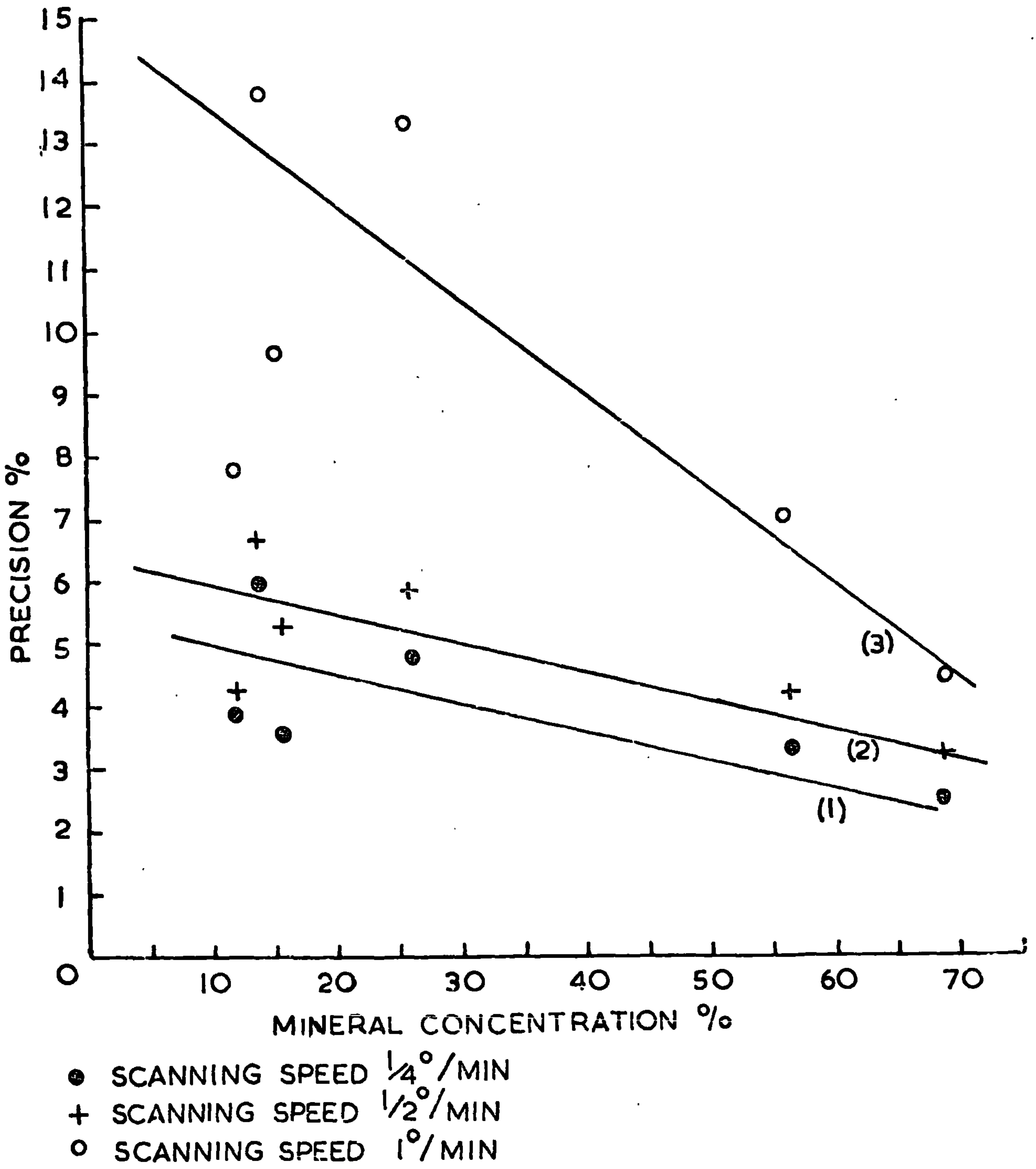
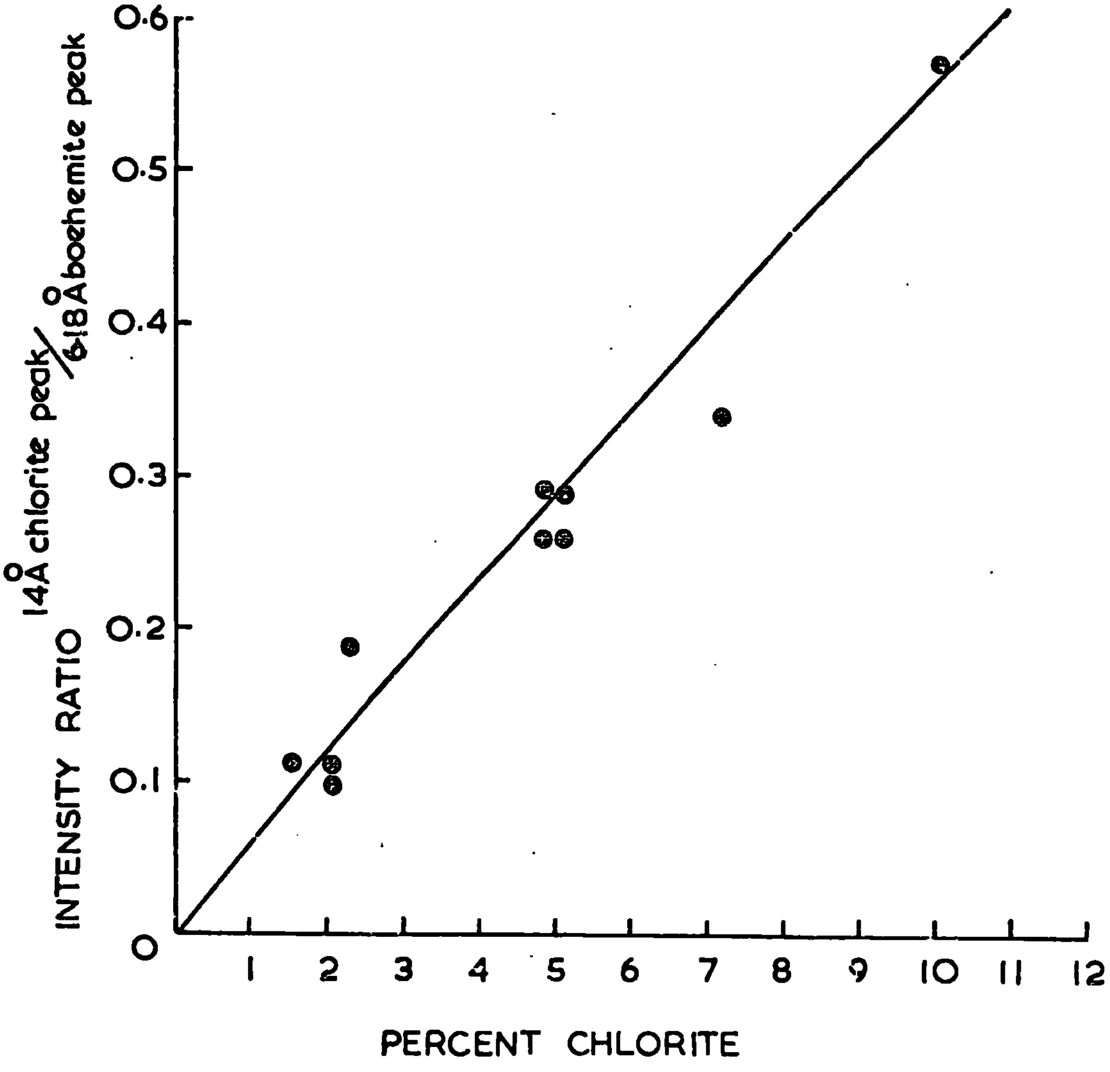
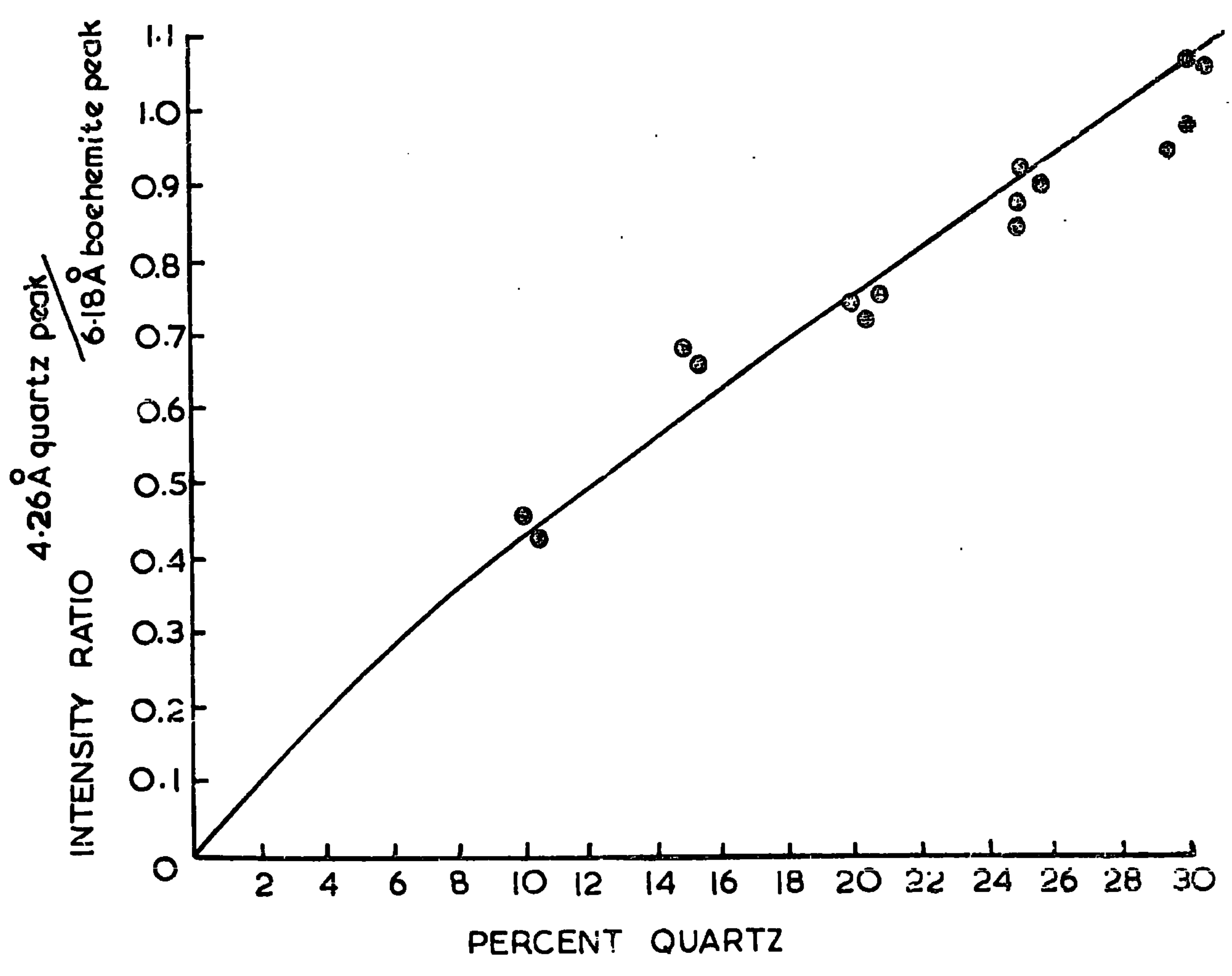


FIG. A1·11 X-RAY DIFFRACTION CHLORITE CALIBRATION CURVE



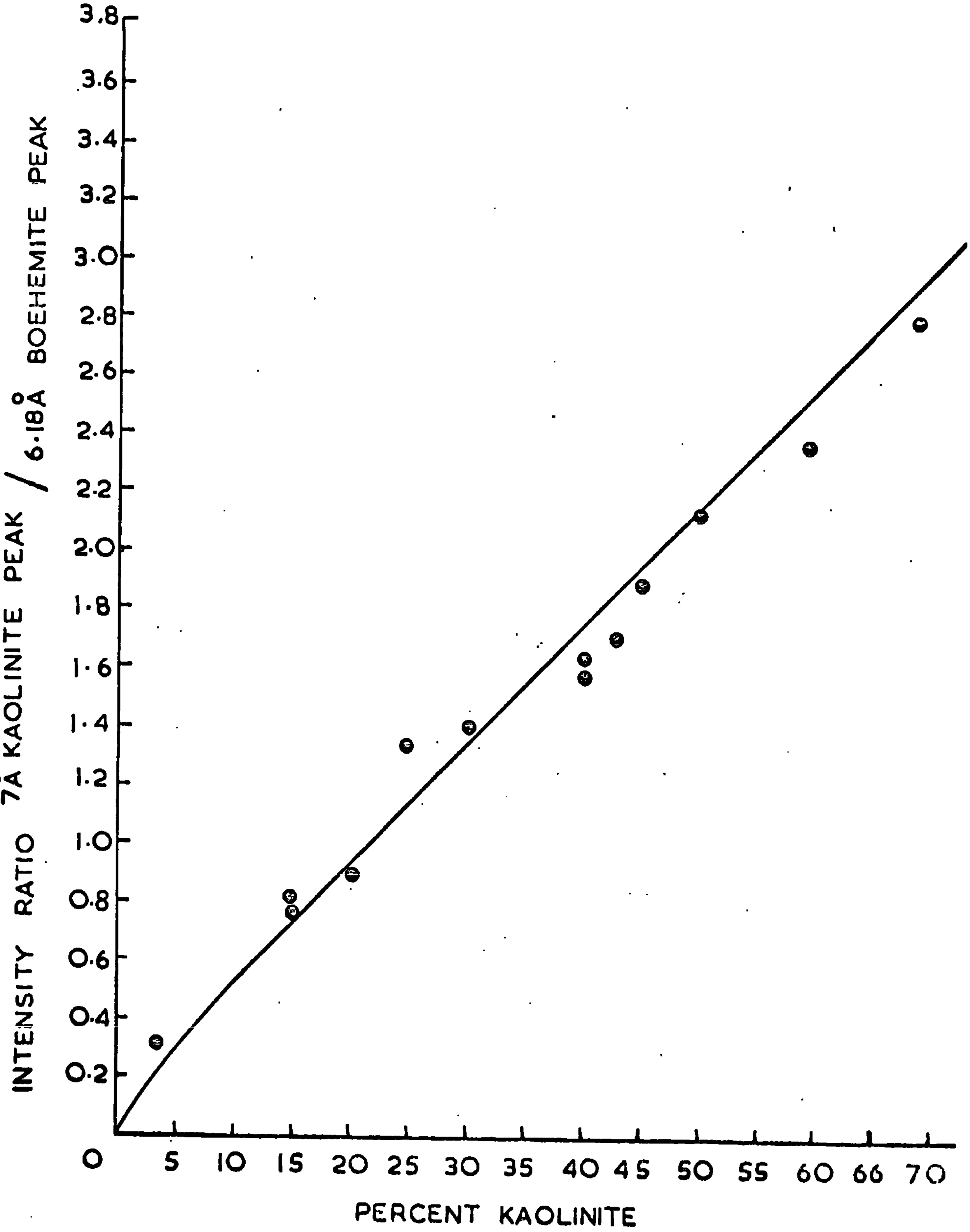
Intensity ratio plotted is column (3) (see table A1·6)

FIG. A1·12 X-RAY DIFFRACTION QUARTZ CALIBRATION CURVE



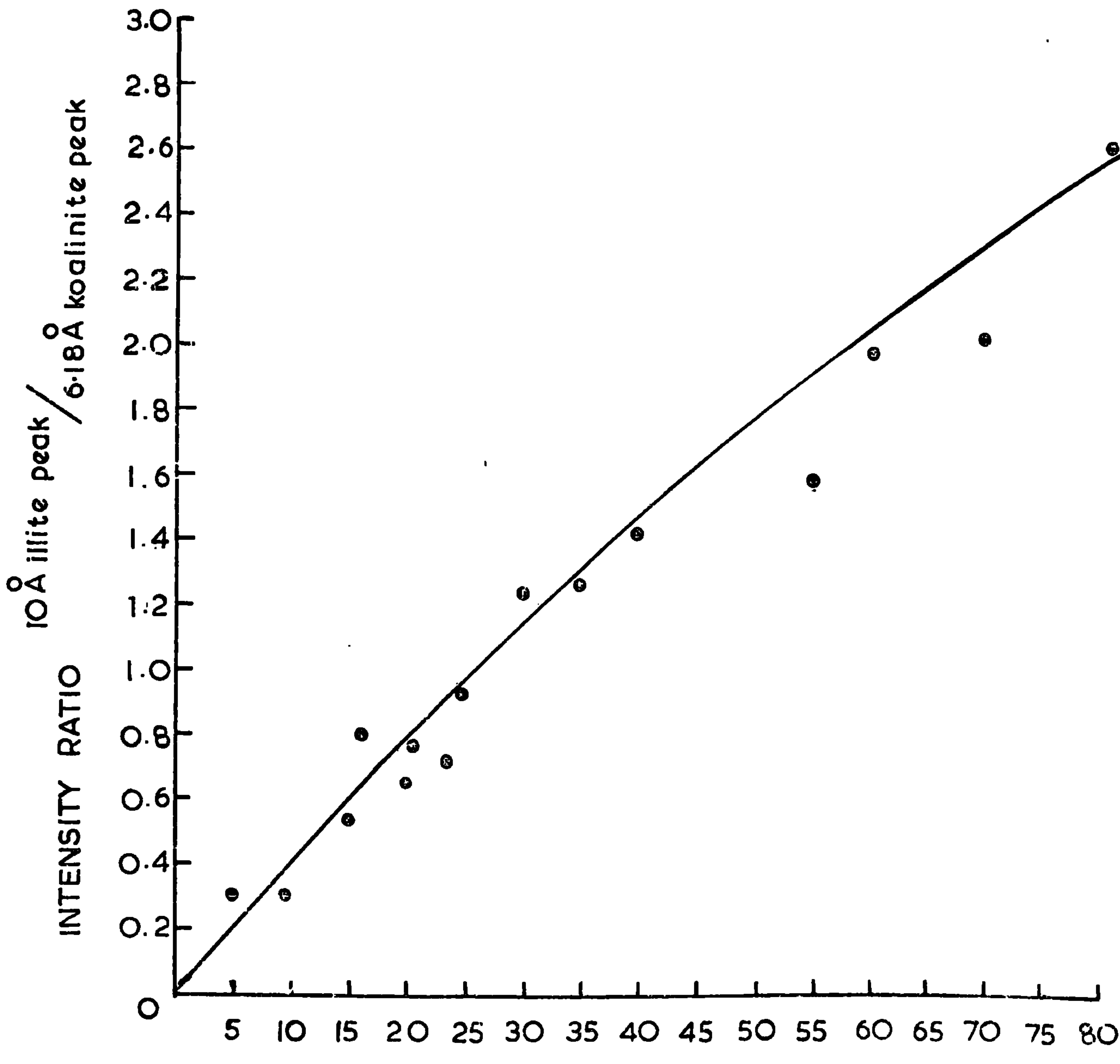
Intensity ratio plotted is column (3) (see table A1·6)

FIG. A1·13 X-RAY DIFFRACTION KAOLINITE CALIBRATION CURVE



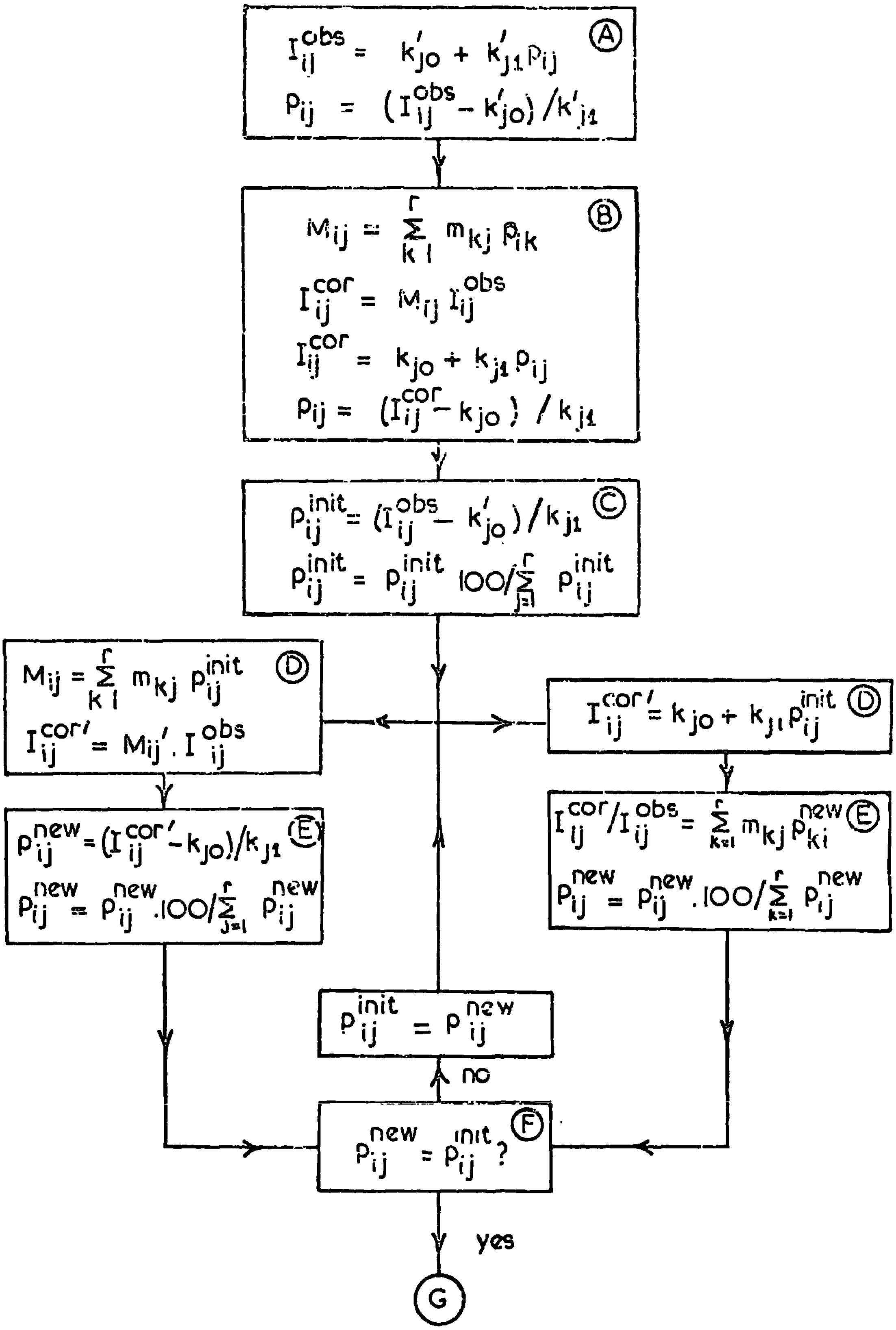
INTENSITY RATIO PLOTTED IS COLUMN (3) (SEE TABLE A1.6)

FIG. A1·14 X RAY DIFFRACTION ILLITE CALIBRATION CURVE



Intensity ratio plotted is column (3) (see table A1·6)

FIG. A1.15 FLOWCHART FOR COMPLEX MATRIX CORRECTION OPTIONS



1.3 REFERENCES TO APPENDIX I

ALLEY, B. J. and MYERS, R. H., (1965), Corrections for matrix effects in X-ray fluorescence using multiple regression methods, Anal. Chem., 37, 1685 - 1690.

ANDERMANN, G. and KEMP, J.W., (1958), Scattered X-rays as internal standards in X-ray emission spectroscopy, Anal. Chem., 30, 1306 - 1309.

BADGER, C. W., (1955), Disintegration of shales in water, Unpublished thesis, Univ. Nottingham.

DAVIS, C. E., and HOLDRIDGE, D. A., (1969), Quantitative estimation of clay minerals by differential thermal analysis, Clay minerals, 8, 193 - 200.

GIBBS, R. J., (1967), Quantitative X-ray diffraction analysis using clay minerals standards extracted from the samples to be analysed, Clay minerals, 7, 79 - 90.

GRIFFIN, O. G., (1954), A new internal for the quantitative X-ray analysis of shales and mine dusts, Rep. Saf. Mines Res. No. 101.

GRIM, R. E., (1947), D.t.a. curves of clay mineral mixtures, Amer. Min., 32, 493 - 501.

GRIMSHAW, R. W., and ROBERTS, A. L., (1953), Quantitative d.t.a. of some minerals in ceramic materials, Trans. Brit. Ceram. Soc., 52, 50 - 67.

GROVES, A. W., (1951), Silicate analysis, 2nd ed. Allen and Unwin, Lond.

HEINRICH, K. F. J., (1966), The electron microprobe, Ed. T.D. McKinley, K. F. J. Heinrich & D. B. Wittry, John Wiley, 296 - 377.

HOFMANN, U., (1956), Clay mineral studies in Germany, 1954 and 1955, Ed. A. Swineford, Clay and clay minerals, 161 - 165.

HOLLAND, J. G., and BRINDLE, D. W., (1966), A self-consistent mass absorption correction for silicate analysis by X-ray fluorescence, Spectrochim. Acta, 22, 2083 - 2093.

KALMAN, Z. H., and HELLER, L., (1962), Theoretical study of X-ray fluorescence determination of traces of heavy elements in a light matrix, Anal. Chem., 34, 946 - 951.

KODAMA, H., BRYDON, J. E., and STONE, B. C., (1967), X-ray spectrochemical analysis of standard silicates using synthetic standards with a correction for interelment effects by a computer method, Geochim. Cosmochim. Acta, 31, 649 - 659.

LIEBHASFSKY, H. A., and WINSLOW, E. H., (1958), X-ray absorption and enhancement, Anal. Chem. 30, 580 - 589.

LUCAS - TOOTH, H. J., and PYNE, C. C., (1964), The accurate estimation of major constituents by X-ray fluorescence analysis in the presence of large interelement effects, Adv. X-ray analysis, 7, 523 - 541.

MACKENZIE, R. C., and MITCHELL, B. D., (1957), Apparatus and technique for differential thermal analysis, Ed. R. C. Mackenzie, Mem. Min. Soc. Lond., Chapter 2.

NORRISH, K., and HUTTON, J. T., (1969), An accurate X-ray spectrographic method for the analysis of a wide range of geological samples, Geochim. Cosmochim. Acta, 33, 431 - 453.

RILEY, J. P., (1958), Simultaneous determination of water and carbon dioxide in rocks and minerals, Analyst, 83, 42 - 49.

ROSE, H. J., ADLER, I., and FLANAGAN, F. J., (1963), X-ray fluorescence analysis of light elements in rocks and minerals., Applied Spectroscopy, 17, 81 - 85.

SABATIER, G., (1954), Determination of heats of transformation by d.t.a., Bull. Soc. franc. Miner., 77, 953 - 968.

SEWELL, E. C., and HONEYBORNE, D. B., (1957), Theory and quantitative use of differential thermal analysis, Ed. R. C. Mackenzie, Mem. Min. Soc. Lond., Chapter 3.

SHAPIRO, L., and BRANNOCK, W. W., (1952), Rapid analysis of silicate rocks, U.S. Geol. Surv. Circ., 165.

SPEIL, S., BERKELHAMER, L. H., PASK, J. A., and DAVIES, B., (1945), D.t.a. of clays and aluminous materials, Tech. Pap. Bur. Min., Wash., No. 664.

TROSTEL, L. J., and WYNNE, D. J., (1940), Determination of quartz (free silica) in refractory clays, Jour. Amer. Ceram. Soc., 23, 18 - 22.

APPENDIX II

STATISTICAL METHODS

2.1 DISTRIBUTION FUNCTIONS

The concentrations of various chemical and elemental components are, as noted by RODIONOV (1965), random quantities with respect to sampling and analysis, for any group of rocks. Thus, geochemical deductions based on comparisons of concentrations of various components are a result of comparison of random variables. Let any random variable x have a distribution function f(x). Now the expectation of the function or random variable is defined as the weighted average value of the function or variable over all possible values of the function or variable. That is,

$$E(x) = \sum_{x=a_1}^{a_n} xf(x) \qquad x = a_1, a_2, \ldots a_n. \tag{1}$$

The moments of a random variable are defined as the expectations of the powers of the random variable. The expectation of the first power of x about zero may be written:-

$$E(x) = \frac{\sum_{i=1}^{n} (x_i - x_0)}{n} \tag{2}$$

This value is the arithmetic mean. The first moment about the mean, it can be seen from (2) will be zero.

The second moment about the mean is given by :-

$$E(x) = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n} \tag{3}$$

This value is called the variance and its square root is the standard deviation. These values are measures of the 'scatter' about the mean. Data can be coverted to a normalised form by the following operation :-

$$^{n}x_i = (x_i - \bar{x})/s_i \qquad (4)$$

Where s_i is the standard deviation and $\bar{x}$ the mean. Data normalised in this way has a mean of zero and a variance of one. The third moment about the mean is called the skewness or assymmetry and is a measure of the symmetry of the distribution function. For symmetrical normalised data the assymmetry is zero. The normal distribution is an example of a symmetrical distribution function. The fourth moment about the mean is called the peakedness or kurtosis and is a measure of the 'height' or peak of the distribution function. For normalised data the normal distribution function has a kurtosis of three. The values of 0 and 3 respectively for the assymmetry and kurtosis of the normal distribution may be used to test the 'normality' of an empirical distribution. Tables of significance for these parameters are given by PEARSON and HARTLEY (1954). Pearsons chi square test can also be used to test the 'fit' of an empirical distribution to the theoretical or a suggested function. Many statisticians prefer the chi square test to the use of moments for the deduction of distribution function. If a histogram of the empirical data is plotted so that the observations fall into r categories then the theoretical number of observations in each category may be deduced from the distribution function f(x). It should be arranged that the theoretical frequency in each category is at least five. To compare the theoretical frequencies e_i with the observed frequencies n_i compute :-

$$\chi^2 = \sum_{i=1}^{r} ((n_i - e_i)/e_i)$$

If the computed chi squared exceeds the value $\chi^2_{a,r-1-g}$ for r -1 -g degrees of freedom, where a is the significance level for the null hypothesis. g = 2 if the mean and standard deviation are used to compute the distribution function. Tables of significance for chi squated are given by PEARSON and HARTLEY (1954).

Table A2.1 shows the tests applied to some data on greywackes, after ONDRICK and GRIFFITHS (1969).

2.2 CORRELATION AND REGRESSION

In linear regression analysis it is assumed that a variable y is a function of some independent variable x, thus :-

$$y = f(x) = a + bx \qquad (5)$$

In polynomial regression y is assumed to be a polynomial function of x, that is :-

$$y = f(x^n) = a + b_1x + b_2x^2 + \ldots b_nx^n \qquad (6)$$

In multiple regression the assumption made is that the variable y is a function of a series of independent variables, thus :-

$$y = f(x_1,x_2,\ldots x_n) = a + b_1x_1 + b_2x_2 \ldots b_nx_n \qquad (7)$$

In all cases if we let y be the estimate of y given by equations (5), (6), or (7), then the error in the estimate of y, e_y, may be written :-

$$e_y = y - y' \qquad (8)$$

If (5), (6), and (7) are regression lines then e_y^2 has been minimised in the determination of the constants.

The solution to (7) is not, in fact, a line but a solid with a representation in n+1 dimensions in vector space. Minimisation of e_y^2 for r observations to give n+1 constants proceeds as follows, taking the simple case of equation (5) :-

$$\sum e_{y_i}^2 = \sum (y_i - bx_i - a)^2 \qquad (9)$$

Where the sums are over i = 1,r.

$\sqrt{\sum e_{y_i}^2 /(r - 2)}$ is called the standard error of estimation. Differentiation of (9) with respect to a and b and equilibration of the results to zero for the minimum gives following pair of equations :-

$$(\sum x_i)a + (\sum x_i^2)b = \sum x_i y_i \qquad (10)$$

$$ra + (\sum x_i)b = \sum y_i \qquad (11)$$

(10) and (11) may be combined in matrix form to give :-

$$\begin{bmatrix} r & \sum x_i \\ \sum x_i & \sum x_i^2 \end{bmatrix} \times \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} \sum y_i \\ \sum y_i x_i \end{bmatrix} \qquad (12)$$

Similarly, the solution of (7) as a regression equation may be written :-

$$\begin{bmatrix} r & \sum x_{1i} & \sum x_{2i} & \cdots \sum x_{ni} \\ \sum x_{1i} & \sum x_{1i}x_{1i} & \sum x_{2i}x_{1i} & \sum x_{ni}x_{1i} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \sum x_{ni} & \sum x_{1i}x_{ni} & \sum x_{2i}x_{ni} & \sum x_{ni}x_{ni} \end{bmatrix} \times \begin{bmatrix} a \\ b_1 \\ \cdot \\ \cdot \\ b_n \end{bmatrix} = \begin{bmatrix} \sum y_i \\ \sum y_i x_{1i} \\ \cdot \\ \cdot \\ \sum y_i x_{ni} \end{bmatrix} \qquad (13)$$

The substitution $x_i = x^i$ yields the regression solution of (6). The X-ray fluorescence analytical results require the application of all three regressions (Appendix I) and the computer programmes to perform the solutions are given in Appendix III.

The relationship between two variables may be expressed in several ways :-

(a) If y is a variable dependent on x and x is an independent variable then the minimisation of AB^2 in Fig. A2.2 gives the y on x regression line.

(b) If x is the dependent variable then minimisation of CD^2 gives the x on y regression line. Fig. A2.1 shows the relationship between the y on x and x on y regression lines.

(c) If neither x nor y are considered to be the dependent variable then minimisation of EF^2 in Fig. A2.2 gives the major axis regression line. Minimisation of the areas of triangles such as GHI gives the reduced major axis regression line. The reduced major axis line is given by :-

$$y = \frac{s_y}{s_x} x + k \qquad (14)$$

Where s_y and s_x are the standard deviations of x and y and k is the intercept constant derived by subsitution of the means $\bar{x}$ and $\bar{y}$ into (14).

In Fig. A2.1 the <u>correlation coefficient</u> r was defined. The equation for the correlation coefficient may be written :-

$$r_{xy} = \text{covariance}\ _{xy}/(\text{variance}_x \times \text{variance}_y)^{\frac{1}{2}} \qquad (15)$$

Where the covariance of x and y is defined as the sum of the cross products of the deviations from the respective means for each observation of x and y, divided by the number of observations. r_{xy} is precisely called the <u>product moment correlation coefficient</u>.

Other correlation coefficients can be defined and one particularly useful in geological data processing is <u>Spearmans rank correlation coefficient</u>. In geological data the case commonly arises when it is required that a measure of the correlation between two variables is required but one or both of the variables have no numeric value but do have a specific order. For example, variables like stratigraphic position, relative age, and rate of deposition may be evaluated only in terms of order. In such cases Spearman's rank correlation coefficient is a valuable statistic. One variable is ordered and is designated a series of rising integers. The other variable is rank so that the highest value has the rank 1, the next highest 2, and so on. The differences between order and rank are calculated and the sum of their squares (d_i^2) is computed. The correlation R is then given by :-

$$R = 1 - \frac{6 \sum_{i=1}^{n} d_i^2}{(n^3 - n)} \qquad (16)$$

Table A2.2 shows the statistic applied to the data of NICHOLLS and LORING (1962) to show a significant increase in the Fe_2O_3 content down the Bersham cyclothem.

EISENHART (1935) indicates two common pitfalls in the application of correlation analysis :-

(a) Use of percentages prevents the consideration of sample size and invalidates any comparison between sample correlation coefficients.

(b) The correlation coefficient is only applicable to quantitative characteristics with real ordering.

Another pitfall pointed out by COLLINS, RUSSEL, and FARQUEHAR (1953) is :-

(c) Extrapolation of linear regression lines beyond the range of the data points.

CHAYES (1960) points out a problem especially important in the use of correlations between variables of fixed sum, for example chemical analyses, :-

(d) Correlations between variables of constant sum must be treated with care since there is an inherent negative correlation as a result of the constant sum.

CHAYES and KRUSKAL (1966) have suggested a possible solution to the constant sum problem and MIESCH (1969) has suggested the subtraction of the null values, derived from CHAYES and KRUSKAL (1966), from correlations between variables of constant sum prior to more detailed statistical analysis.

EISENHART (1939) has pointed out that in multiple regression analysis :-

(e) If the values of x in equation (7) are chosen, that is y is the independent variable and the x's are a series of dependent variables, then the least squares minimisation is meaningless.

2.3 FACTOR ANALYSIS AND CLUSTER ANALYSIS

The principal aim of factor analysis is to reduce an observed set of relationships between many variables to a simpler set of relationships among fewer variables or <u>factors</u>. The associations between pairs of variables are usually measured by the correlation coefficient, however, any similar statistic may be used. Two techniques are commonly used to assess the associations between variables :-

(a) The Q mode technique, which correlates two individual samples on the basis of, usually a large number of, measured variables.

(b) The R mode technique, which correlates pairs of variables for a large number of samples.

Table A2.3 illustrates the difference between the two techniques. The Q-mode technique has been widely used in palaeontology for elucidating the factors defining and distinguishing particular species. R-mode factor analysis has also been applied to studies in palaeontology and sedimentology and more recently applications to the field of geochemistry have been made. SPENCER (1966) applied factor analysis, the R-mode technique, to the elucidation of the factors affecting the distributions of elements in a Silurian graptolite band. This study was made on a very small sample and only orthogonal factors were investigated. CAMERON (1967) applies the R-mode technique to a large sample of dolomitic reef limestones and the study includes the discussion of correlated factors. SPENCER et al. (1968) apply the same technique to some shallow water deposits and discuss the use of a factor analytical model as a regression. Cluster analysis, a less mathematical and more easily applied multivariate technique, does not seem to have been applied to the field of geochemistry to the writer's knowledge.

Cluster analysis is perhaps the fastest and most easily applied simplification of data for a series of intercorrelated variables yet it is notable for its absence from the literature of geochemical interpretation. CATTELL (1944) and TRYON (1939) give details of the method of cluster analysis which simply involves the extraction of intercorrelated groups or <u>clusters</u> from the correlation matrix. The term factor is reserved for the more rigorous vector analysis to be described later. CATTELL (1944) considers the method superficial by comparison to the vector analysis. Cluster analysis however does have the outstanding advantage over factor analysis in that its results are directly comparable from one study to the next. In factor analysis this is virtually impossible. A cluster is defined as a group of intercorrelated variables such that the correlations between all possible pairs of that group are greater than or equal to some arbitarily selected level of correlation. MILLER and KAHN (1962) indicate that for many problems in geology cluster analysis may be prefered because :-

(1) The research worker is at all times in close touch with his original variables.

(2) The clusters are more easily and simply interpreted.

If the correlation between two variables is represented by, say, unit vectors then the correlation coefficient is equal to the cosine of the angle between the two vectors. Factors are extracted from the correlation matrix by a series of matrix and vector operations. The principal component solution is obtained by extraction of eigenvalues from the correlation matrix. This is a standard mathematical technique. The principal component solution is a solution where the maximum possible fraction of the total variance of the data is accounted for by the first factor, the maximum of the remaining variance on the second factor and so on. The variance of any variable is made up of variance due to the variation of other variables and variance due to error or variation of variables not measured. The former variance is called the communality. If communalities instead of unities are entered in the diagonals of the correlation matrix and factors extracted then the resultant solution is called a principal factor solution. Fig. A2.2 shows the representation of correlation when communalities are used.

It can be seen that the use of communalities in no way affects the value of the correlation coefficient but does affect the position of the variables in vector space. From the principal component or principal factor solution a rotation of the factor axes has been devised by KAISER (1958). The varimax rotation is an orthogonal rotation, that is all pairs of factor axes remain orthogonal during the rotation. The solution arrived at by varimax rotation using the varimax criterion of KAISER (1958) is a 'best fit' of the factor axes to the variables in vector space. In comparison with the principal component solution then, the variables are closer to the factor axes. Factor loadings are the coordinates of the variables relative to the factor axes. Thus in the varimax solution, factor ladings tend to 1 or 0. It is difficult to assign physical significance to principal factors for several reasons (CATTELL (1965)). However, having determined the dimension of vector space, rotation of factor axes in a non-orthogonal sense may be made. If this rotation is performed so that the axes correspond to dominant clusters of variables interpretation is simplified since each cluster is identified with a particular factor. HARMAN (1960) describes many methods by which such oblique rotation may be made. The promax rotation of HENDRICKSON and WHITE (1964) was used to perform the rotation and the parameter kmin which may be mentioned describes the degree of permitted obliqueness. Fig. A2.3 illustrates the differences between the three types of solution described, for the six variables A, B, C, D, E, and F in two dimensional space. The loadings of the variable D are illustrated. A measure of the effects of the various factors on a particular sample, in the case of the R-mode technique, or on a variable, in the case of the Q-mode technique, may be obtained as <u>factor scores</u>. They were computed by the short method described by HARMAN (1960).

If we let a_{kj} be the loading of the j^{th} variable on the k^{th} factor, for an R mode analysis, and z_{ij} be the value of the j^{th} variable on the i^{th} sample, and F_{ik} be the value of the k^{th} factor score on the i^{th} sample, then we may write :-

$$z_{ij} = a_{1j}F_{i1} + a_{2j}F_{i2} + \ldots\ldots + a_{mj}F_{im} + a_jU_{ij} \qquad (17)$$

Where m is the total number of common factors and U is the specific factor for a particular variable. It can be seen that equation (7) and (17) are similar and the factor pattern of (17) may be treated as a multiple regression where the a's are the coefficients, the z's are the dependent variables and the F's are the independent variables. If the factors can be interpreted in physical terms then it may be possible to estimate factor scores and hence the value of variables. SPENCER et al. (1968) showed that a knowledge of the mineralogical composition, pH, and median grain size, for samples could provide a very good approximation for the chemical composition of a sample for both major and trace elements.

2.31 EXAMPLE OF THE USE OF CLUSTER ANALYSIS

Cluster analysis was applied to the interpretation of the chromite data of ENGIN and HIRST (1970). The data consists of 62 analyses of chromites for the following 12 elements :- Cr, Al, V, Ti, Si, Fe, Mg, Ca, Cu, Ni, Zn, and Mn. CATTELL (1944) lists four methods of extracting clusters from the correlation coefficient matrix :-

(1) The Ramifying Linkage method.

This method is the simplest and proceeds as follows:- The first step is to write out the linkages (the correlations greater than some arbitary specified level) for each variable on a separate card. Thus for the chromite correlation matrix shown in Table A2.4 the first card would show :

Cr links with Al, V, Fe, Zn, Mn.

One now takes up the card for Al and inspects it for linkages with variables to the right of Al on the Cr card :

Al links with V, Ni, Zn, Mn, (Cr)

V is common to both lists so one proceeds to the card to V where the list contains :

V links with Ti, Fe, Zn, Mn.(Cr, Al)

The variable Zn is common to the three lists and so the Zn card is selected revealing that :

Zn links with Mn.(Cr,Al, V, Fe)

Mn appears on all four cards and the cluster Cr - Al - V - Zn - Mn. has been extracted. One now begins with Al and repeats the process until all the possibilities have been exhausted.

(2) The Matrix diagonal method.

Althought the Ramifying Linkage method is simple, when the correlation matrix is large the number of linkages makes the investigation of each linkage very time consuming. As in the previous method some arbitary level of significance is selected for a linkage. The linkages may be further graded on the basis of the size of the correlation. The object of the Matrix Diagonal method is to manipulate the order of the variables in the matrix so that all linkage correlations lie as near as possible to the matrix diagonal. This method has no simple repetitive prescription to bring about solution and trial and error methods must be adopted. Furthermore it is incapable of dealing with situations such as three variables each entering three distinct clusters.

(3) The Correlation Profile method. (Tryons method).

This method is fully described by TRYON (1939) and consists of "correlating the correlations". That is the variables of a cluster must have their columns (or rows) of correlation coefficients in the matrix positively correlating, above agreed figure. The higher the level of intercorrelation the more distinct is the cluster. The method does provide added information about the clusters extracted however it is no more rapid than the two previous methods.

(4) The Approximate Delimitation method.

This method provides a short cut to an approximate extraction of clusters from large matrices. The procedure is as follows :

(a) Single linkage lists are prepared as in method (1)

(b) Each list is systematically paired with all other lists and whenever the two variables have two or more common linkages, the pair is recorded on a new card. If the second member of the pair appears on the single linkage list for the first variable then it is underlined on the new card. Each underlined variable on the new card is certain to be a member of at least a triad and the cards are called triangular linkage lists.

(c) The triangular linkage lists are less numerous than the single lists. The next step aims to bring together larger clusters. Systematic matching of triangular linkage lists enables those with essentially similar members to be brought together in approximate cluster lists.

(d) Finally each approximate cluster list is tested by reference to the original single linkage lists or the correlation matrix.

It is important that any cluster search method be flexible and any variable which is just excluded from a cluster on the basis of one correlation in, say, four failing at some arbitary level may be included. The clusters extracted from the chromite data by method (1) were :-

(a) Cr - Al - V - Zn - Mn
(b) V - Ti
(c) Si - Mg
(d) Mg - Ni
(e) Cr - V - Fe - Zn - Mn
(f) Ca
(g) Ni - Al
(h) Cu

Clusters (a) and (e) could be merged into one and (c), (d), and (g) are very closely related. Fig. A2.5 shows the relationships between clusters and variables by means of a Venn diagram.

The interpretation of the clusters is broadly in agreement with the interpretation placed on the data by ENGIN and HIRST (1970). The clusters may be split into two groups for interpretation :-

(i) Clusters which are a result of variations in the crystal chemistry of the chromites. (a, b, e)

(ii) Clusters which are a result of impurities. (c, d, f, g, h).

The clusters are interpreted as follows :-

(a), (b), and (e) are interpreted in terms of variations in the chromites. The two large clusters (a) and (e) show that as Cr decreases with differentiation Al, Fe, Zn, Mn, and V, show an increase. The splitting off of Al and Fe from the main group is thought to reflect the different sites the two major substituents enter. The V - Ti cluster is interpreted as Ti entering the chromite lattice for V.

(c), (d), (f), (g), (h), and (i) are interpreted in terms of impurities. The Al - Ni cluster and the Ni - Mg cluster are interpreted as a chlorite impurity and the Ni - Mg and Mg - Si clusters are thought to reflect the presence of serpentine impurities. The independence of Ca is thought to reflect tremolite impurity and the non-correlation of Ca with Si is due to the minor nature of tremilite compared to serpentine as an impurity. The independence of Cu reflects the presence of chalcopyrite as a sulphide impurity. The interpretation of the clusters is indicated in Fig. A2.5.

2.32 EXAMPLE OF THE APPLICATION OF R MODE FACTOR ANALYSIS

Analyses of some 32 samples of phosphate bearing strata from Jordan for 21 chemical variables were used to demonstrate the application of R - mode factor analysis. The mineralogy and petrology of the samples and details of their localities and stratigraphical positions are given by SAADI (1969). The data was analysed, using the program shown in Appendix III- Computer programmes, and a principal component, varimax, and four promax oblique solutions, together with the six associated sets of factor scores, were obtained in 54 seconds on the N.U.M.A.C. IBM 360/67 computer. Eight factors, representing some 93.4 percent of the total variance of the data, were extracted. It is evident that the bulk of the variance (55.2 percent) is explained in two factors (See Table A2.5). On passing from the varimax to the promax solution it can be seen from Tables A2.5 and A2.6 that the minor loadings are removed from factors one, two and five leaving only a single loading on each of these factors. Factor three becomes a bipolar factor with only two opposed loadings, having lost some lesser loadings. Factor four loses one minor loading and the H_2O^- loading is considerably reduced. Factor six is very stable and remains virtually unchanged. Factor seven loses most of its negative loadings and become essentially homopolar, C and Mn loadings are lost and the Ba loading is reduced. Factor eight loses loading for Si, Ca, Na,and Cl, and the loading for Mg is reduced. Most of the strong loadings are increased from varimax to promax. The eight factors extracted may be summarised as follows :-

1. Anionic adsorption.
2. Oxidation potential.
3. Silica precipitation.
4. Residual pore water.
5. Sulphate precipitation.
6. Carbonate precipitation. (Supply of shelf sea water.)
7. Supply of phosphate in solution.
8. Detrital clay supply.

Factor one - Anionic adsorption.

Factor one is a minor factor accounting uniquely for a large part of the variance of Cl. The loading is positive. The factor has significant correlations with factors three and seven, the corrlations being negative, and factor one also has a significant positive correlation with factor eight. These correlations suggest that the factor is related to detrital clay but opposed to the supply of organic debris. It is tentatively suggested that Cl is adsorbed on mineral surfaces and essentially clay surfaces. However, the analysis of Cl by X.R.F. is not highly sensitive and the nature of the method involves the analysis of a thin surface film of sample. Cl is one of the elements most likely to be transferred to the samples by repeated handling. The uniqueness of the Cl factor may be a function of such random analytical error. Another source of error likely to affect Cl lies in the method of sample preparation for X.R.F. Pellets of powder are prepared by use of a hydraulic ram and under pressure Cl is likely to be mobilised and become segragated on the surface of the pellets, however, the control represented by factor one may be anionic adsorption but may equally well be an expression of analytical error.

Factor two - Oxidation potential.

Like factor one, this factor has a single positive loading, in this case for C. However, unlike factor one, the analytical determination of C is thought to be subject to errors an order of magnitude below the observed variance and the data is considered to show a 'real' variation subject to geochemical control. The preservation of C in sedimentary rocks is a function of two processes :-

1. Rate of burial. C may be preserved in sediments,

even if they have accumulated under oxidising conditions, if the rate of burial exceeds the rate of oxidation.

2. Oxidation potential. C may be preserved in slowly accumulated sediments if the conditions are sufficiently reducing to prevent the destruction of carbonaceous material by oxidation.

The stratigraphical evidence points to a condensed sequence and hence relatively slow depostion for the phosphate bearing strata. It is therefore thought that under such conditions, the main control of carbon variation is oxidation potential. The correlation with factor seven shows supply of organic debris and oxidation potential to be related. It is thought that the accumulation of carbonaceous and phosphatic debris on the floor of the basin of deposition tended to create a local zone of slightly acid and reducing conditions. Under such conditions phosphate may dissolve or be precipitated and nodular accretion may be favoured if pH were sufficiently high for precipitation to occur.

Factor three - Silica precipitation.

Factor three is a bipolar factor with a high positive loading for Si and an opposing negative loading for Ba. The sediments analysed are essentially clay-carbonate-phosphate-silica assemblages. Ba is commonly associated with clays both as a structural replacement for K and as an adsorbed cation. Phosphate, especially bone debris, is known to have a vast surface area and Ba is the type of large cation liable to be adsorbed. In both phosphate and carbonate Ba can structurally replace Ca withouth a great deal of rearrangement. It can thus be seen that silica is the only phase present in significant amounts which positively inhibts the incorporation of Ba into the sediments. The bipolar nature of factor three is thought to be a function of this inhibition. Factor three has been interpreted as a silica precipitation factor. It is thought that silica has been biogenically precipitated by organisms like radiolaria, diatoms, and sponges since the saturation of sea water with silica is very unlikely. The majority of the silica in the rocks is either biogenically precipitated or detrital. Factor three shows a negative correlation with factor eight, the detrital factor, and this, owing to the negative loading of Si on factor three, indicates that the two factors behave sympathetically. Two interpretations of this correlation are possible :-

1. The silica is partially detrital and therefore shows a correlation with factor eight.

2. The correlation is a function of the slow deposition of the siliceous sediments and their relative proximity to shoreline, so permitting the incorporation of detritus.

If 1 were the case it is thought that a Si loading on factor eight would be appropriate. This is not observed in the promax solution and 2 is thought to be the more realistic interpretation. The correlation with factor seven shows the diluent action of silica relative to phosphate when the silica acts as a cement.

Factor four - Residual pore water.

Factor four shows high positive loadings for Na and Mg and lesser loadings of the same sense for Cl and H_2O^-. Mn and F have low negative loadings. The Mn loading is thought to be insignificant and its dismissal as such demonstrates one of the inherent dangers in the use of factor analysis. On studying a factor pattern one tends to assume that factor loadings are significant above a certain level for all variables. This is not true. A factor loading derived from a principal component solution includes possible error variance. The error variance may be assumed to be at least the size of the analytical precision. The square of the factor loading is the fraction of the total variance explained by a particular factor. For Mn all the determined values are close to the detection limit and the error variance is high. Loadings of less than 0.50 are thought to be insignificant for this element. Having dismissed the Mn loading, all the other loadings are for elements commonly found in, and characteristic of, sea water and pore water. Factor four is therefore interpreted as a function of trapped pore water and more specifically of porosity or void ratios. The correlations with factor eight indicates an increase in porosity with detrital content and the factor scores for factor four are in reasonable agreement with estimate porosities on the basis of grain size and values for various rock types quoted in the literature. F is thought to have a negative loading because of its tendency to be incorporated in minerals, probably phosphate and clay, at the expence of H_2O^- during diagenesis.

Factor five - Sulphate precipitation.

Factor five is the third unique factor and has a single negative loading for SO_3. SO_3 like Mn has a small variance relative to the precision and the error variance may be large. The correlation with factor seven may be interpreted as $(SO_4)^{2-}$ for $(PO_4)^{3-}$ in the apatite lattice. This interpretation is supported by the mineral chemistry and SAADI (1969) indicated that the refractive index of the phosphate mineral was related to SO_3 content. If this were truly the case a loading of SO_3 on factor eight would be expected. Two conclusions may be reached from this situation :-

1. SO_3 occurs as a separate mineral phase intimately associated with the phosphate.

2. The SO_3 is included in the phosphate lattice secondarily.

The non-detection of a sulphate phase in the separates seems to exclude 1, and 2 is thought to be the better interpretation of the available data. Part of the unique variation of SO_3 is undoubtedly due to a sulphate phase detected in the whole rocks. The low variance and low precision of the SO_3 analyses prevent the extraction of any more specific conclusions.

Factor six - Carbonate precipitation.

Factor six has high positive loadings for Ca and CO_2 and a lesser positive loadin for H_2O^+. Small negative loadings for Si and F are also present. Factor six is unique amongst the eight factors in that it shows no correlations, that is, it is almost a totally independent factor. Factor six is thought to represent normal shelf sea water of slightly oxidising and alkaline character from which sedimentation of biogenic and precipitated shelf limestones can occur. In such an environment phosphate sedimentation will be overwhelmed by carbonate deposition. A relatively small fall in pH will result in a tendency for calcite to dissolve instead of precipitate. The loadings of Si and F may be a function of pH, Si tending to be less soluble at low pH and F tending to extend the stability of phosphate in sea water by reducing its solubility. Silica and carbonate are the major cementing materials present in the phosphates and the good preservation of phosphatic fossils in the siliceous material may indicate that the two phases have similar stability fields. The tendency for more rounded phosphate pellets to occur in the carbonate cemented beds may indicate shallower water origin for these deposits relative to the siliceous phosphates. If this is the case then the absence of detrital material from the limestone and calcareous phosphates can be explained in two ways :-

1. The rate of deposition was high and no time was available for detrital accumulation.

2. Deposition was not necessarily slow but fine detritus was removed by wave action which would also explain the tendency of the phosphate grains to be more rounded.

Both explanations are equally valid and combined with the possibility of variation in detrital supply the situation is complex.

Factor seven - supply of phosphate in solution.

This factor has high positive loadings for P, U, F, Y, and H_2O^+ and lesser positive loadings for Ca, Ba and H_2O^-. Na shows a slight negative loading but is insignificant for this particular element. Supply of phosphate would promote organic activity and thus controls the amount of organic debris produced. The organic debris is mainly phosphate and the Sr, U, Y, and Ba loadings are considered to indicate that these elements replace Ca in the phosphate lattice. The H_2O^+ and F loadings are interpreted as elements present in the 'hydoxyl' position of apatite. The H_2O^- loading is thought to be a function of the huge surface area and adsorptive capacity of bone phosphate or freshly precipitated phosphate. Economic concentrations of phosphate will only accumulate if conditions are such that a flood of carbonate sedimentation is inhibited. It is therefore assumed that a fall in pH in a basin with adequate supply of phosphatic material would promote phosphate concentration, if the rate of detrital supply were small. Factor seven, like factor six, is strongly related to pH but not related to factor six. The interactions between the two factors may be considered in terms of the mixing of two distinct bodies of water. Factor six represents normal, oxygenated, slightly alkaline, shelf-sea water and factor seven oxygen free, slightly acid, phosphatic, siliceous, upwelling, deep oceanic water. The resulting pH and Eh from the mixing of these waters are the major controls on sedimentation. Since the influence of factor six increases with pH and that of factor seven decreases with pH it is reasonable to suppose that the differences in factor scores from factor six to factor seven will provide a relative estimate of pH for each sample. Table A2.8 shows the derived relative pH values compared with the lithology. The figures quoted for derived pH are believed to be an approximate function of pH though not necessarily a linear one.

Factor eight - Detrital clay.

This factor has high positive loadings for K, Ti, Al, Fe and H_2O^- and lesser positive loadings for Mg and Mn. All these elements are commonly found in clay minerals and the factor scores for factor eight correlate strongly with the estimated total clay based on an average Al/clay ratio of 0.28. The relative abundances of K and Ti are of the expected order relative to Al but the Fe content is high. It is thought that much of the iron was carried into the basin of deposition as iron oxide hydroxide coatings on clay minerals (CARROLL, plotted against estimated total clay, and the log of estimated total clay. The correlation of factor seven with factor eight is explained in terms of proximity to detrital source and the diluent effect of detritus on phosphate. Three factors affect the detrital contents of the sediments ;-

1. Rate of detrital deposition.
2. Rate of chemical and biological precipitation.
3. Proximity to shoreline.

Superimposed on these three controls are the effects of wave and current action in removing 'fines' from the inshore sediments.

Origin and genesis

The detrital fraction of the deposits is well identified by factor eight but accounts for less then five percent of all but three of the samples examined. Thus during phosphate deposition detrital supply was low. The near absence of eroded detritus is even more strongly emphasised when the slow rates of accumulation envisaged for phosphates are considered. The phosphate rich rocks are essentially bioclastic accumulations together with chemical and biogenic precipitates. The abraded nature of the phosphate pellets indicate a fairly high energy environment, especially for the more calcareous deposits. Removal of 'fines' by wave and current action may partially contribute to the absence of detritus but a slow rate of detrital deposition is still essential. The Eh conditions are thought to have varied from slightly reducing, for the deeper water more carbonaceous sediments, to fairly oxidising for the shallow water limestone and phosphate deposits. When pure phosphates accumulated pH was probably slightly lower than for the formation of the calcareous sediments. KRUMBEIN and GARRELS (1952) indicate this should occur but F fixation by phosphate may well extend its stability range at low pH. The siliceous deposits probably also required a low pH to inhibit limestone sedimentation.

KAZAKOV (1937) proposed a theory of upwelling, deep, oceanic, waters for the supply of siliceous, phosphatic, cold, more acid, water. Such upwellings have been recognised by BRONGERSMA - SANDERS (1948). A general account of some Turkish phosphorites, based on this theory, is given by SHELDON (1964). The theory is that water rich in Si and P, dissolved at depth under pressure, promote the growth of a rich phosphatic fauna in the shallow, near surface, oxygenated, shelf zone. Mortality of such a fauna would lead to a zone of decaying organic matter on the sea bed and this in turn would create a shallow water reducing environment. The creation of such an environment explains the black shaleglauconite-phosphorite association. Uranium may be fixed during this phase of deposition. The cherts are poor in carbon and this may indicate shallower water, more oxidising conditions of deposition. Their fairly high detrital content may indicate relative proximity to shoreline or the addition of fine grained detrital material by current action. The more abraded nature of the pellets in the calcareous phosphates may indicate shallower water than the siliceous deposits for their deposition. Fixation of F from sea water may account for the stability of the phosphates during cementation. The limestones are typical shelf sea deposits formed when the pH rose sufficiently to allow a flood of carbonate sedimentation.

Climatic factors may also be involved in stablising the delicate balance of physico-chemical conditions necessary for economic phosphate accumulation. Temperature may well be effective at the surface where oxygen and carbon dioxide may be removed as gases, by evaporation, whereas $(PO_4)^{3-}$ remains and is concentrated. This mechanism may also tend to increase the pH of shallow shelf sea water relative to the already more acidic deep ocean water, which may be made acidic by decay of organic matter on the deep sea floor. STRAKHOV (1962) recognised a correlation between phosphorite deposition and former arid zones. This author indicated that strong trade winds were responsible for deep oceanic upwellings bearing phosphate and that such arid conditions were characterised by high Ca contents in the water thus stimulating both phosphorite and limestone deposition.

KLEMME (1958) gives a tectonic interpretation of the Mediterranean area during the Cretaceous and Eocene. It is apparent that the phosphate deposits of Jordan were formed in a shelf area adjacent to the Afro-Arabian continent. BENTOR (1953) suggests that the equivalent Israeli deposits were laid down in subsiding synclinal basins produced by small scale folding during the Campanian.

BUSHINSKI (1964) suggests that phosphorite deposits may be independent of upwelling zones, at least as a source of phosphate. River water is considered to be the primary source of phosphorus and phosphorites are said to be formed by phosphorus, concentrated in and deposited from, bottom muds. The theories of KAZAKOV (1937) and BUSHINSKI (1964) differ in one important respect; the source of the phosphorus. Both authors are agreed on the importance of biogenic concentration and the shallow depth of phosphorite deposition.

The reconstructions shown in Figs. A2.7, A2.8, and A2.9 are generalised and the influence of phosphorus carried by river water may be underestimated. The low detrital contents of the Jordanian phosphates may well indicate, however, that in this case the influence was small. Phosphorites are deposited through the interaction of three bodies of water. The interaction necessary to produce economic phosphorite is not thought to be unique, indeed it is almost certainly not so, but the balance of physico-chemical conditions is thought to be delicate and therefore rarely sustained. Fig. A2.7 shows the three sources of supply. Fig. A2.8 shows the envisaged pattern of pH and Eh for phosphorite deposition. Fig. A2.9 shows the suggested resultant pattern of sedimentation.

Conclusions

Eight factors were deduced by factor analysis to account for the variation of twenty one chemical variables in thirty two phosphate bearing rocks from Jordan :-

1. Anionic adsorption. A relatively unimportant factor accounting for much of the variance of Cl and also possibly an error factor.

2. Oxidation potential. This factor explains most of the variance of carbon.

3. Silica precipitation. The first of the three important factors. Much of the variance of Ba and Si is explained.

4. Residual pore water. Variations in Na, Mg, Cl, F, H_2O^- are explained in terms of this factor. Mn has a loading which is dismissed as insignificant.

5. Sulphate precipitation. Only the variance of SO_3 is explained by this factor which like factor one may be a function of analytical error.

6. Carbonate precipitation. Another important factor accounting partially, or wholly, for the variances of Ca, CO_2, Si,F, H_2O^+.

7. Supply of phosphate in solution. The third important factor controlling much of the variance of P, Sr, F, Y, H_2O^+, Ca, Ba.

8. Detrital clay. The final factor influencing K, Ti, Al, Fe, H_2O^-, Mn, Mg.

The interaction of the more important factors leads to the construction of a model basin of deposition which adequately explains the observed chemical data within the tectonic framework interpreted by other authors. Three essential criteria must be satisfied for the economic accumulation of phosphate to occur :-

1. Detrital supply must be very low to prevent arenaceous and argillaceous sedimentation which would dilute any phosphate formed. The slow inflow of water is also essential since strong current action would take any phosphate contained in the river water out into the deep ocean before significant biogenic fixation could occur.

2. The pH must be sufficiently low to inhibit a flood of carbonate sedimentation which, like detrital sedimentation, would dilute any phosphate deposited.

3. Upwelling waters, perhaps fairly rich in Si and P, and probably slightly acid and cold, must be available. Such a current effectively seals the depositional basin to the seaward side and leads to the retention and biogenic assimilation of any phosphorus available. The rich fauna is found in upwelling regions is essential in the fixation of P and the creation of P rich bottom muds.

The abundance of Cretaceous and Eocene phosphorites in the Mediterranean area indicates that during this period conditions favourable to phosphorite deposition prevailed. This is analogous to the deposition of chalk in north-western Europe during the Cretaceous when the appropriate conditions were prevalent. Non-deposition of phosphorites in current that upwelling regions implies that one of the critical conditions is not satisfied just as all shelf seas do not deposit chalk.

The foregoing interpretation is the authors contribution to a joint paper submitted for publication in Ecomomic Geology. T.A.K. Saadi is the co-author, (REEVES and SAADI (1971)).

TABLE A2.1

STATISTICAL TESTS OF THE HYPOTHESES OF NORMALITY AND LOGNORMALITY FOR THE DISTRIBUTIONS OF SIO2, K2O, AND LA IN 119 ANALYSES OF THE RENSELLAER GREYWACKE. (After Ondrick and Griffiths (1969)).

Distribution model										
Normal					Element	Lognormal (e)				
Mean	S.D.	Skew	Kurt	Chi		Mean	S.D.	Skew	Kurt	Chi
70.6	6.67	-0.19*	4.48	13.9*	SiO_2	4.27	0.09	-0.45	3.79	n.q.
2.20	0.98	1.06	5.10	n.q.	K_2O	1.12	0.30	0.01*	3.40*	12.6*
60.2	27.2	1.01	4.34	n.q.	La	4.02	0.44	-0.23*	3.00*	19.0*

n.q. = not quoted.

* indicates values not significantly different from the value theoretically obtained if the hypothesis were true.

TABLE A2.2

APPLICATION OF SPEARMAN'S RANK CORRELATION COEFFICIENT

Sample	BC9	BC8	BC7	BC6	BC5	BC4	BC3	BC2	BC1
% Fe_2O_3	1.69	1.74	1.69	0.60	0.66	0.60	0.12	0.53	0.45
Rank	3	1	2	5	4	6	9	7	8
Order	1	2	3	4	5	6	7	8	9
Difference	2	-1	-1	1	-1	0	2	-1	-1
Difference^2	4	1	1	1	1	0	4	1	1
Depth (ft)	280	275	273	270	265	260	255	250	247

$$\sum d^2 = 14 \quad n = 9$$

$$1 - \frac{6\sum d^2}{n^3 - n} = 1 - \frac{6 \times 14}{729 - 9} = 1 - \frac{7}{60} = 0.883$$

The figure of 0.883 is significant at the 99.9% level. The true product moment correlation of Fe_2O_3 with depth is 0.875 which is also significant at the 99.9% level.

TABLE A2.3

RELATION BETWEEN Q AND R - MODE FACTOR ANALYSIS TECHNIQUES

SAMPLE	VARIABLE 1	VARIABLE 2	VARIABLE 3	.....	VARIABLE m	
1	x_{11}	x_{12}	x_{13}	.....	x_{1m}	Correlation between samples gives Q - mode.
2	x_{21}	x_{22}	x_{23}	.....	x_{2m}	
3	x_{31}	x_{32}	x_{33}	.....	x_{3m}	
.	.	.	.		.	
.	.	.	.		.	
.	.	.	.		.	
n	x_{n1}	x_{n2}	x_{n3}	.....	x_{nm}	
	Correlation between variables gives R - mode.					

TABLE A2.4

CORRELATION MATRIX FOR CHROMITE DATA. (AFTER ENGIN AND HIRST, 1970)

ELEMENT	Cr	Al	V	Si	Ti	Mg	Fe	Ca	Ni	Zn	Cu	Mn
Cr	1.00											
Al	-0.93	1.00										
V	-0.76	0.68	1.00									
Si				1.00								
Ti			-0.60		1.00							
Mg				0.41		1.00						
Fe	-0.62		0.53				1.00					
Ca								1.00				
Ni		0.44				0.51			1.00			
Zn	-0.73	0.57	0.58				0.85			1.00		
Cu											1.00	
Mn	-0.73	0.59	0.47				0.63					1.00

TABLE A2.5

VARIMAX FACTOR MATRIX*.

FACTOR	1	2	3	4	5	6	7	8	COMMUNALITY
SiO_2			-0.76			-0.37		0.28	0.930
Al_2O_3							-0.40	0.88	0.953
Fe_2O_3				0.26				0.91	0.936
P_2O_5							0.92		0.953
CaO						0.73	0.50	-0.29	0.945
SrO					-0.26		0.88		0.948
BaO			0.67				0.57		0.861
MgO		0.26		0.51				0.64	0.910
Na_2O				0.75				0.44	0.888
K_2O							-0.32	0.88	0.948
TiO_2								0.88	0.943
MnO	0.29		-0.27				-0.43	0.69	0.882
SO_3					-0.89		0.32		0.945
F				-0.26		-0.32	0.78		0.942
Cl	0.82			0.28				0.43	0.978
U_3O_8							0.91		0.963
Y_2O_3							0.78		0.939
CO_2						0.92			0.939
C		0.88					0.41		0.976
H_2O^+						0.34	0.84		0.902
H_2O^-				0.38			0.30	0.74	0.920
% VAR.	5.0	5.1	6.8	6.4	5.9	8.9	29.2	26.0	93.4

*Loadings less than 0.25 represent less than 6.25% of the variance of an element and are omitted from the matrix.

TABLE A2.6

PROMAX OBLIQUE MATRIX KMIN = 4.*

FACTOR	1	2	3	4	5	6	7	8
SiO_2			-0.89			-0.31		
Al_2O_3								0.96
Fe_2O_3								1.01
P_2O_5							1.01	
CaO						0.71	0.47	
SrO							0.90	
BaO			0.75				0.38	
MgO				0.47				0.30
Na_2O				0.85			-0.28	
K_2O								0.94
TiO_2								0.95
MnO				-0.30				0.57
SO_3					-0.89			
F				-0.26		-0.32	0.80	
Cl	0.94			0.27				
U_3O_8							0.99	
Y_2O_3							0.70	
CO_2						0.94		
C		0.93						
H_2O^+						0.34	1.01	
H_2O^-				0.29			0.42	0.75

*Loadings less than 0.25 have been omitted.

TABLE A2.7

CORRELATIONS BETWEEN PROMAX OBLIQUE FACTORS KMIN = 4.*

FACTOR	1	2	3	4	5	6	7	8
1	1.00							
2		1.00						
3	-0.33		1.00					
4				1.00				
5					1.00			
6						1.00		
7	-0.40	0.33	0.45		-0.30		1.00	
8	0.55		-0.51	0.40			-0.39	1.00

* Correlations less than 0.25 are omitted.

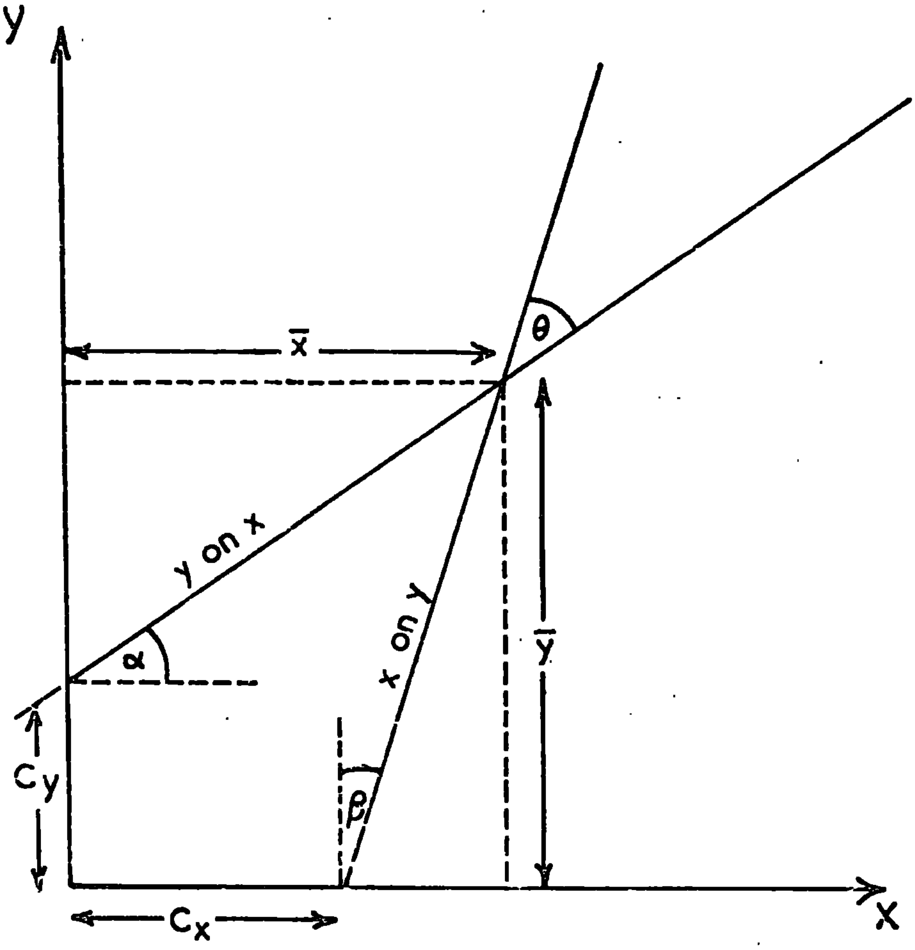
TABLE A2.8

RELATIONSHIP OF LITHOLOGY TO pH DERIVED FROM FACTOR SCORES

Sample	Factor scores		Difference	Lithology
	Factor 6	Factor 7	(pH)*	
56 B	2.11	-1.66	3.77	Limestone
63	1.80	-1.65	3.45	Limestone
53	1.18	-2.24	3.42	Limestone
58	1.46	-1.63	3.09	Limestone, argillaceous
61 B	0.66	-0.72	1.38	Cherty limestone
56 A	0.29	-0.68	0.97	Calcareous chert
37	0.72	0.35	0.37	Calcareous phosphate
62	0.68	0.44	0.24	Calcareous phosphate
40	0.43	0.24	0.19	Calcareous phosphate
59	0.29	0.32	-0.03	Calcareous/Siliceous phos.
49	0.68	0.82	-0.14	Calcareous phosphate
61 A	-2.28	-1.98	-0.30	Chert
50	0.31	0.66	-0.35	Calcareous phosphate
60	-2.51	-2.18	-0.38	Chert
54	0.19	0.62	-0.43	Phosphate
57	0.11	0.56	-0.45	Calcareous/Siliceous phos.
46	0.23	0.74	-0.51	Siliceous phosphate
43	0.13	0.66	-0.53	Siliceous phosphate
55	0.09	0.64	-0.55	Phosphate
41	-0.21	0.44	-0.65	Siliceous phosphate
45	0.01	0.70	-0.69	Siliceous phosphate
52 B	0.06	0.75	-0.69	Phosphate
35	-0.83	-0.08	-0.75	Siliceous phosphate
44	-0.26	0.59	-0.85	Phosphate
52	0.04	0.94	-0.90	Phosphate
66	-0.44	0.50	-0.94	Phosphate
38	-0.31	0.82	-1.13	Phosphate
65	-0.72	0.45	-1.17	Siliceous phosphate
47	-1.24	-0.05	-1.19	Siliceous phosphate
36	-0.30	1.01	-1.31	Phosphate
64	-1.58	-0.17	-1.41	Siliceous phosphate
51	-0.79	0.75	-1.54	Siliceous phosphate

* Relative not absolute estimate.

FIG A2.1 PHYSICAL SIGNIFICANCE OF REGRESSION PARAMETERS



WHERE $y = m_y x + C_y$ $m_y = \tan \alpha$

$x = m_x y + C_x$ $m_x = \tan \beta$

correlation coefficient = $\cos \theta$

FIG. A2·2 VARIOUS METHODS OF FITTING A STRAIGHT LINE TO SCATTERED POINTS

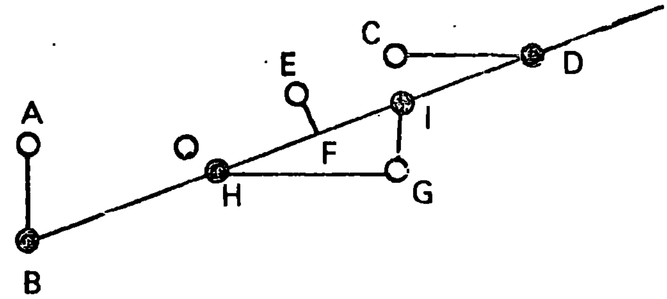
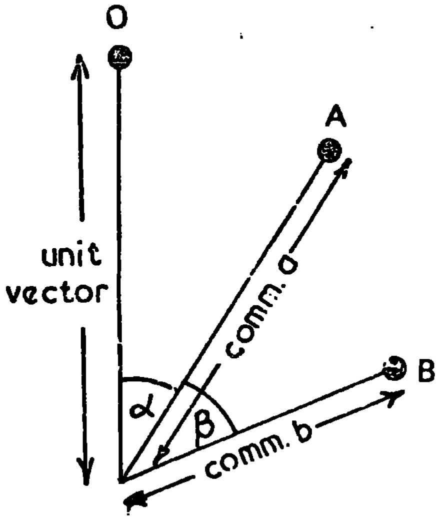


FIG. A2·3 PHYSICAL REPRESENTATION OF CORRELATION AND COMMUNALITY



Let O be a unit vector

comm. a = communality of a

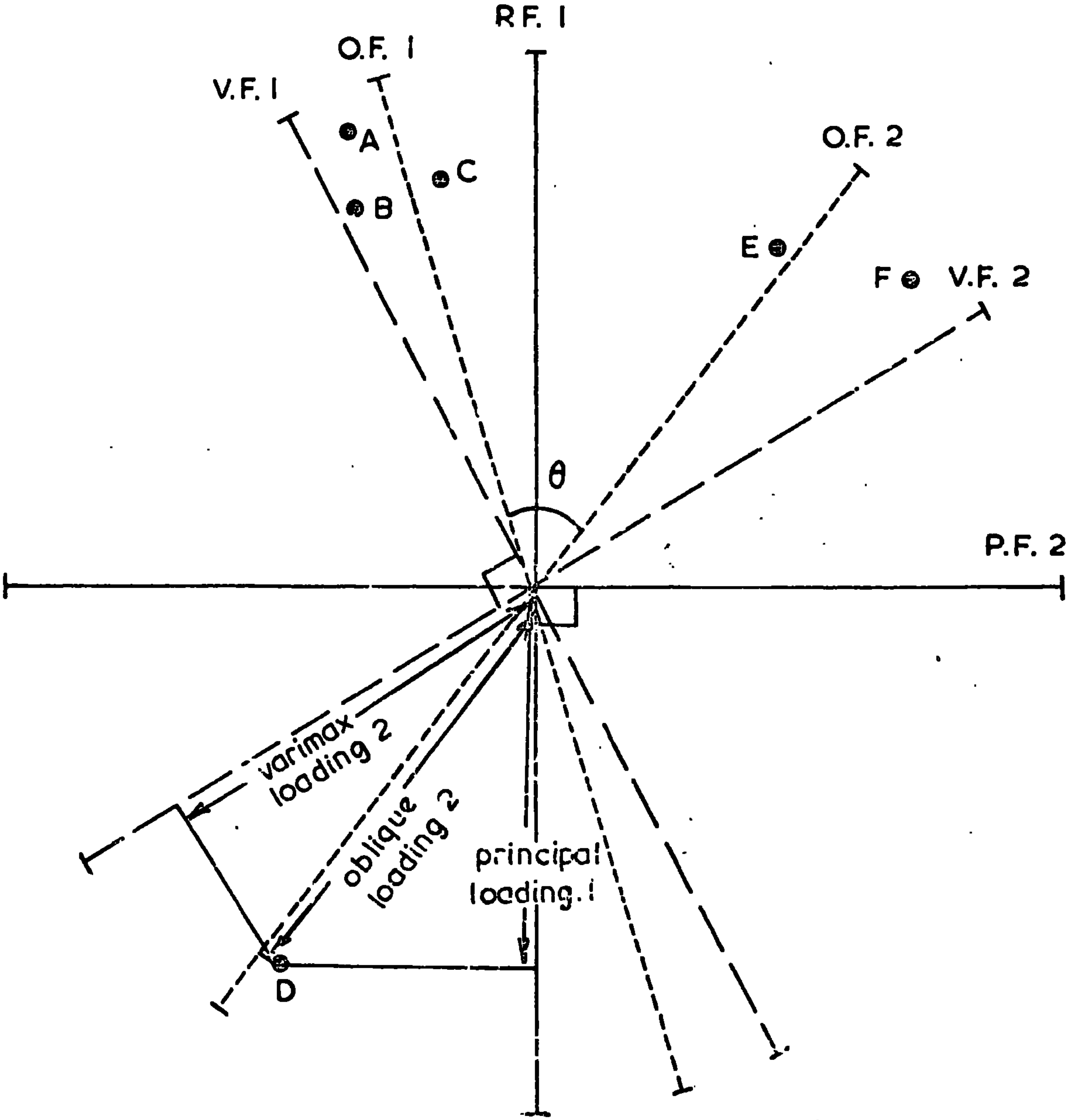
comm. b = communality of b

$r_{AO} = \cos \alpha$

$r_{BO} = \cos (\alpha + \beta)$

$r_{AB} = \cos \beta$

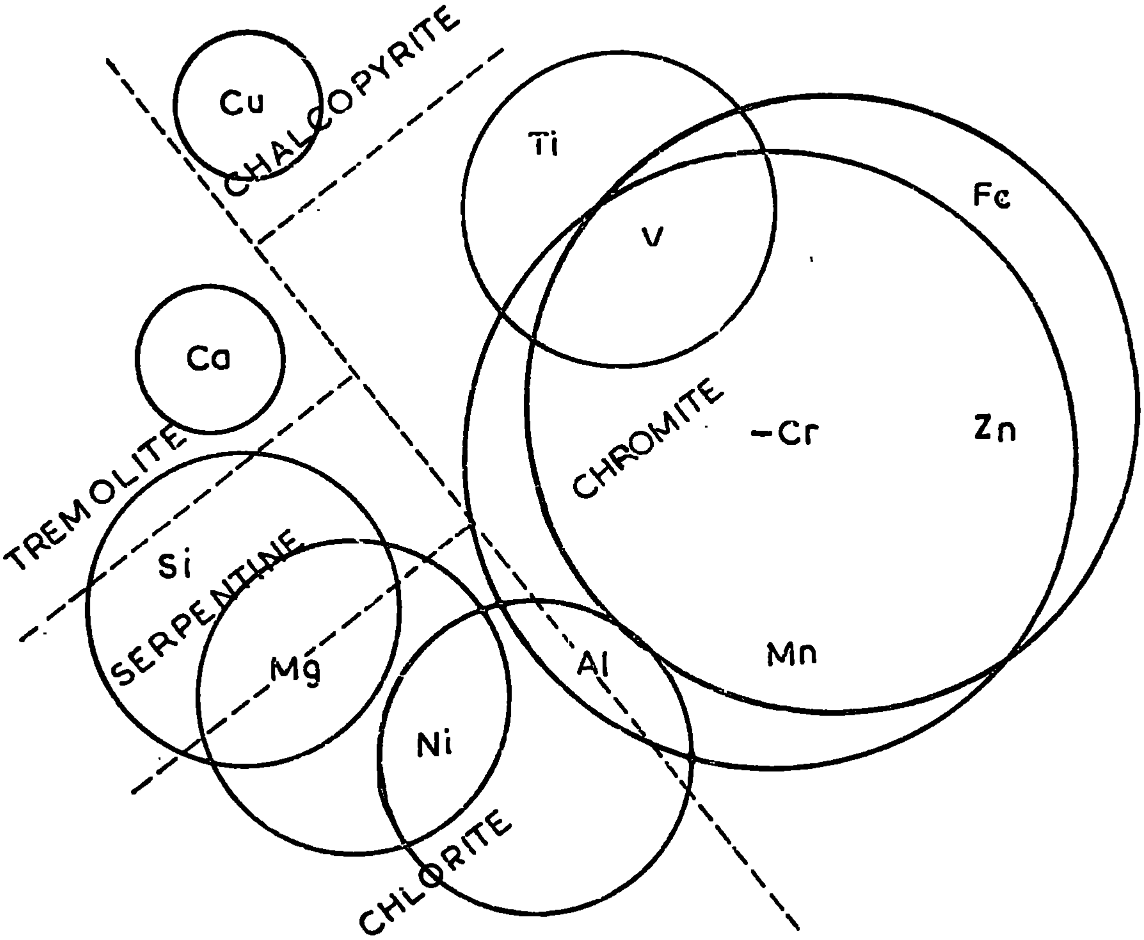
FIG. A2·4 RELATIONSHIPS OF VARIOUS FACTOR AXES DEMONSTRATED IN TWO DIMENSIONS.



Cos θ correlation between oblique factors
P.F. principal factors (orthogonal)
V.F. varimax factors (orthogonal)
O.F. oblique factors

The various loadings of the variable D are illustrated

FIG. A2·5 VENN DIAGRAM SHOWING RELATIONSHIPS BETWEEN VARIABLES AND CLUSTERS IN CHROMITE DATA.



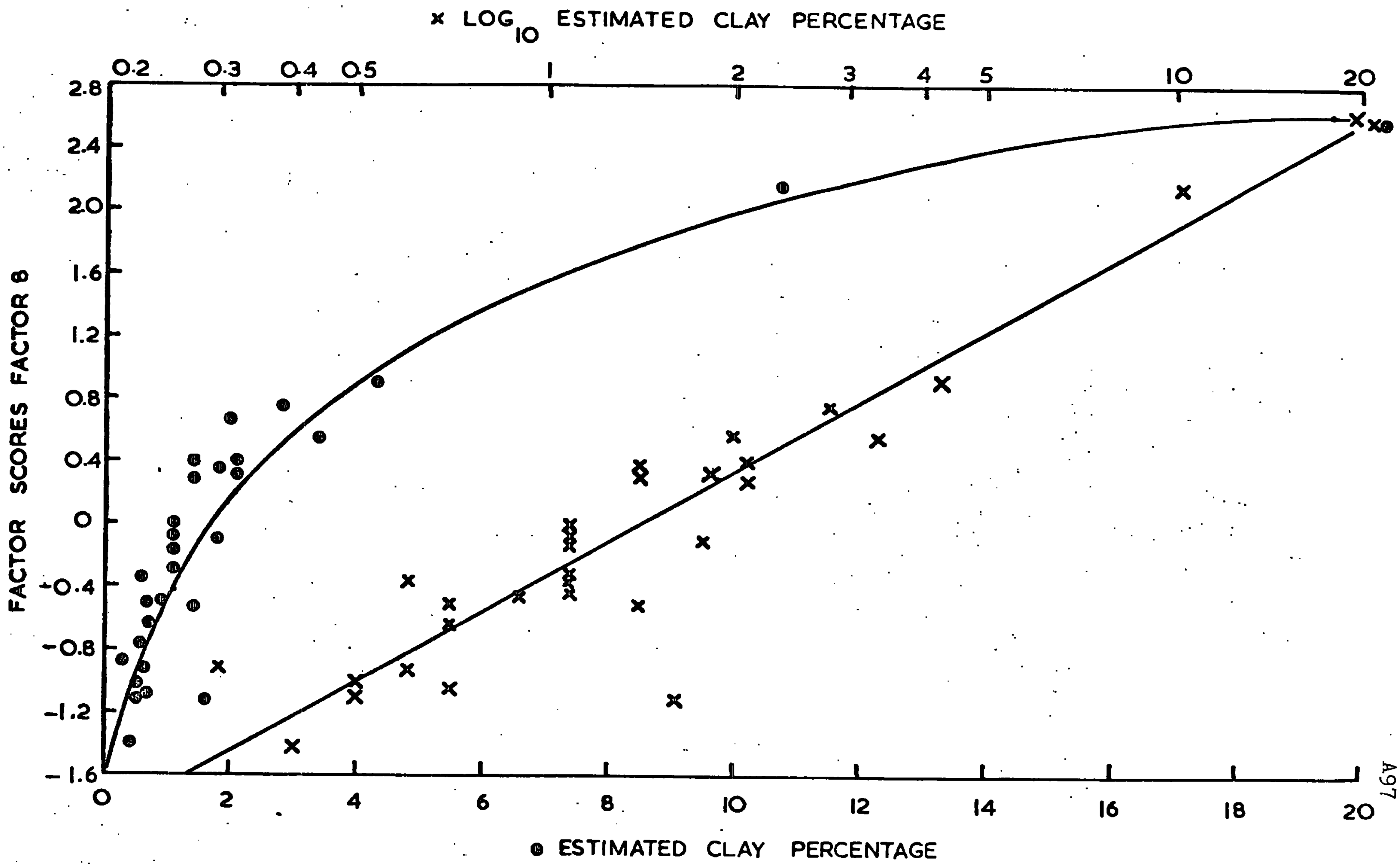


FIG. A2.6 FACTOR 8 FACTOR SCORES V ESTIMATED TOTAL CLAY

FIG. A2·7 SUPPLY TO BASIN OF SEDIMENTATION

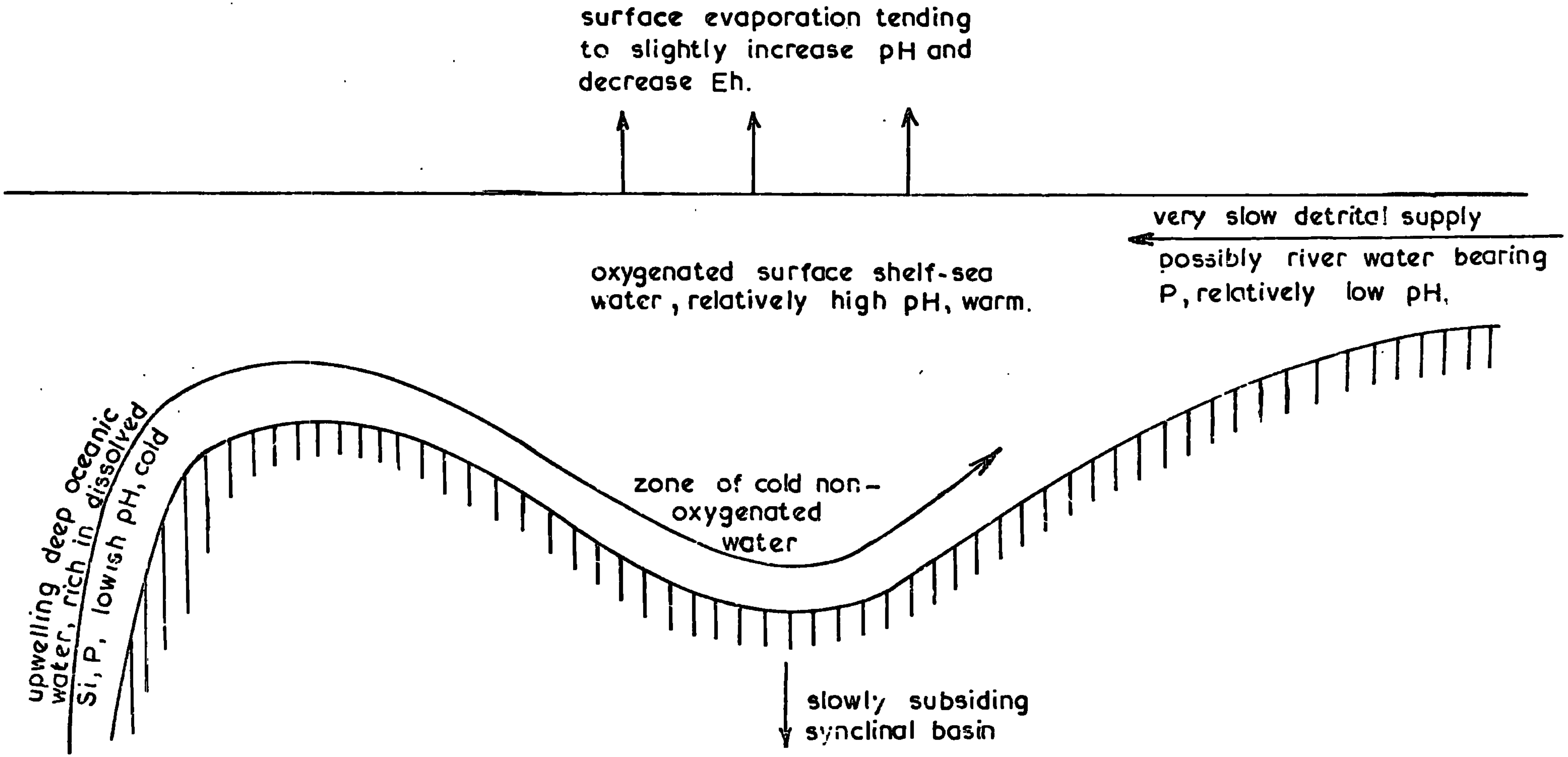


FIG. A2·8 PHYSICO-CHEMICAL CONDITIONS OF DEPOSITION

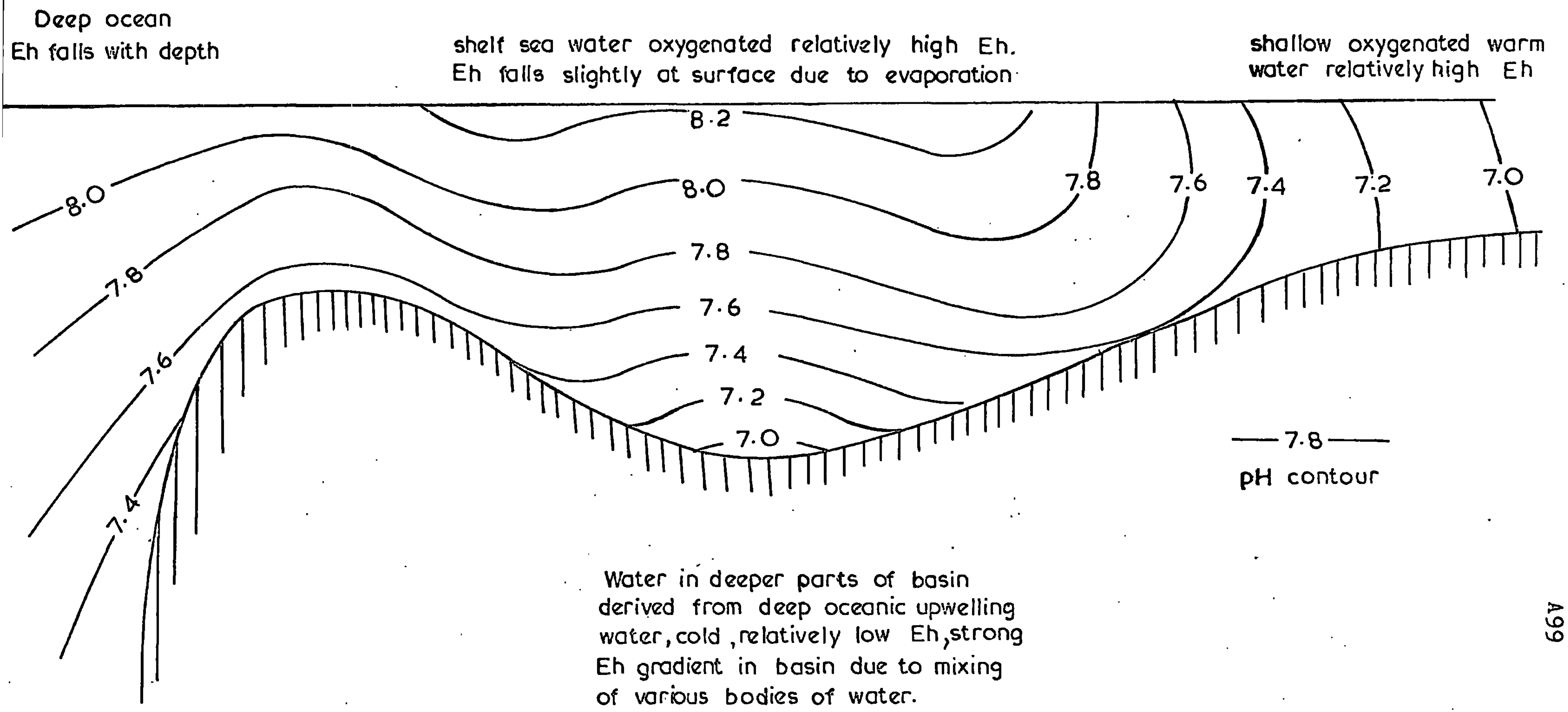
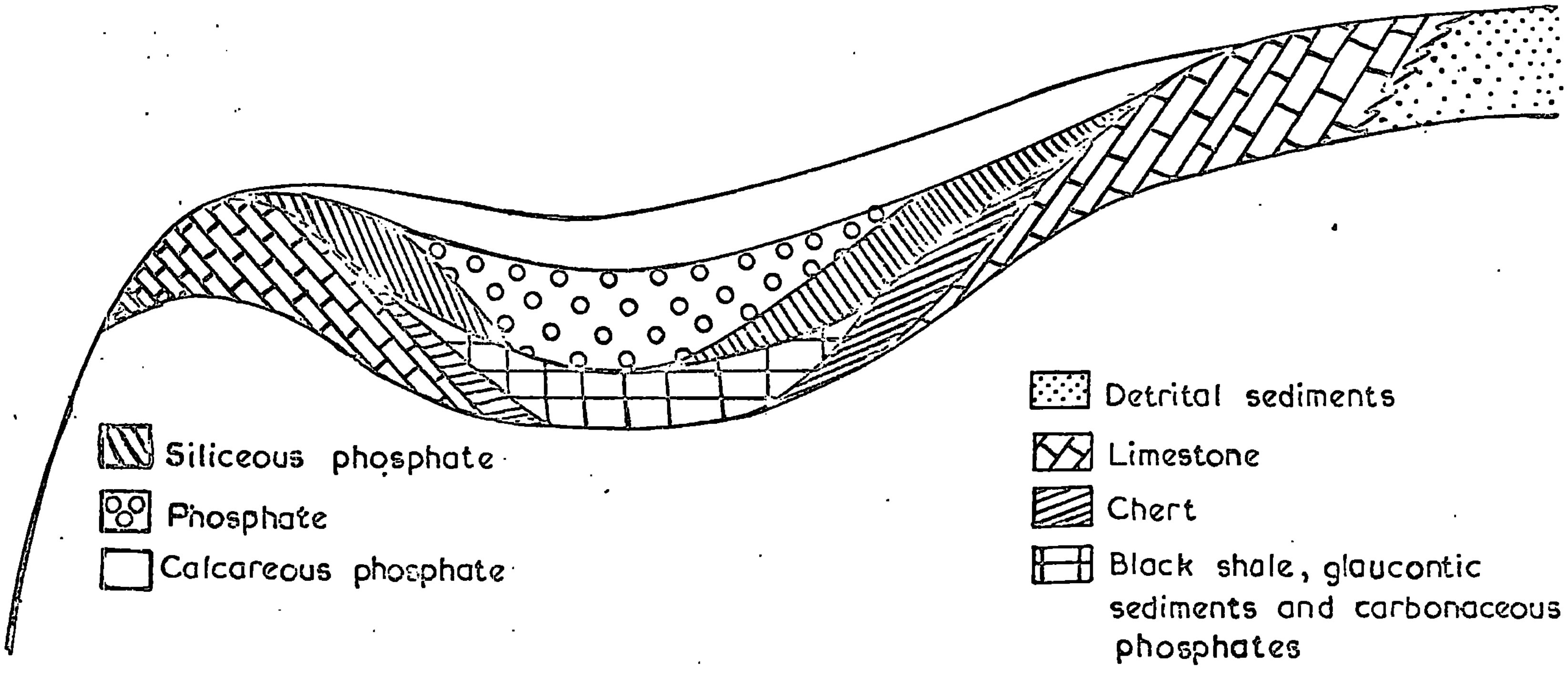


FIG. A2·9 SUGGESTED GENERAL PATTERN OF SEDIMENTATION



2.4 REFERENCES TO APPENDIX II

BENTOR, Y. K., (1953), Relations entre la tectonique et les depots de phosphates dans le Neguev israelien, Internat. Geol. Cong., 19th, Algiers, Comptes rendus, sec. 11, pt. 11, 93 - 101.

BRONGERSMA - SANDERS, M., (1948), The importance of upwelling water to vertebrate paleontology and oil geology, K. Nederlandsche Akad. van Wentensch. afd. Natuurk, Tweede Sect., 45, 112 -

BUSHINSKI, G. I., (1964), On shallow water origin of phosphorite sediments, Internat. Sedimentol. Cong., 6th, Belgium, In Deltaic and shallow water deposits, Ed. Van Straaten.

CAMERON, E. M., (1968), A geochemical profile of the Swans Hills reef, Canad. Jour. Earth Sci., 5, 278 - 309.

CARROLL, D., (1958), The rôle of clay minerals in the transportation of iron, Geochim. Cosmochim. Acta, 14, 1 - 27.

CATTELL, R. B., (1944), A note on correlation clusters and cluster search methods, Psychometrika, 9: 3, 169 - 184.

CATTELL, R. B., (1965), Factor analysis : an introduction to essentials, 1 & 2, Biometrics, 190 - 215 & 425 - 435.

CHAYES, F., (1960), On correlation between variables of constant sum, Jour. Geophysical Res., 65, 12, 4185 - 4193.

CHAYES, F., and KRUSKAL, W., (1966), An approximate statistical test for correlations between proportions, Jour. Geology, 74, 5, 692 - 702.

COLLINS, A., RUSSEL, T., and FARQUEHAR, J., (1953), Maximum age of elements and age of the earths crust, Canad. Jour. Physics, 31, 402 - 418.

EISENHART, C., (1935), A test for significance of lithological variation, Jour. Sed. Pet., 5, 137 - 145.

EISENHART, C., (1939), The interpretation of certain regression methods and their use in biological and industrial research., Ann. Math. Statist., 10, 162 - 165.

ENGIN, T., and HIRST, D. M., (1970), The Alpine chrome ores of the Andizlik-Zimparalik area, Fethiye, southwest Turkey, Trans. Inst. Min. Met., 79, B16 - B27.

HARMAN, H. H., (1960), Modern factor analysis, Chicago Univ. Press.

HENDRICKSON, A. E., and WHITE, P. O., (1964), Promax: a quick method for rotation to oblique simple structure, Brit. Jour. Statis, Psychol., 17, 65 - 70.

KAISER, H. F., (1958), The varimax criterion for analytical rotation in factor analysis, Psychometrika, 23, 187 - 200.

KAZAKOV, A. V., (1937), The phosphorite facies and the genesis of phosphorites, in Geological investigations of agricultural ores, USSR, Lenningrad Sci. Inst. Fertilizers and Insectofungicides Trans. (USSR), 142, 95 - 113. (Special issue published in English for 17th Internat. Geol. Cong.)

KLEMME, H. D., (1958), Regional geology of the Circum-Mediterranean region, Am. Assoc. Petroleum Geologists, 42, 477 - 512.

MIESCH, A. T., (1969), The constant sum problem in geochemistry, In Computer applications in the earth sciences, Ed. D. F. Merriam, Plenum Press.

MILLER, R. L., and KAHN, J. S., (1962), Statistical analysis in the geological science, John Wiley.

NICHOLLS, G. D., and LORING, D. H., (1962), The geochemistry of some British Carboniferous sediments, Geochim. Cosmochim. Acta, 26, 181 - 223.

ONDRICK, C. W., and GRIFFITHS, J. C., (1969), Frequency distribution of elements in Rensselaer graywacke, Troy, New York, Bull. Geol. Soc. Am., 80, 509 - 518.

PEARSON, E. S., and HARTLEY, H. O., (1954), Biometrika tables for statisticians, Cambridge University Press, 1, 238.

REEVES, M. J., and SAADI, T.A. K., (1971), Factors controlling the deposition of some phosphate bearing strata from Jordan, Econ. Geol. (In Press).

RODIONOV, D. A., (1965), Distribution functions of element and mineral contents of igneous rocks, Consultants Bureau, New York.

SAADI, T. A. K., (1969), Mineralogy, crystal chemistry and genesis of some Jordanian phosphate ores, Unpublished M.Sc. thesis, Durham.

SHELDON, R. P., (1964), Exploration for phosphorite in Turkey - a case history, Econ. Geol., 59, 1159 - 1175.

SPENCER, D. W., (1966), Factors affecting element distributions in a Silurian graptolite band, Chem. Geol., 1, 221 - 249.

SPENCER, D. W., DEGENS, E. T., and KULBICKI, G., (1968), Factors affecting element distributions in sediments, In Origin and distribution of the elements, Ed. L. H. Arhens.

STRAKHOV, N. M., (1962), Fundamentals and theory of lithogenesis, 3 Acad. Sci. USSR, 95.

TRYON, R. C., (1939), Cluster analysis, Edwards Bros.

APPENDIX III

COMPUTER PROGRAMMING

3.1 DATA PROCESSING SCHEME

Some 24 PL1 procedures were written for the purpose of geological data processing. Essentially four main programmes were used :-

(a) XRFR This programme performs various corrections to X-ray fluorescence data.

(b) DISP This programme provide visual display of the data in the form of histograms, and bivarient and trivarient plots of various kinds.

(c) MULT This programme performs stepwise multiple regression analysis of data.

(d) FACT This programme performs either Q or R mode factor analysis of data.

In the case of the seatearth analyses, data was obtained from five sources :-

(a) Field observations. Sample descriptions, geographical locations, stratigraphical horizons, and borehole depths were among the data in this category.

(b) Wet chemical analysis. Five chemical variables were determined by gravimetric and flame photometric methods.

(c) Physical analysis. Determination of liquid and plastic limits, densities and grain size distributions were among data of this category.

(d) Mineralogical analysis. X-ray diffraction and differential thermal analysis were employed for this purpose and both quantitative and qualitative data obtained.

(e) Instrumental chemical analysis. The majority of the data were obtained by X-ray fluorescence analysis.

Of the five sources of data only (a) is obtained directly in a form suitable for coding. All other data sources required some sort of arithmetic manipulation in order to obtain the data in a form suitable for analysis. (b), (c), and (d) involved relatively simple processing carried out on a programmed desk calculator. The X-ray fluorescence data, however, was subjected to computer processing in the programme XRFR. Analysis of the distributions and correlations within various subgroups and the whole data were obtained by the programme DISP. DISP was also used to display the data graphically. MULT and FACT were employed for more detailed statistical analysis. Fig. A3.1 shows the scheme of data processing used.

3.2 DESCRIPTION OF PROCEDURES AND THEIR FUNCTIONS

Table A3.1 lists the important procedures and links them with the main programmes in which they are called. In XRFR much of the data is read in by a special procedure called DATR. In all other programmes the data is read by the main programme. Flowcharts for the four main programmes are given in Figs. A3.2, A3.3, A3.4, and A3.5. These charts are only presented as rough guides to the operations and options available in the programmes and do not necessarily reflect the true programme structure. The input and output facilities of the programmes are dealt with by comment statements within the programmes. Table A3.2 lists the functions of the 24 procedures.

TABLE A3.1

COMPUTER PROCEDURES AND THEIR ASSOCIATED MAIN PROGRAMMES.

MAIN PROG	XRFR			
MAIN PROG		MULT		
MAIN PROG			DISP	
MAIN PROG				FACT
PROCEDURE	DATR			
PROCEDURE	LINR		LINR*	
PROCEDURE	SREG			
PROCEDURE	RMAC			
PROCEDURE	TCOR			
PROCEDURE	CORL	CORL	CORL*	CORL
PROCEDURE	STRG	STRG*		
PROCEDURE	MINV	MINV		MINV
PROCEDURE	MOUT	MOUT	MOUT	MOUT
PROCEDURE	POUT			
PROCEDURE	TOUT			
PROCEDURE		SOUT		
PROCEDURE			TRAN	TRAN
PROCEDURE			FREQ	
PROCEDURE			HIST	
PROCEDURE			PLOT	
PROCEDURE				EIGN
PROCEDURE				VRMX
PROCEDURE				PRMX
PROCEDURE				SCOR

* Indicates that slight modifications have been made to the procedure.

TABLE A3.2

BRIEF DESCRIPTION OF FUNCTIONS OF COMPUTER PROCEDURES

PROCEDURE	FUNCTION
XRFR	Main procedure of XRF correction programme.
MULT	Main procedure of multiple regression programme.
DISP	Main procedure of data display programme.
FACT	Main procedure of factor analysis programme.
DATR	Data reading procedure for XRF correction programme.
LINR	Linear regression used in XRFR and DISP.
SREG	Second order polynomial regression used in XRFR.
RMAC	Computes total rock matrix corrections in XRFR.
TCOR	Computes interelement interferences in XRFR.
CORL	Computes means, variances, standard deviations, maximums, minimums, skewness, kurtosis, and correlation coefficients, used in all programmes.
STRG	Stepwise multiple regression procedure used in XRFR and MULT.
MINV	Gauss - Jordan matrix inversion used in all but DISP.
MOUT	Matrix output procedure used in all programmes.
POUT	Calibration output procedure used in XRFR.
TOUT	Analysis output procedure used in XRFR.
SOUT	Regression output procedure used in STRG within MULT.
TRAN	Data transformation procedure used in DISP and FACT.
FREQ	Computes frequency distributions in DISP.
HIST	Compiles and prints histograms in DISP.
PLOT	Compiles and plots graphs in DISP.
EIGN	Computes eigenvalues and eigenvectors in FACT.
VRMX	Performs varimax factor rotation in FACT.
PRMX	Performs promax oblique factor rotation in FACT.
SCOR	Computes factor scores in FACT.

FIG. A3·1 DATA PROCESSING SCHEME

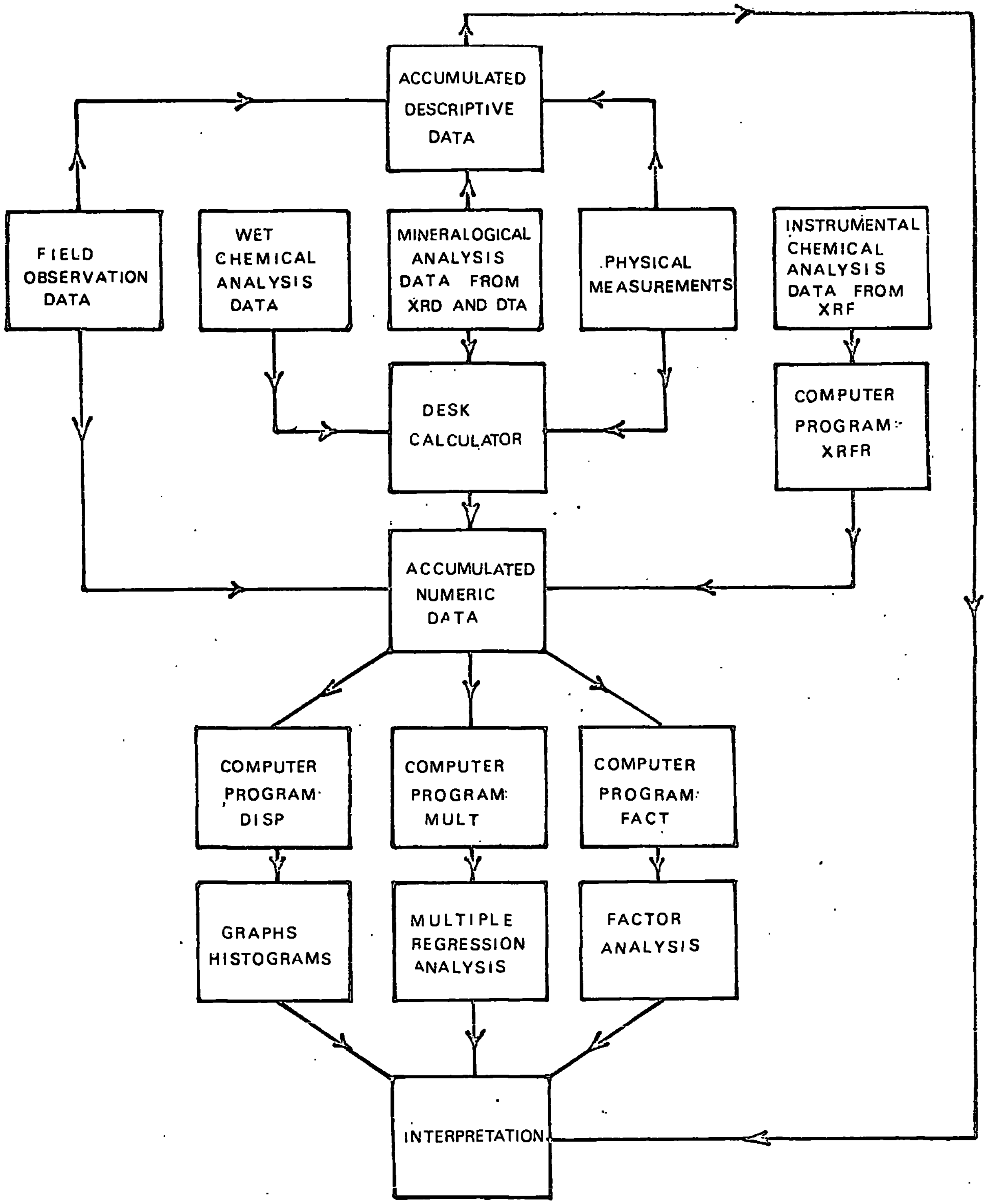


FIG. A3·2 FLOWCHART FOR XRFR

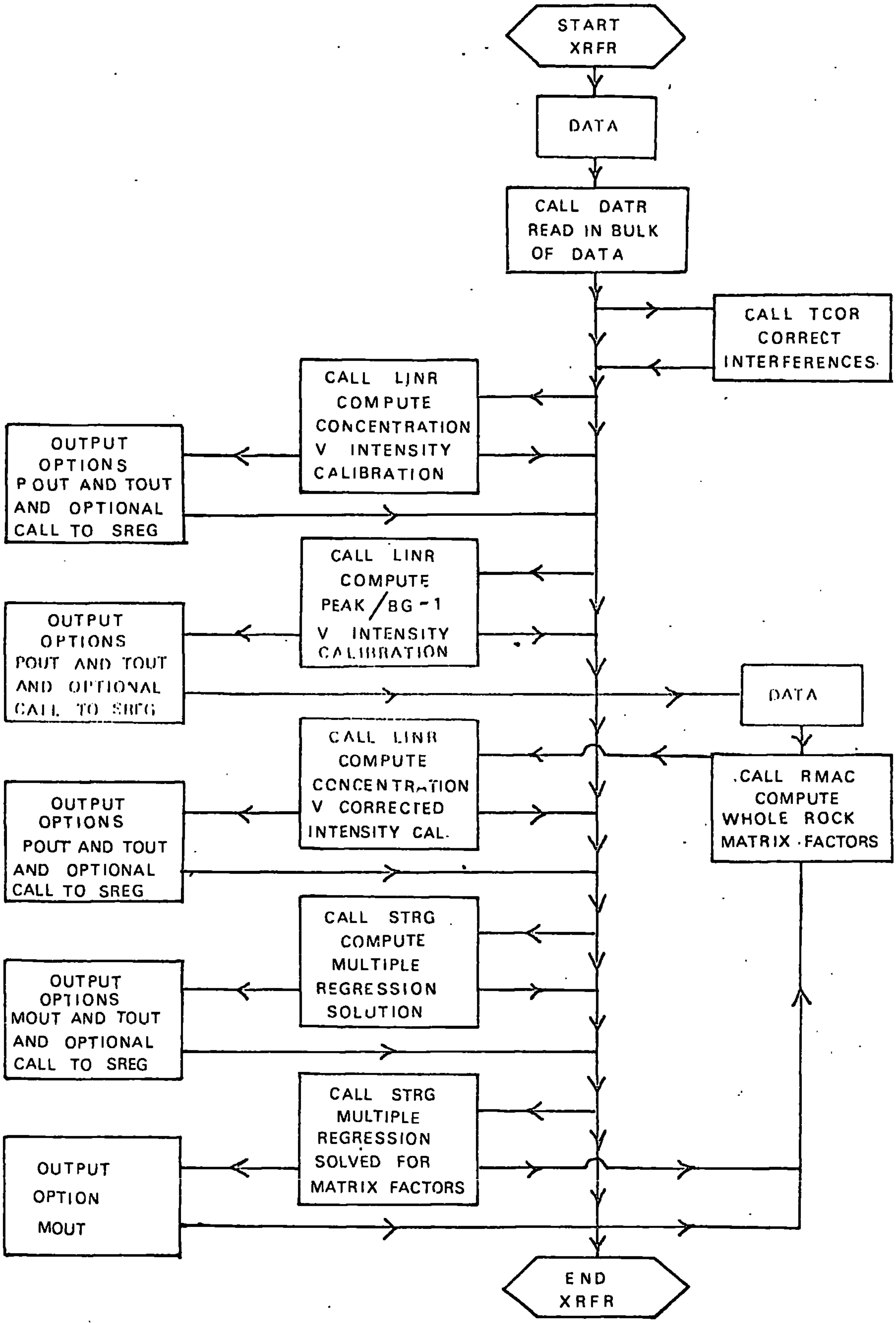


FIG.A3.3 FLOWCHART FOR PROGRAM MULT

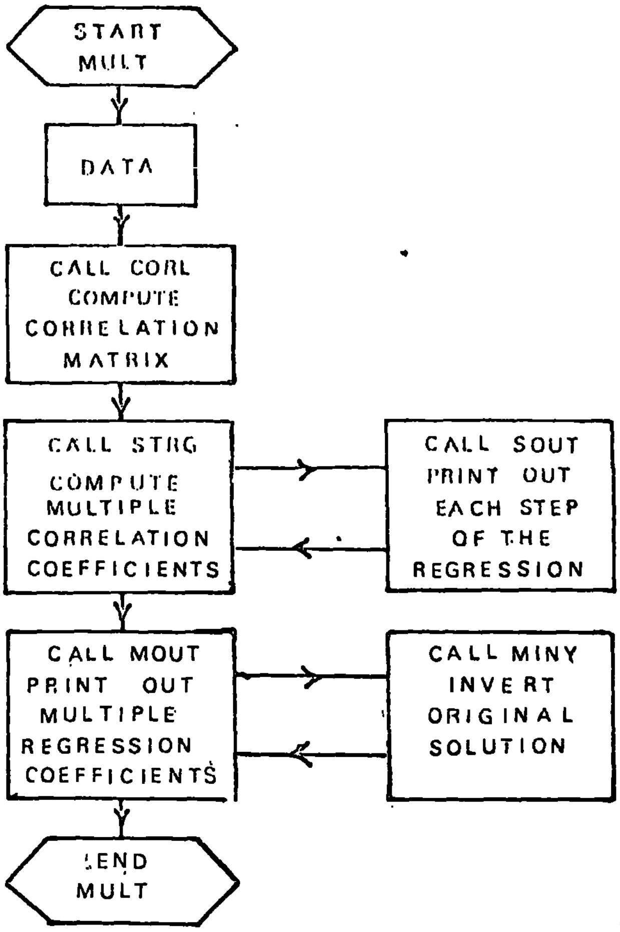


FIG.A3.4 FLOWCHART FOR DISP.

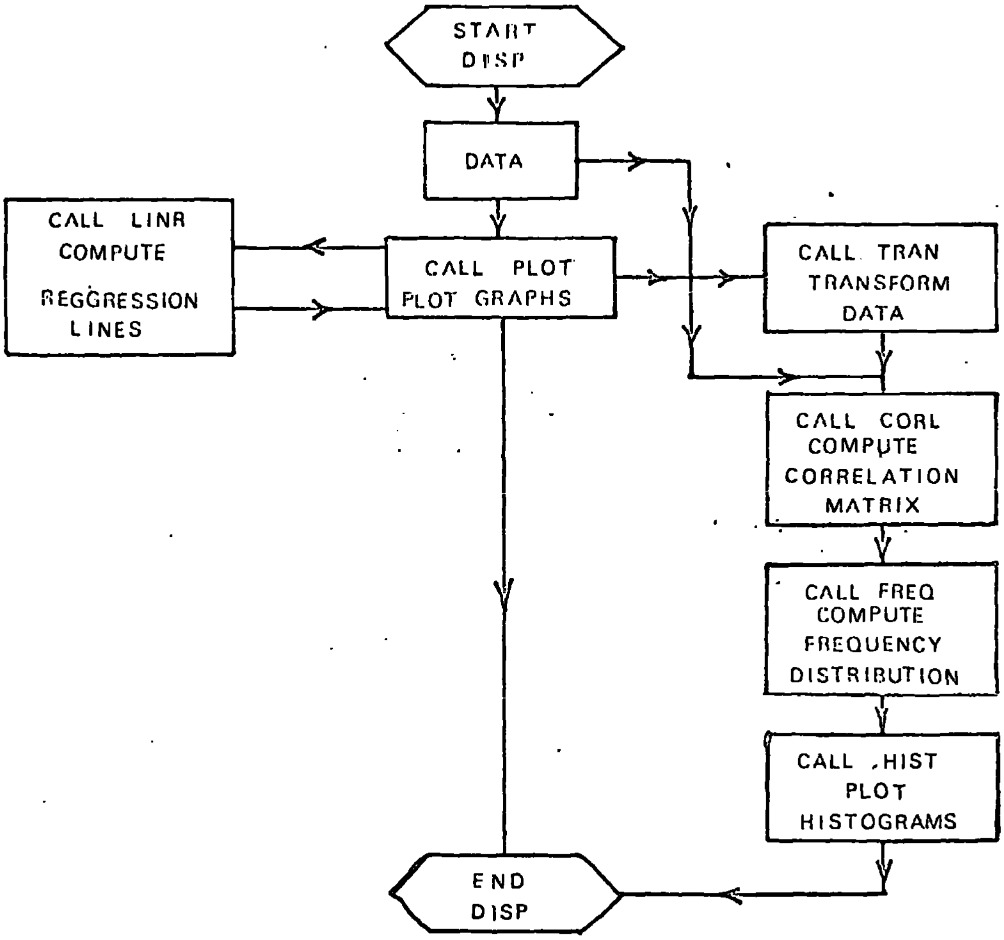


FIG. A3.5 FLOWCHART FOR FACT