Geocheinical studies of sediments from the gulf of paria, venezuela; and the Atlantic ocean north of the Faeroe islands

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Thesis presented for the Degree Doctor of Philosophy in the

University of Durham.

by

Melville K. Sarginson

Geochemical studies of sediments from the Gulf of Paria, Venezuela; and the Atlantic Ocean north of the Faeroe Islands.

Bede College.

Submitted: September, 1970.

I am not one who was born in the possession of knowledge;
I am one who is fond of antiquity, and earnest in seeking it there.

Confucius 551-479 B.C.

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ABSTRACT

Section 1 is concerned with the geochemistry of sub-samples taken from a suite of 5 piston cores collected over the southern part of the Iceland-Faeroes Rise in the North Atlantic Ocean. The samples were taken in 1968 during Cruise No. 14 of the R.V. Meteor of the Deutsches Hydrographisches Institut.

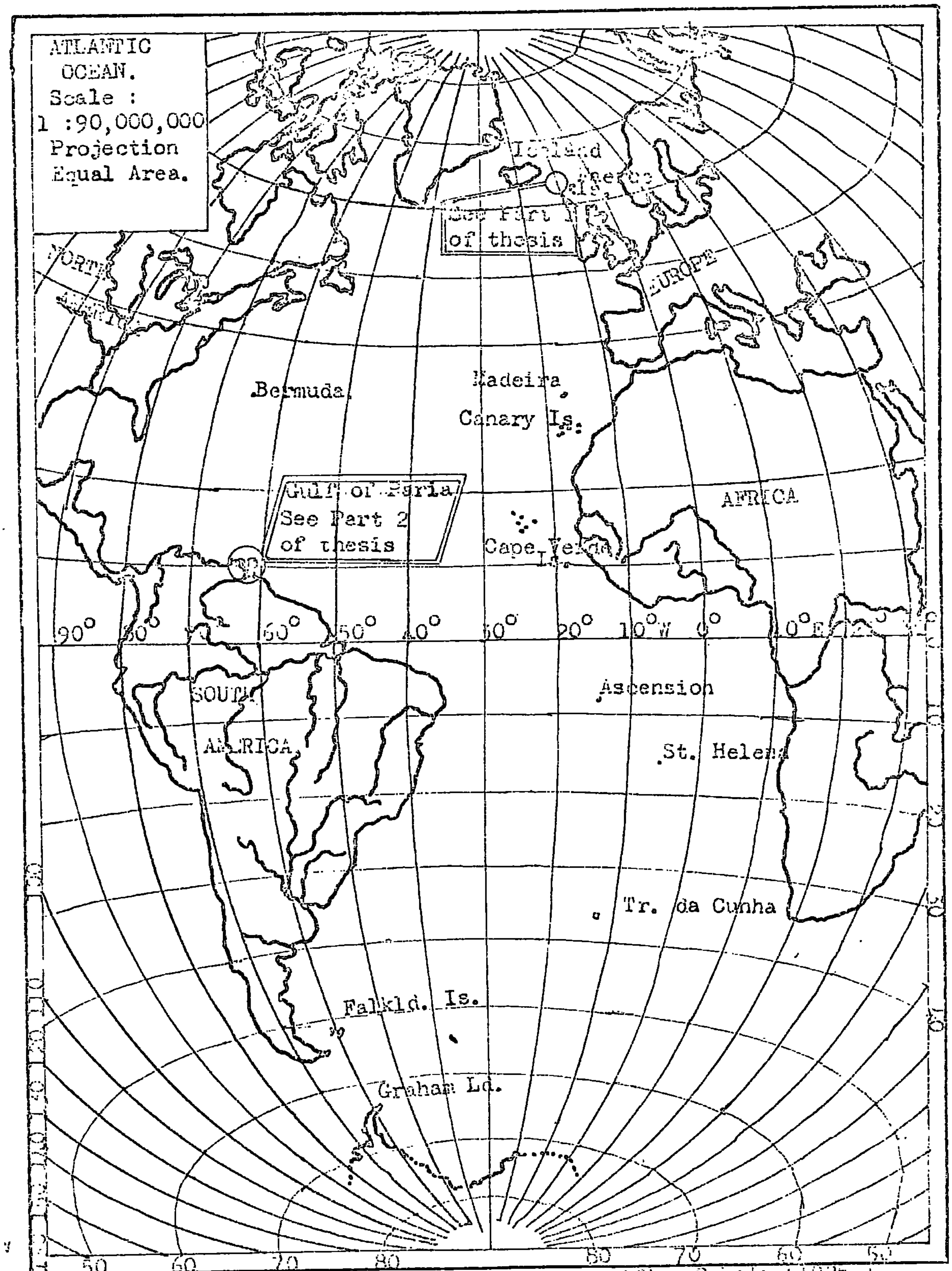
The Iceland-Faeroes Rise appears to have acted as a barrier, resulting in a high proportion of terrigenous material in the sediment accumulating on the eastern side. The sediment east of the Rise contains a relatively high proportion of material derived from a source area which includes metamorphic rocks. True marine sedimentation, i.e., precipitation of $CaCO_3$, becomes important in the stations west of the Rise. Iceland appears to have overprinted the sediments by the introduction of volcanic glass, the greater proportion of which occurs in the cores east of the Rise. The distribution of volcanic debris may have resulted in part from the prevailing westerly winds. Bottom currents flowing westwards over the Rise appear to have carried either the fine fraction of the volcanic glass or its alteration products into the Atlantic Basin.

Section 2 deals with the geochemistry and mineralogy of a suite of sediment samples collected from the Boca Vagre estuary on the southern margin of the Gulf of Paria. These sediments were collected in 1963 during Cruise 35 of the R.V. Chain, of Woods Hole Oceanographic Institution. Variation in the major element geochemistry and mineralogy are studied in the light of earlier works on the geochemistry and sedimentation rates in the area. The results indicate a distinct change in sedimentation over the

pro-delta region, which is reflected in the amount of resistant material in the sediment, and also in the amount, and possibly the composition of the hydrolysate fraction. Variations in pH, and sedimentation rate noted by earlier workers, are reflected in the carbonate content, which shows an increase out into the Gulf. Changes observed in the minor element population are consistent with an increase in the content of the hydrolysate fraction. The proportion of illite and montmorillonite in the hydrolysate fraction would appear to be constant, from evidence provided by the results of Factor Analysis.

VI

Figure 1.11



After Schott (1926.)

SECTION 1

GECHEMICAL STUDIES OF SEDIMENTS FROM THE ATLANTIC OCEAN NORTH OF THE FAEROE ISLANDS.

CHAPTER 1.1

Introduction

Location

The area from which the samples were collected lies within the polygon situated between latitude 61 and 64° North, longitude 6 and 13° West, and embraces the southern half of the Iceland-Faeroes Rise. The latter feature separates the eastern Atlantic Ocean from the Norwegian Sea, being a prominent ridge lying at a depth of between 100 and 200 metres near the Faeroe Islands, increasing to 400 - 500 metres further north. The Iceland-Faeroes Rise belongs to the ridge system extending approximately 2,000 km from eastern Greenland to northern Scotland. Its relationships and location can be seen in FIGURE 1.11. This submarine ridge has two transverse extensions, the larger one known as Reykjanes Ridge, which is part of the Mid-Atlantic Ridge, while the smaller has Rockall Bank and the Faeroes as its higher parts. Between the Faeroes and Rockall, the ridge is dissected by a number of deep water channels; for example the Faeroe Bank Channel.

Previous Work

There has not been a great deal of work published on the geology or geochemistry of the sediments from this area of the Atlantic Ocean and Norwegian Sea; most published work relates to the physical oceanography of the area.

Steele et. al. (1962) studied the deep water currents of the eastern Atlantic Ocean. The Faeroe Bank Channel has been quite extensively studied. Lee (1963) and Crease (1965) have examined the velocity of bottom waters, and the resulting sedimentation, Harvey (1965) has investigated the topography, while Stride et. al (1967) and Bott et. al. (1967) discuss the origin of the channel. The mixing of the Norwegian Sea and Atlantic Ocean water and flow over the Iceland-Faeroes Rise, were studied by Steele (1967).

A recent general review of the Norwegian Sea area is contained in Volume five of a report of the United States Naval Oceanographic Office Marine Geophysical Program 1965-67, where the bathymetry slope and track charts are discussed. Saito et. al. (1967.) describe a core collected in the Norwegian Sea basin during the course of this programme.

One of the earliest descriptions of sediment samples from the area is that given by Chumley (1910) on the samples collected during the Michael Sars North Atlantic Deep Sea Expedition of 1910. The samples described, although from the south and south east of the Faeroe Islands, are of general interest. More recently, Correns (1939) gives a map of the North Atlantic Ocean, showing the distribution of calcium carbonate in the bottom sediments of the whole area of the Iceland-Faeroes Rise. In Graham and Moberg (1944), two stations are indicated in the Iceland-Faeroes region from the last Cruise of the Carnegie, when data were collected on the phosphate content, and pH of the sea water.

Moving further east, Holtedahl (1955, 1959) describes the lithology, foraminiferal content, grain size, and carbonate content of a suite of core samples collected from the Norwegian Sea. These results are of value for purposes of comparison with the general stratigraphy of the cores obtained for this present study. Berry and Johns (1966) provide information on the mineralogy of 52 sediment cores collected over the North Atlantic and Arctic Ocean, four of which lie in the area of the Iceland-Faeroes Rise. The results provide an insight into the possible origin of the sediments.

This brief review would not be complete without a mention of the work done by Russian scientists in this area: Lavrov, Klenova et. al. (1969) have done piston coring in this general area, but no results are yet available.

Location of samples and their collection

The sediments studied were taken as sub samples from piston cores collected at the stations indicated on FIGURE 1.12 during Cruise 14 of R.V. *Meteor*. Details of these stations are provided in Table 1.1A.

Cruise 14 was organised by the Deutsches Hydrographisches Institut, Hamburg, being the first of several Cruises planned for the sea area between Iceland and the Faeroe Islands. The object of these investigations is to conduct a geological and geophysical survey of the area. The main purpose of this, the first Cruise, was to study the detailed bathymetry of the ridge, although this had to be restricted to the south-eastern half, because of the short time available. A continuation of this work, together with other investigations, is planned for 1970.

Figure 1.12

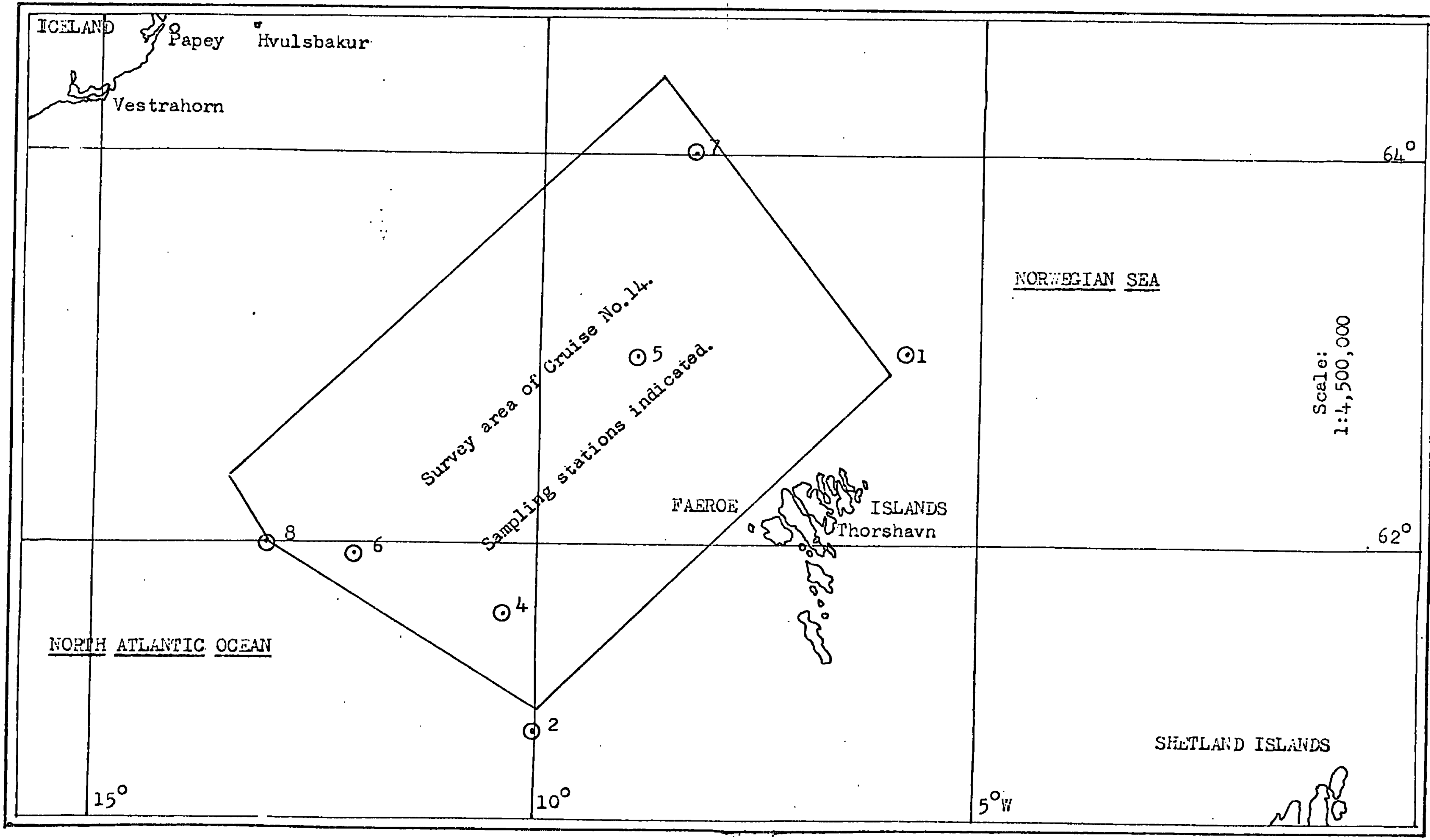

ICELAND
Papey
Hvulsbakur
Vestrahorn
64°
NORWEGIAN SEA
Scale:
1:4,500,000
Survey area of Cruise No.14.
Sampling stations indicated.
1
2
4
5
6
7
8
FAEROE ISLANDS
Thorshavn
62°
NORTH ATLANTIC OCEAN
SHETLAND ISLANDS
15°
10°
5°W

TABLE 1.1A

STATIONS CRUISE No. 14

DATE	STATION	TIME	LATITUDE	LONGITUDE	DEPTH	NOTES
1968	No.	GMT	NORTH	WEST	METRES	
July 6th	1	1758	62°57.5'	5°49.0'	1408	Box Sampler
		2015	59.2'	43.6'	1413	Piston Corer
July 7th	2	1814	61°08.4'	10°06.5'	1120	Box sampler
		1903	08.5'	06.8'	1122	Water samples
		1955	08.9'	06.8'	1120	Piston corer
July 8th	3	1324	62°58.5'	6°07.2'	1594	Water samples
July 14th	4	0924	61°42.4'	10°15.4'	1177	Box sample
July 18th	5	2057	62°59.8'	8°50.0'	451	Box sample
July 22nd	6	0840	61°57.0'	12°08.5'	1237	Box sample
		0946	58.0'	08.6'	1227	Piston corer
August 1st	7	0820	64°05.0'	8°14.8'	1259	Box sample
		0919	04.9'	14.9'	1244	Water samples
		1007	04.7'	15.1'	1237	Piston corer
August 2nd	8	0719	62°01.5'	13°05.0'	1256	Box sample
		0815			1256	Water samples
		0913			1259	Piston corer

On this Cruise, Meteor was making a contribution to the survey work of the International Overflow Program, started in 1960 by R.V. Gauss and FRV Anton Dohrn, in conjunction with seven ships of other nations. The object of these investigations was a study of the overflow of Arctic waters over the Iceland-Faeroes Rise.

The survey work carried out during Cruise 14 included, a continuous gravity and magnetic survey across the ridge, under the supervision of Dr. U. Fleischer of the Deutsches Hydrographisches Institut. Water samples were collected at some stations for the investigation of their tritium and carbon 14 content, by the Second Department of Physics, University of Heidelberg. Special equipment for the study of the rare gas content of the atmosphere was also tested, by Messrs. Buechen and Rudolf from the Department of Meteorology and Geophysics, Frankfurt a.M. The latter was in preparation for the Atlantic Expedition of the Meteor planned for 1969. Askania-Werk, manufacturers of sea gravimeters, used the Cruise to test a prototype of a new, more compact, sea gravimeter, Gss3, under the supervision of Ing. E. Thebis. Its performance during the Cruise was compared with that of the two older Askania models fitted as standard equipment on the Meteor. All gravimeters were kept running continuously throughout the Cruise from Hamburg, until Heligoland on the return leg of the Cruise. This allowed correction for drift in the instruments, as the absolute value for gravity is known at these points. Experiments in communications and navigation, begun on a previous Cruise in the

Cop

southern part of the North Atlantic Ocean, using the American satellite ATS-3, were continued. Scientists from the Deutsche Versuchsanstalt fuer Luft und Raumfahrt conducted these experiments, in co-operation with the National Aeronautics and Space Administration (N.A.S.A.); when direct communication was effected with the United States. Also taking part in these satellite experiments were representatives from the Deutsches Hydrographisches Institut, Deutsche Bundespost, and Rohde u. Schwarz, a private company. Investigations into the efficiency of the anti-roll tanks on the *Meteor* were planned, under the supervision of Dr. Wuehrer of Escher Wyss GmbH., the original manufacturers. The experiments were, however, curtailed because of the good weather encountered during most of the voyage.

Navigation is, of course, possibly the most important factor in an oceanographical survey, and the *Meteor* was equipped to make use of the usual navigational systems - Decca, Loran and Direction Finder radio. In fact, the Decca Navigator was used during the North Sea crossing, Radar when near the Faeroe Islands, and Loran "A" for the bulk of the survey.

The geological sampling equipment used on the *Meteor* during the Cruise was
a. The Reineck Box Sampler.
b. The Kullenberg piston corer.

The Reineck box sampler was used at all stations to discover the nature of the sediment cover; this was to prevent damage to the more expensive piston corer, should the bottom sediment prove to be too coarse, or absent. As shown in Table 1.1A, at two stations, the box sampler only, was used, because of the coarse nature of the sediment found; no attempt was, therefore, made to use the piston corer. Details of the construction and mode of operation of the box sampler are given by Reineck (1963). This apparatus can collect a rectangular core, 0.45 m deep by 0.20m by 0.30m., providing undisturbed sediment samples suitable for the study of sedimentary structures, animal burrows, as well as geotechnical properties, such as shear strength, and water content. With additional apparatus, oriented box samples may be collected.

Two types of corer were carried, the <u>Bandy</u> and the <u>Caribic</u>. Both of these were of the Kullenberg type (Kullenberg, 1947) the only difference being that the latter is of German manufacture, and uses plastic liners, while the <u>Bandy</u> corer is of American manufacture. Details of the <u>Caribic</u> corer are given for reference:

Caps ·
Cap

Core barrel length : 5, 10m and multiples.
Maximum drive weight : 600 kg
Trigger weight : 60 kg
Length of tube on trigger weight : 0.2m
(During Cruise 14, core barrels of 5m only were used.)

The coring programme was quite successful since at each of the stations where the equipment was used, useful cores were recovered.

Table

<u>Lengths of cores recovered</u> (For details of depth and co-ordinates see TABLE 1.1A

Station 1	4.5m
Station 2	4.5m
Station 6	3.5m
Station 7	3.3m
Station 8	4.4m

The cores were logged, then cut into metre lengths, sealed and labelled, before being stored in a refrigerated room on the Meteor, where a constant temperature of fifteen degrees Centigrade was maintained. A portion of each of the box samples was also retained, either in polythene bags (for shells and rock fragments) or in lengths of plastic tubing. A brief description, with the core logs, is included in the section headed Mineralogy.

Meteor sailed from Hamburg on July 2nd and returned there on August 7th, 1968. A call was made at Heligoland on the return voyage, when the gravity survey was completed. After the Cruise, all the samples were shipped back to Durham for work to begin in September, 1968.

Objects of this study

The object of the coring programme was to study the sediment distribution over the southern part of the Iceland-Faeroes Rise. It was also hoped that the influence of adjacent areas of land, the submarine topography and associated bottom currents on the accumulating sediment would be elucidated from the results of geochemical and mineralogical studies of the sediments. The geographical location of the cores are shown in FIGURE 1.12. The nature of sediment accumulating at stations 1 and 7, east of the ridge might be expected to show a higher proportion of terrigenous matter than those to the west. Station 2, situated between Faeroe Bank and Bill Bailey Bank, might be expected to show the influence of deep water currents on sedimentation. Station 4, on the other hand, situated on the higher slopes of the ridge, was selected to investigate the nature of the sediment cover higher on the ridge. For a study of the geotechnical properties of the sediments, portions of the piston core samples were passed on to Dr. P.B.Attewell, Reader in Engineering Geology at Durham. The results of these studies are given in the theses of Dixon (1969) and Mahdi (1969).

CHAPTER 1.2

MINERALOGY

In this chapter, it is considered relevant to give descriptions of the cores taken on board the Meteor, and the general scheme of sub-sampling adopted. The geographical co-ordinates depth of sea water, dates of collection and lengths of cores at the stations were presented in Table 1.1A in the last chapter.

GENERAL DESCRIPTION

Station one The core consisted mainly of a uniform greyish green clay, only the upper 25 x 10^{-3}m. of the core differed, being reddish brown in colour.

Station two The core showed slightly more variation than at Station one, in that the top 0.2m appeared slightly coarser in texture than the underlying fine grained sediment. At approximately 0.4m. from the top of the core, the sediment had a distinct spiky appearance and feel when passed between the fingers. Under the microscope, abundant opal fibres were found in the sediment. A quantity of these were separated and sent to the Palaeontology Department of the British Museum of Natural History for identification. These fibres were identified as sponge spicules, they belong to the phylum Porifera, class Desmospongea, Order Choristida, Family ? Geodiidae. This was the limit of possible identification, since only megascleres were found and sent for identification. The two types of sponge spicules are megascleres and microscleres; the former constitute the skeletal framework of the animal, while the latter occur scattered through the soft tissue of the sponge; the latter do in fact, show variation between the individual genera. The family Geodiidae are found to be predominant on the continental shelf and slope areas of the world, being recorded from the Arctic Ocean, North and South Atlantic, Indian Ocean, Mediterranean, Red Sea, and the Pacific Ocean from S.E. Asia to New Zealand. Their presence is, therefore, neither unique nor unusual.

Station three No geological sampling was undertaken at this station, only water samples were collected.

Station four Although no piston core was collected, a quantity of shell fragments and rock debris were recovered in the box sampler. The rock fragments of quartzite and schist, varied in size from 40×10^{-3}m x 25×10^{-3}m to 5×10^{-3}m. diameter. The shell fragments were identified as plates from large goose barnacles, they vary in size from 1 to 2×10^{-2}m. Bryozoans encrust the inner surfaces of many of these plates. Since the Bryozoans encrust the inner surfaces of the plates, they obviously post-date the original barnacles. The position of the bryozoan encrustation within the curved plates suggest shelter and protection from the bottom currents at this station. Associated with these shell fragments was a coarse silt consisting of some sand grains, some sponge spicules, but mainly the tests of foraminifera. A number of unidentified small gastropods, and bivalye shell fragments were also found at this station.

Station five Only a box sample was collected, the sediment being a coarse silt which contained numerous rock fragments. Fourteen fragments were separated, and four sectioned, the smallest being 10 x 10^{-3}m x 7.5 x 10^{-3}m., the largest 5 x 10^{-2}m. They were subangular or rounded in appearance, and of basaltic composition. When collected, the bulk of the silt had a dark grey-green colour, with some light brown patches with a slightly coarser grain size. The coarse rock fragments showed superficial weathering as a white coating. The larger pieces and the silt fraction were divided into two halves, one of which was brought back to Durham.

Station six Both a box sample and piston core were collected. The length of the core was 3.5m but this had been broken into two lengths of 2.75 and 0.75m respectively, probably a result of incomplete penetration of the sediment by the corer. On pulling the corer out of the sediment, the piston would first be drawn up to the end of the core barrel. There would thus be a reduction in pressure below the piston, so that the sediment column would be pushed up by the sea water, as it entered the bottom of the core barrel, equalising the pressure. Some flushing of the sediment could also occur. The sediment column did not, however, appear to be disturbed, apart from the break in the column. Klenova (1969. verbal communication.) stated that under similar circumstances, her co-workers had obtained piston cores, which they believed, had been highly disturbed by similar processes. Their cores appeared superficially quite homogeneous, but on division, consisted of a coat of the upper brown layers of sediment, surrounding a core of the lower grey coloured sediment, like a rolled jam pudding.

Station six The sediment collected here was homogeneous in appearance, consisting of a reddish brown, silty clay giving way, with an abrupt change at 0.02m to a greyish green clay containing some well rounded pebbles. The clay was tenacious and fine grained, while the rock fragments were basalt and tuff.

Station seven This piston core had a length of 3.31m. Distinct variation with depth was apparent, the upper 0.05 - 0.06m of the core consisted of a grey to brown clay, which passed into a coarse, pale brown sandy horizon. At 0.07m this passed into an homogeneous grey clay. There was a noticeable lack of larger clastic fragments in the sediment collected at this station.

Station eight The piston core collected here was 4.44m long. The top of the core consisted of a brown silty clay, with a distinct boundary visible at a depth of 0.03m. Below this boundary, the sediment consisted of a grey silty clay which contained small rounded pebbles varying in diameter between 20 and 40 x 10^{-3}m.

DISCUSSION

It is interesting to compare the lithological variation seen in the cores from stations 1 and 7 with the description given by Holtedahl (1955, 1959) for a suite of cores collected from further east in the Norwegian Sea. The 25 x 10^{-3}m of reddish brown clay at the top of the core from station 1 may be the lateral equivalent of either the light brownish grey marl, or the brownish clay described by Holtedahl (op. cit.). Core one was collected to the east of the boundary, marked on FIGURE 39, ibid., further substantiating this suggestion, and was also the core collected from the greatest depth (1413m) on the Meteor Expedition. Holtedahl (op.cit) has recognised this horizon in cores collected from water depths greater than 1,000m. The absence of this pale horizon in the cores from the other stations may be due to the action of bottom water currents flowing west over the Iceland-Faeroes Rise, i.e. erosion balancing sedimentation. Worthington (1970. Fig.2) and Dietrich (in Lee 1963) regard this flow of water as being purely gravitational, and suggests a velocity of 5 x 10^{-2}m. sec^{-1} near the bottom at 700m depth. Steele (1959, 1961., in Lee 1963) however, considers that the overflow includes both gravitational and geostrophic components, and suggests that a velocity of 1.6 x 10^{-2}m. sec^{-1} is more realistic. Measurements carried out during the Overflow Programme in 1960 indicated that near Iceland the bottom currents reached 2.5 x 10^{-2}m. sec^{-1}. (Joseph 1960 in Lee 1963). Whichever of the values for the velocity are taken, it is obvious that there is an appreciable overflow of bottom water, which would affect sedimentation at the present day.

It seems logical, in view of the lithological similarities to draw correlations between the lithology of the Meteor cores one and seven, with those of Holtedahl (1955) to the east. The stiff grey clay of the former stations, containing occasional pebbles, suggests that this is the lateral equivalent of the blue grey clay, which makes up the deeper portion of the cores described by Holtedahl (op.cit) below approximately 0.01m. (see Cores 5, 6 p. 150 ibid.). The overall carbonate content, however, is not as high in the Meteor cores, and the Trask sorting coefficients are lower, indicating better sorting (Pettijohn 1957, p.37) than in those examined by Holtedahl (op. cit.). These sorting coefficients are tabulated on the next page.

TABLE 1.2A

TRASK SORTING COEFFICIENTS

Calculated from Dixon, 1969.

Station one (Meteor)	Sorting Coefficient	Median diam (x m^{-6}.)
0.04 - 0.05m	2.67	25
0.14 - 0.15	1.67	40
0.24 - 0.25	4.20	10
0.34 - 0.35	1.58	80
0.42 - 0.43	1.73	60
Station seven (Meteor)		
0.04 - 0.05	5.00	90
0.14 - 0.15	2.67	20
0.24 - 0.25	2.42	15
Station five (Holtedahl 1955 pp.146)		
0.044 - 0.049m	9.1	16
0.092 - 0.100	8.8	20
Station six (Holtedahl op. cit.)		
0.040 - 0.047m	-	2.5
0.090 - 0.095	7.3	25

It is obvious from these results that all of the Meteor samples are reasonably well sorted and although the horizons which have been studied are not as closely spaced down the core as those of Holtedahl (op cit.) variation with depth would be readily seen. The sediments from stations 1 and 7 show better sorting than those described by Holtedahl (op.cit.), this may result from sorting during transportation from the east, i.e., these are reworked glacial marine sediments, and hence better sorted than those sediments described by Holtedahl (op. cit.) further east.

The cores collected in the west of the sampled area, would not be expected to correlate with cores from the Norwegian Sea because of the influence of the intervening Iceland-Faeroes Rise and the open Atlantic Ocean basin. Apart from some anomalous horizons, the sorting seen in these cores is relatively uniform with depth. The degree of sorting increases westwards away from the Iceland-Faeroes Rise. This substantiates the earlier suggestion concerning the effect of the Iceland Faeroes Rise with only the finer material being carried far to the west.

The core from station 2 shows two features which are not observed in the other cores. This core has a relatively high carbonate content and a high concentration of opaline sponge spicules at a depth of approximately 0.415m. The position of this station on the edge of the submarine channel between Faeroe Bank and Bill Baileys Bank, may account in part for the nature of the sediment. If this channel were followed by a northwestward flowing current, similar to that in the adjacent Faeroe Bank Channel, then the floor of the channel which is at a depth of between 360 and 550m., would act as a sediment dam, preventing or reducing the amount of terrigenous material being carried over from the Norwegian Sea into the Atlantic Ocean basin. For details of water current flow between the two sea areas, (see Lee.(1963) and Worthington.(1970). The relatively high carbonate content may thus represent a stage when the supply of terrigenous material was either reduced or cut off. This may have occurred during a glacial period, when erosion of the continental areas would be at a minimum. A study of the fauna within the sediment particularly with respect to the numbers and types of the Microfossils present may clarify this point. It is of interest that Charlesworth (1957) suggests a land connection between Scotland and Greenland, linking Iceland and the Faeroe Islands. He suggests that this may have existed during the Pliocene, when colder waters were deflected into the North Sea. During the Quaternary, its effect would have been to close the Arctic basin from the warmer North Atlantic Ocean waters.

CONCLUSIONS

A number of conclusions may be drawn from the results of mineralogical studies. First of all the higher concentration of detrital material east of the Iceland-Faeroes Rise, which seems to have acted as a sediment dam, causing the amount of detrital matter in the sediment to be reduced to the west. The rock fragments present in the sediment from stations west and east of the Rise may have been derived from the Faeroe Islands in part (basalt, tuff. Stations 5, 6 and 8.) as well as Scandinavia (quartzite, schist. Station 5 and 8).

It is possible to see similarities in the vertical variation in the cores from stations 1 and 7, and those of Holtedahl (1955).

Differences in the carbonate content and degree of sorting may be explained in terms of erosion and redeposition by bottom currents of sediment of a type similar to that described by Holtedahl (op.cit.).

From the bottom current pattern of the Norwegian Sea (Worthington, 1970), a source area to the north and east seems quite possible. The absence of the pale brown clay described by Holtedahl (op. cit.) may have resulted from a balance between erosion and sedimentation.

The greater content of carbonate present in the sediment to the west of the area results from the influence of the Iceland-Faeroes Rise, and Atlantic Ocean basin, as mentioned earlier.

The content of carbonate in core two, where it increases with depth, may indicate a low stand in sea level, possibly during a period of glacial advance on the continental areas, causing a reduction in the amount of clastic material entering the basin of deposition.

SAMPLING SCHEME

Systematic sub-sampling into 0.01m lengths was carried out on the cores for two reasons. The first was because each core had considerable uniformity, with little vertical variation, and secondly, because some sub-samples were required for a study of their geotechnical properties.

For these reasons, the whole cores were cut into 0.01m lengths, then resealed in polythene sheet to retain the interstitial water.

The sub-samples from the horizons selected for geochemical and mineralogical work were treated in the following manner. After being unwrapped, the outer centimetre was removed with a palette knife in order to avoid any contamination which may have occurred during coring. The sub-sample was then placed in a dessicator, which was then evacuated. This method of treatment, proposed by Nicholls (1967. pers. comm.) has advantages over simple air drying, or oven drying usually employed for unconsolidated sediments. When a core is air dried, it is usually cut into two halves, which are then left open, usually for some months. During the process of drying capillary action may cause the migration of some elements such as magnanese, magnesium and calcium to the outer surfaces, which if, discarded before analysis, will introduce an obvious source of error. Secondly, if a sample is to be used in clay mineral studies, heating, even to 50°C, may cause alteration, such as loss of interlayer water.

For details of the pretreatment given to the Geotechnical samples, see : Dixon (1969) and Mahdi (1969).

TABLE 1.2B

HORIZONS SAMPLED FOR MINERALOGICAL AND CHEMICAL ANALYSIS

Core station one	Sample No.	Core station two	Sample No.
0.01 - 0.02 ×10m	1-2	0.01 - 0.02 ×10 m.	2-2
0.03 - 0.04	1-4	0.03 - 0.04	2-4
0.11 - 0.12	1-12	0.11 - 0.12	2-12
0.13 - 0.14	1-14	0.13 - 0.14	2-14
0.21 - 0.22	1-22	0.21 - 0.22	2-22
0.23 - 0.24	1-24	0.23 - 0.24	2-24
0.31 - 0.32	1-32	0.31 - 0.32	2-32
0.33 - 0.34	1-34	0.33 - 0.34	2-34
0.41 - 0.42	1-42	0.41 - 0.42	2-42
0.43 - 0.44	1-44	0.43 - 0.44	2-44

Core station six	Sample No.	Core Station seven	Sample No.
0.01 - 0.02 ×10m.	6-2	0.01 - 0.02 ×10 m.	7-2
0.03 - 0.04	6-4	0.03 - 0.04	7-4
0.11 - 0.12	6-12	0.11 - 0.12	7-12
0.13 - 0.14	6-14	0.13 - 0.14	7-14
0.21 - 0.22	6-22	0.21 - 0.22	7-22
0.23 - 0.24	6-24	0.23 - 0.24	7-24
		0.30 - 0.31	7-31

Core station eight	Sample No
0.01 - 0.02 ×10 m.	8-2
0.03 - 0.04	8-4
0.11 - 0.12	8-12
0.21 - 0.22	8-22
0.31 - 0.32	8-32
0.41 - 0.42	8-42

The dry sub-samples, on removal from the dessicator, was divided longitudinally, one half was retained for microscopical examination, and possible grain size analysis, while the other was crushed for chemical and mineralogical analysis.

GRAIN SIZE ANALYSIS

This has not been investigated in the geochemical sub-samples since the grain size distribution through the cores has been dealt with by Dixon (1969) who has presented the relevant cumulative percentage curves.

X-RAY DIFFRACTION STUDIES

Prior to analysis, one half of the section was crushed for 15 minutes in a Tema swing mill, to reduce the overall grain size of the sample to approximately 400 mesh (B'S.I.), and also produce a fine homogeneous powder. For a detailed discussion of the effects of grain size on X-ray diffraction intensities, see Klug and Alexander (1954 pp. 193-197).

When analysing a sample by X-ray Emission Spectrography, the overall grain size of the sample is found to be important in most methods currently in use, as shown by the work of Claisse and Samson (1962), and Bernstein (1963). These workers studied the effects of particle size, and found that for any X-ray wavelength, a sample gives fluorescent intensities independent of particle size, only for very fine or very coarse particles. Between these extremes, which vary from sample to sample, and with the wavelength of the primary radiation under consideration, the intensity of secondary radiation is found to depend in a complex manner on the mineral phases present, and on the shape of the particle distribution curve, so that quantitative analysis is unreliable.

There are three reasons for using a fine powder:

1. The number of available crystallites giving reflections must be large enough to give a sufficiently high precision.

2. To reduce the possibility of preferred orientation.

3. To reduce the micro-absorption of X-rays by crystallites to a minimum.

Brindley and Udagawa (1959) studied the effect of prolonged grinding on the peak diffraction intensity of quartz, and found that a thin layer of disturbed material was produced on the surface of individual quartz grains. This contributed to the absorption of the X-rays, but did not enhance the intensity of reflections. This thickness was estimated to be of the order of 0.03 x 10^{-6}m. With particles of smaller size than 2 x 10^{-6}m., the intensity was found to be diminished, while with those greater than 40, extinction also produced a reduction in intensity. This process of extinction results from reflection by atomic planes, so that the intensity of the incident beam is decreased. Brindley and Udagawa (op. cit.) concluded that a grinding time of between a half and one hour should give optimum diffracted intensity, whereas after 16 hours, an 80 percent reduction would occur in the intensity of the reflections. With those results in mind it was decided to crush all the samples for a uniform grinding time of fifteen minutes. This was considered a suitable length of time because of the unconsolidated nature of the sediment, and the content of minerals of hardness less than quartz. Grinding for longer periods, would probably reduce the crystallinity of the clay minerals in a similar manner to that found when dealing with the Paria samples in Part II of this thesis.

After a cursory microscopic examination of the samples, it was immediately obvious that the mineralogy was more varied than that of the sediment of the Gulf of Paria. In addition to the variable proportions of quartz, clay and carbonate, amorphous silica in the form of opal sponge spicules, some feldspar and volcanic glass fragments were common constituents, particularly in stations 1 and 7.

It was decided therefore, to restrict the determinative mineralogy to two mineral species, quartz and opal. Quartz was determined by X-ray diffraction, while an attempt was made to determine opal by Infra-red spectroscopy.

X-RAY DIFFRACTION ANALYSIS

A set of artificial standards could not be used satisfactorily as in Section II, because of the marked variation in the mineralogy from core to core. It was thus decided to prepare sets of spike standards using two types of matrix, one carbonate poor, the other carbonate rich, to allow for gross variations in matrix. For this purpose, horizons 1-34 from station 1, and horizon 2-44 from station 2, were selected as being suitable base matrices. The overall range of the quartz content was expected to be between 10 and 20 percent, so that five standards covering this range were prepared. The peak intensity of the Quartz 1010 reflection at 4.26×10^{-10}m. was used in the analysis. The intensity of the reflection was plotted against the amount of quartz added, thus providing a calibration curve. The quartz used for this purpose was obtained by crushing a sample of Brazilian Rock Crystal, which was then passed through a 200 mesh (BSI) bolting cloth.

Correlation coefficients of calibration curve

0.9632	1-34
0.9839	2-44

Only a slight difference in gradient for the calibration curve could be seen, hence matrix effects were not significant. All standards were mixed in $14 \times 10^{-6} m^3$. mixing vials for one hour on a Glen Creston mixing mill to ensure homogeneity.

Operating conditions for Philips PW 1051 1 Kilowatt Diffractometer

Copper anode

Tube rating : 1 kilowatt. Operating at; 40 Kv 20 ma.

Goniometer scan speed : 1° per minute.

Settings : Rate meter : 4 Time Constant : 2

No discrimation.

Sample holder : Philips PW 1064. Rotating.

Precision

Sample 1-12 Wt percent Quartz

22 Mean = 22 percent
20 Standard deviation = ± 1 percent
21 Relative deviation = 5 percent
22
23
21

No internal standard was used for this work, as the advantages resulting would be marginal. The results of the quartz analyses are tabulated at the end of this chapter.

TABLE 1.2C

QUARTZ DETERMINATION BY X-RAY DIFFRACTION IN METEOR SAMPLES

Sample No.	Wt percent Quartz	Sample No.	Wt percent Quartz
1-2	9	2-2	10
1-4	n.d.	2-4	17
1-12	22	2-12	22
1-14	n.d.	2-14	12
1-22	33	2-22	4
1-24	26	2-24	8
1-32	16	2-32	22
1-34	24	2-34	n.d.
1-42	8	2-42	4
1-44	40	2-44	4
7-2	30	6-2	20
7-4	13	6-4	12
7-12	17	6-12	8
7-14	5	6-14	14
7-22	5	6-22	7
7-24	4	6-24	11
7-31	n.d.		
		8-2	10
		8-4	12
		8-12	2
		8-22	7
		8-32	6
		8-42	15

n.d. not determined

It is obvious that when the results of the quartz analysis are considered, the concentration of quartz is higher in stations 1 and 7 than 2, 6 and 8. A study of the coarse fraction of the sediment indicates the presence of strained quartz grains, suggesting metamorphic derivation. It seems reasonable, therefore, to suggest Scandinavia as a possible source of the detrital quartz present in the sediment. The bottom current pattern of the Norwegian Sea of Worthington (1970) would support this suggestion.

Carbonate

The common carbonate which occurs in argillaceous rocks is $CaCO_3$, usually in the form of calcite or aragonite. On the basis of X-ray diffraction examination, the dominant carbonate species present in the *Meteor* Atlantic samples is calcite. According to Deer, Howie and Zussman (1966), most inorganic calcites are free from substitution. Chave (1952) however, indicates where Mg is able to substitute for Ca in calcite, a decrease in cell size results. This results when more than 4 mol. percent $MgCO_3$ is present in the crystal lattice. This substitution appears to be more common in the skeletal calcite of organisms, as shown by Dodd (1967), where the amount of substitution is given for the different phyla. According to Dodd (op. cit.), between 9 and 12 mol. percent $MgCO_3$ may become incorporated in the skeletal calcite of foraminifera, 2 - 4 mol. percent $MgCO_3$ in that of barnacles and 8 - 10 mol percent $MgCO_3$ in bryozoa.

Since the remains of all of these invertebrates have been found in the sediment samples from the *Meteor* cores, some Mg substitution would be expected in the calcite. In this connection, diffractograms were obtained for samples 2-32, 2-34, 2-42 and 2-44 and a crushed barnacle plate, over the angular distance 20 - 30° 2 θ, using Si metal as internal standard, Cu radiation. The positions and d spacing of the calcite $d_{(104)}$ reflection was examined and compared with the calibration curve of Goldsmith and Graf (1958), p.57., it appeared that the calcite in these samples contained approximately 2 mol. percent $MgCO_3$.

Clay minerals

On the basis of a qualitative X-ray examination, by the procedure suggested in Warshaw and Roy (1961), the presence of the following clay minerals has been noted in the sediments: Illite, Montmorillonite, Kaolinite and possibly Chlorite.

Any attempt at the recalculation of the chemical analyses along the lines of Nicholls (1962), Imbrie and Poldervaart (1959), would be difficult to accomplish satisfactorily, in view of the presence of volcanic glass, and the variable amounts and type of detrital feldspar in the sediment. For details of the clay mineralogy of some samples from the Iceland-Faeroes area, the work of Biscaye (1964), Berry and Johns, (1966) should be consulted.

Amorphous silica

Amorphous silica, in the form of opaline sponge spicules, as mentioned earlier, is a conspicuous constituent in the sediment collected at station 2. Apart from the zoological identification the mineralogical nature of these was investigated by a number of methods. The refractive index of these spicules was determined as 1.45 by the immersion method described by Larsen and Bermen (1934). This value falls within the range given for opal in the determinative tables of these authors. The X-ray diffraction pattern obtained from a smear mount prepared from these spicules showed a lack of crystalline structure, with a very broad peak between 17 and 19° two theta (Cu radiation.).

In the literature, there are a number of methods presented for the quantitative determination of opal in marine sediments. A method employing X-ray diffraction is given in Calvert (1966), while Soviet workers employ a method of double extraction by 5 wt percent sodium carbonate solution (anon.1957), Chester and Green (1968) and Chester and Elderfield (1968), describe methods using infra-red spectroscopy, whereby the wavelength region between 10 and 15 x 10^{-6}m is made use of. Opal has two absorption bandheads at 9.20 and 12.55 x 10^{-6}m. respectively, but since the former bandhead is common to all silicate minerals, the latter must be used. Using a similar method to that described in Chester and Elderfield (1968), an attempt was made to determine the amount of biogenic opal contributed to the sediment at station2. The method, however, gave inconclusive results, one of the apparently insoluble problems being the high background in the infra-red spectrum produced by finely divided clay material. This would obviously influence the percentage transmission of the sample disc, and consequently would interfere with any quantitative analysis attempted.

CHAPTER 1.3

CHEMICAL ANALYSIS

Analysis for carbon, carbonate and total water.

Organic carbon, was determined by the wet combustion method described by Groves (1951. pp 114-117). This method makes use of the oxidation of the carbon to carbon dioxide by a hot chromic-phosphoric acid mixture, the gas so produced being absorbed in weighed soda-lime tubes.

Carbonate may be determined by a similar method, as in Groves (op.cit.pp 108-114) or by the method of Shapiro and Brannock (1955b). The latter method can be satisfactorily used when the samples contain less than 1 wt percent carbon dioxide. In the sub-samples from the Meteor cores, the carbonate content is in general considerably higher than 1 wt percent and the method of Groves (op.cit.) was used.

Analysis for total water followed the method described by Riley (1958), where samples are inserted into a combustion tube at 1,100°C. Some samples were also analysed using the modified Penfield method described by Shapiro and Brannock (1955a). The results of these analyses are shown in Table 1.3F at the end of this chapter.

X-ray Emission Spectrography

X-ray Emission Spectrography has been used for the analysis of both light elements in major amounts and heavy elements in minor amounts. Light elements include those elements which have atomic numbers less than Ti, atomic number 22. (See: Liebhafsky et. al. 1960 p.215). These are usually referred to as the major elements when dealing with the commoner type of geological materials. Elements such as Fe, atomic number 26, and Mn, atomic number 25, are also included in the list of major elements, although they would strictly belong to the heavy elements.

The sources of error encountered when using this method of analysis, are listed and discussed in Liebhafsky and Winslow (1958) and will not be discussed further here. Other useful sources of reference, concerning X-ray Emission analysis are: Andermann and Kemp (1958) - Use of scattered X-rays as an internal standard. Baird et. al. (1963) - Na, Mg, analysis. Claisse and Samson (1962) Effects of heterogeneity in sample on analysis, Davis (1958) - Temperature effects on spectrometer. Henke (1964) - Na, F, O_2, N, C and B analysis. Liebhafsky et. al. (1960) - General text on method. Rose et. al (1962) - Use of heavy absorber and sample fusion method. Rose et. al. (1963) - Analysis for the light elements. Norrish and Chappell (in: Zussman 1967) - sample fusion method.

MAJOR ELEMENT ANALYSIS

The following elements were analysed: Si, Al, Mg, Fe, Ca, K, Ti, P and S. An attempt was made to analyse for Na, but due to a number of factors, this was not successful. The range of soda content within the sedimentary standards was inadequate, and more important, the salt content of the sediments tended to form a surface film on the briquettes, resulting in a greatly enhanced count rate for Na, with suppression of the other elements.

It was found that this salt could be removed by washing the samples with distilled water, enabling more reliable analyses to be made for all major elements except Na: the washed samples were not subsequently used in minor element analysis.

Standards

A series of sedimentary rocks, which had been previously analysed by wet chemical methods at Sheffield, Spears (1964), were used as standards. These provided the range of composition required, details of which are given in the Table 1.3C below.

Prior to major element analysis, the samples are made into bricquettes; for theoretical considerations of this technique, see Liebhafsky and Winslow (1958), and for practical considerations, Norrish and Chappell (In: Zussman, 1967). The inert polyvinylalcohol cement Mowiol, suggested by Holland and Brindle (1966), was not used since bricquettes could be made directly by the application of a pressure of 5 tons per square inch (77.2215 MN/m^2.) maintained for three minutes. Bricquettes thus prepared were found to be more uniform in comparison with some made with Mowiol, where there appeared to be surface segregation effects.

The operating settings for the Philips 1212 Automatic Spectrograph, are given in Table 1.3A, and the results of the analyses appear at the end of this chapter. Intensity data for the samples and standards together with chemical analyses of the standards, and mass absorption coefficients were processed by a computer program. Some allowance must also be made for soda, water carbon dioxide, and carbon. These are given empirical mass absorption values, since their omission from the scheme would not be realistic. The program allows direct calibration between the fluorescent intensity, and weight percentage oxides, followed by

Table 1.3A.

Machine settings for Major Element Analysis using Philips 1212 Automatic X-ray Emission Spectrograph.

Element.	Analytical line.	2θ	Wavelength.	Anode.	Voltage.	Current.	Counter.	Collimater.	Crystal.
Si.	K alpha.	109.1°	7.12×10^{-10}m.	Cr.	60 Kv.	8 ma.	Flow.	Coarse.	P.E.
Al.	K alpha.	145.0°	8.34×10^{-10}m.	Cr.	60 Kv.	24 ma.	Flow.	Coarse.	P.E.
Fe.	K alpha.	85.72°	1.94×10^{-10}m.	Cr.	60 Kv.	8 ma.	Flow + Scint.	Coarse.	P.E.
Mg.	K alpha.	81.355°	9.89×10^{-10}m.	Cr.	50 Kv.	40 ma.	Flow.	Coarse.	Gypsum.
Ca.	K alpha.	45.14°	3.36×10^{-10}m.	Cr.	20 Kv.	8 ma.	Flow.	Coarse.	P.E.
K.	K alpha.	50.58°	3.74×10^{-10}m.	Cr.	40 Kv.	8 ma.	Flow.	Coarse.	P.E.
Ti.	K alpha.	36.58°	2.75×10^{-10}m.	Cr.	40 Kv.	8 ma.	Flow.	Coarse.	P.E.
S.	K alpha.	75.78°	5.37×10^{-10}m.	Cr.	50 Kv.	40 ma.	Flow.	Coarse.	P.E.
P.	K alpha.	89.56°	6.155×10^{-10}m.	Cr.	50 Kv.	40 ma.	Flow.	Coarse.	P.E.[1]

P.E.[1] Pentaerythritol.

Table 1.3B.

Machine settings for Minor Element Analysis using Philips 1212 Automatic X-ray Emission Spectrograph.

Element.	Analytical line.	2θ	Wavelength.	Anode.	Voltage.	Current.	Counting time.	Counter.	Analyser xtal.
Ba.	K alpha.	15.53°	0.39×10^{-10} m.	W.	80 Kv.	24 ma.	40 seconds.	Scint.	LiF_{110}
Zr	K alpha.[+]	32.05°	0.788×10^{-10} m.	W.	80 Kv.	24 ma.	40 seconds.	Scint.	LiF_{110}
Sr	K alpha	35,83°	0.88×10^{-10} m.	W	80 Kv.	24 ma.	40 seconds.	Scint.	LiF_{110}
Rb.	K alpha	37.96°	0.99×10^{-10} m.	W	80 Kv.	24 ma.	40 seconds.	Scint.	LiF_{110}
Zn.	K alpha.	60.56°	1.44×10^{-10} m.	W	60 Kv.	32 ma.	100 seconds.	Scint.	LiF_{110}
Cu	K alpha.	65.53°	1.54×10^{-10} m.	W.	60 Kv.	32 ma.	100 seconds.	Scint.	LiF_{110}
Ni.	K alpha.	71.25°	1.66×10^{-10} m.	W.	60 Kv.	32 ma.	100 seconds.	Scint.	LiF_{110}

[+] Correction applied for interference by Sr K beta peak (at 31.92° 2θ.) cf. Norrish and Chappell (In : Zussman, 1967.)

TABLE 1.3C

Element	Range of composition wt percent oxide	Correlation coefficient
SiO_2	9.63 - 67.03 percent	0.974
Al_2O_3	5.57 - 24.50 percent	0.968
Total Fe as Fe_2O_3	1.65 - 10.04 percent	0.977
MgO	0.75 - 8.35 percent	0.998
Cao	0.10 - 26.64 percent	0.999
K_2O	0.82 - 4.54 percent	0.946
TiO_2	0.30 - 1.21 percent	0.981
S	0.01 - 5.31 percent	0.931
P_2O_5	0.03 - 13.78 percent	0.996

normalisation, and application of mass absorption corrections.

The recommended soda value of Turekian and Wedepohl (1961) was used for the Meteor cores, and that of Hirst (1962) for the sediments from the Gulf of Paria (see Section II).

MINOR ELEMENT ANALYSIS

The elements analysed included Ba, Zr, Sr, Rb, Zn, Cu and Ni.

According to Kalman and Hiller (1962) Cr and V are enhanced in matrices which contain greater than 10 wt percent Fe_2O_3. For this reason, and because of line interference on V by Ti, and Mn, Optical Emission spectrography was used for the determination of Cr and V.

Two series of standards were used, one had a shale matrix, and the other a carbonate rich matrix. The standards were prepared by spiking one of the samples to be analysed, with a series of weighed amounts of Specpure compounds of the elements under consideration, to cover the expected range of concentration. This addition method is considered to be more realistic than constructing standards in an artificial matrix. The method of Kalman and Hiller (1962) was used, in which the radiation scattered by the sample is used as an internal standard. These authors derived a mathematical expression relating the intensity of radiation at the fluorescent peak to that scatted at a chosen wavelength in its vicinity, and the concentration of the trace element present. The use of the scattered radiation as internal standard, allows correction for instrumental, sample and absorption effects. (Andermann and Kemp, 1958.).

The samples used as base matrices for the standards were selected after studying spectrometer traces for a number of the samples run over the angular distance 14 - 80° 2θ. Samples generally showing low contents of the minor elements, were selected.

Johnson Matthey Specpure compounds were used in the preparation of the addition standards, and the range of these standards is given in Table 1.3D, together with the correlation coefficients obtained when the intensities of the analytical lines obtained, were plotted against content to produce the calibration curves. All standards had previously been mixed for 6 hours in a large Spex mixing vial before use. Since the carbonate content is markedly higher in Station 2, one of the sub-samples from this core was used to prepare carbonate bearing standards.

TABLE 1.3D

DETAILS OF STANDARDS USED IN MINOR ELEMENT ANALYSIS BY X-RAY EMISSION SPECTROGRAPHY

Standards

Element	Range of concentration	Correlation coefficient
Ba	371 - 196 ppm[1]	0.9989
	985 - 410 ppm[2]	0.9934
Zr	435 - 140 ppm[1]	0.9996
	494 - 209 ppm[2]	0.9969
Sr	1341 - 1106 ppm[1]	0.9986
	369 - 120 ppm[2]	0.9754
Rb	123 - 18 ppm[1]	0.9895
	455 - 123 ppm[2]	0.9994
Zn	226 - 38 ppm[1]	0.9971
	501 - 163 ppm[2]	0.9997
Cu	282 - 61 ppm[1]	0.9929
	325 - 36 ppm[2]	0.9923
Ni	173 - 19 ppm[1]	0.9905
	375 - 78 ppm[2]	0.9879

[1] Carbonate matrix

[2] Shale matrix

Accuracy of X-ray Emission analysis

No comparison has been made directly with International Standards, but some of the analyses obtained for Ba by X-ray Emission analysis were compared with those obtained by Optical Emission spectrography ; these are presented in Table 1.3E. The latter analyses were then compared with results obtained from analysis of the Tanganyika Tonalite T-1 by Optical Emission Spectrography. The results of this comparison are given in Table 1.3H, later in this chapter. There is obvious agreement between the analytical results of the present work and the published values of various authors.

In X-ray Emission Spectrography the use of Ba K alpha as the analytical line, meansthat the background reading lies on the edge of the Tungsten continium (15° 2θ.). This is an important reason for checking the Ba analyses.

TABLE 1.3E

Barium analyses

Sample No.	X-ray Emission Spectrography	Optical Emission Spectrography
1-2	390 ppm	260 ppm
1-4	261	235
1-12	480	355
1-32	340	225
1-42	430	338
2-2	437 ppm	420 ppm
2-4	378	400
2-12	409	390
2-32	386	340
2-42	184	280
6-2	360 ppm	470 ppm
6-4	314	415
6-12	360	380
6-14	292	300
6-24	272	340
7-2	400 ppm	255 ppm
7-4	395	405
7-12	330	450
7-14	336	285
7-31	520	270
8-2	330 ppm	370 ppm
8-12	290	350
8-22	390	420
8-32	310	430
8-42	350	380

TABLE 1.3F

Precision of X-ray Emission Analysis for Minor Elements

During the analysis, one of the samples/standards was used as a monitor, serving as a check on instrumental stability. This has provided data on the precision of the method over an extended period of about three days.

Ba Standard x-j No. of determinations = 13
Average content = 426 ppm
Standard deviation = ± 5.35 ppm
Relative deviation = 1.26 percent

Ni Standard x-d+ No. of determinations = 4
Average content = 361 ppm
Standard deviation = ± 13 ppm
Relative deviation = 3.6 percent

Cu Standard x-j No of determinations = 15
Average content = 53 ppm
Standard deviation = ± 3.15 ppm
Relative deviation = 5.9 percent

Zr Standard x-d+ No of determinations = 4
Average content = 475 ppm
Standard deviation = ± 3.33 ppm
Relative deviation = 0.71 percent

Sr Sample No. 8-4 No of determinations = 4
Average content = 285 ppm
Standard deviation = ± 2.4 ppm
Relative deviation = 0.84 percent

Rb Sample No. 8-4 No of determinations = 4
Average content = 43 ppm
Standard deviation = ± 1.11 ppm
Relative deviation = 2.6 percent

Zn Standard x-j No of determinations = 15
Average content = 173 ppm
Standard deviation = ± 6.33 ppm
Relative deviation = 3.6 percent

Despite the fact that four repeat analyses are not really adequate, for its estimation, precision of the method is obviously high. For all of the elements except Ba, two background positions were used, to allow for slope in the background. Individual correction factors were obtained from a solution of an equation defining the general background slope.

The results of the minor element analysis by this method are given in Table 1.3J at the end of this chapter.

OPTICAL EMISSION SPECTROGRAPHY

This technique was used in the determination of the following trace elements : B, V, Cr and Ba. All determinations were made on a Hilger and Watts Large Automatic Spectrograph Type E.742; photographic plates were then measured with the Hilger and Watts Non-Recording Microphotometer.

This method of analysis has been held by some workers to be qualitative or at best, semi-quantitative due to low precision generally obtainable. Since elements such as B, Cr and V could not be determined, or not determined satisfactorily by X-ray Emission Spectrography, it was decided to make use of Optical Emission Spectrography, with the added advantage of a check on the Ba determined by X-ray Emission.

Boron

The operating conditions for the Spectrograph are discussed in Table 1.3G. Only selected horizons were analysed for B, but these are included in the Table 1.3J at the end of this chapter.

A series of standards were prepared using Johnson Matthey Specpure compounds. Ahrens and Taylor (1961) pp 158-159) indicate the inadequacies of the use of addition standards in Optical Emission Spectrography, hence the use of an artificial matrix for the standards. Ahrens (1955) suggests that synthetic silicate mixtures be sintered for several hours in a furnace in order to improve burning quality, and the precision of the discharge. However, in view of the danger of contamination,this was not carried out for the present work. The base mixture was, however, mixed for six hours in a large Spex mixing vial before being used in the preparation of the standards.

For important details of the analytical method, see Table 1.3G. After the standards had been arced, the densities of the spectral lines on the photographic plate were measured, and used to prepare the necessary calibration curves. The densities of the analytical lines, and those of the internal standard being measured by means of the microphotometer. This measurement, a galvonometer deflection, is used to construct the calibration curve, either as d, galvanometer deflection, or as the Seidel function , $\log(d^o/d-1)$, where d^o is the galvo. reading for clear glass, i.e., full scale deflection for the galvanometer d is the galvo. deflection obtained on the analytical line. Tables of ratio d^o/d are given by Mitchell (1948) for $d^o = 50$, and details of the Seidel function are given in Ahrens (1955, pp. 10, 13.)

The first calibration curve is constructed by plotting d for weak lines against d for strong lines. The advantages of the use of Seidel function is that an extended linear relationship is obtained for weak lines, compared with a curve constructed from

TABLE 1.3G

The Determination of Boron in sediments

For analytical details for this element, see Jones (1969). The only details which differ in the present work are in the exposure time, which was found to give optimum results at 1 minute, with no pre-burn. All other details are similar. Better precision has, however, been obtained in the present work.

Precision of analysis

Sample 6-2 (Meteor)

Average content = 60 ppm
No. of determinations= 3
Standard deviation = ± 3.16 ppm
Relative deviation = 5.2 percent

plotting galvonometer deflection only. An emulsion calibration curve is then constructed, which relates either deflection or the Seidel function to relative line intensity. In the batch calibration method, this curve is constructed for each plate (emulsion) batch, and is used to obtain log intensity ratios of $\frac{\text{element line}}{\text{int. std. line}}$ for all the standards and unknowns. These intensity ratios are then used to produce the calibration curve, relating content of element (in ppm.) in the standards and the log intensity ratio for the analytical lines.

Vanadium, Chromium and Barium

These elements were treated together using Pd as the internal standard. Details of the analytical method are presented in Table 1.3H. Although these three elements belong to the same group of involatile elements (Ahrens 1955 p.85) as Boron, it will be noted that there are difference in detail between the analytical methods used for these elements. The method of batch calibration was used, as described above for B.

The precision of the B analyses is given in Table 1.3G, Cr, V and Ba in Table 1.3H. The precision is low compared to X-ray methods, but is considered satisfactory for the present study.

TABLE 1.3H

The Determination of Cr, V and Ba in sediments

Details of the analytical method are similar in general to those given in Taylor (1962) and Ahrens and Taylor (1961), except that an exposure time of two minutes, after a preburn of ten seconds gave optimum results, consistent with adequate precision.

Precision of analysis

Sample No. 1.42 (Meteor)

		Ba	V	Cr
No of determinations	=	4	5	5
Average value	=	338 ppm	126 ppm	95 ppm
Standard deviation	=	± 40 ppm	± 18 ppm	± 9 ppm
Relative deviation	=	11.9 per cent	14.3 per cent	9.5 percent

Accuracy		Ba	V	Cr
Tanganyika Geological Survey Msusule Tonalite T-1		3	2	1
Published values	:	490 ppm	120 ppm	35 ppm
This work	:	445	130	49

References :

[1] Rooke: in Thomas (1962)

[2] Bowden: in Thomas (1962)

[3] Ingamells and Suhr (1963)

Table 1.3I.

Major element data for <u>Meteor</u> samples.

Sample.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	S	P_2O_5	CO_2	C	H_2O
1-2	47.48	9.71	9.79	3.81	12.03	1.10	1.84	0.33	0.24	5.51	0.36	6.41
1-4	47.69	11.99	11.41	3.76	12.60	1.12	2.10	0.03	0.21	1.54	0.36	3.97
1-12	61.95	10.54	7.67	2.64	6.41	2.21	1.58	0.22	0.15	2.18	0.03	1.14
1-14	61.83	12.53	7.42	1.67	5.11	2.76	1.38	0.00	0.06	0.40	0.25	3.48
1-22	59.37	12.99	5.44	2.41	7.55	2.35	0.94	0.00	0.16	1.24	0.63	3.97
1-24	58.01	11.70	6.12	2.25	7.81	2.22	0.93	0.00	0.13	2.89	0.21	4.79
1-32	57.64	8.70	7.63	3.18	9.40	1.60	1.58	0.23	0.22	4.39	0.12	1.92
1-34	61.61	10.00	4.72	2.11	9.61	2.10	0.98	0.00	0.10	2.60	0.07	3.14
1-42	55.72	9.34	4.89	3.22	8.05	1.71	0.94	0.34	0.19	2.80	0.24	9.38
1-44	61.42	10.84	5.31	2.25	7.67	2.25	1.00	0.00	0.09	1.68	0.95	3.55
Average.	57.27	10.83	7.04	2.73	8.62	1.94	1.35	0.23	0.16	2,52	0.32	4.81
2-2	43.61	12.98	6.12	2.94	12.67	2.31	0.85	0.00	0.20	5.71	0.30	9.59
2-4	48.46	13.46	6.78	3.01	13.71	2.64	0.93	0.03	0.12	3.43	0.04	4.40
2-12	47.46	11.98	5.15	2.53	12.73	2.47	0.72	0.00	0.19	8.93	0.00	5.04
2-14	42.65	11.44	6.52	2.74	17.82	2.33	0.97	0.10	0.15	5.61	1.77	4.85
2-22	31.82	7.83	4.58	2.53	23.76	1.66	0.59	0.32	0.38	17.34	0.22	5.56
2-24	35.66	10.23	4.62	2.32	22.02	2.04	0.66	0.14	0.20	14.48	0.24	4.44
2-32	42.94	10.28	4.86	2.17	16.81	1.98	0.68	0.02	0.24	12.86	0.00	4.32
2-34	14.58	5.21	2.78	1.41	32.53	1.17	0.47	0.07	1.72	30.85	0.68	4.91
2-42	14.48	0.64	2.99	1.45	27.25	0.68	0.36	0.66	0.59	41.62	0.01	4.99
2-44	21.21	5.27	3.19	1.69	33.89	1.16	0.52	0.42	0.39	24.90	0.52	3.62
Average.	34.29	8.93	4.76	2.28	21.35	1.84	0.68	0.22	0.42	16.57	0.47	5.17
6-2	47.99	11.30	7.52	3.92	10.88	2.25	1.13	0.35	0.19	4.67	1.25	5.15
6-4	50.04	12.54	7.37	3.16	11.94	2.30	1.28	0.05	0.11	4.16	0.50	3.56
6-12	48.08	10.58	6.86	3.45	10.49	1.81	1.07	0.18	0.20	3.69	0.67	9.73
6-14	48.90	10.48	7.68	2.64	15.63	2.71	1.04	0.00	0.60	5.12	0.13	2.35
6-22	47.73	12.73	8.96	4.40	10.82	1.57	1.51	0.26	0.18	2.39	1.00	5.29
6-24	49.33	10.34	7.65	2.77	16.76	2.33	1.21	0.00	0.53	3.67	0.42	2.29
Average.	48.67	11.32	8.00	3.39	12.75	2.16	1.20	0.21	0.30	3.95	0.66	4.72

All concentrations in Weight percentages.

Table 1.XI (continued.)

Sample.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	S	P_2O_5	CO_2	C	H_2O
7-2	61.37	9.16	5.62	2.56	7.73	1.91	1.03	0.15	0.33	2.39	0.36	3.31
7-4	63.89	9.75	4.99	1.95	8.12	3.03	0.91	0.00	0.50	0.97	0.47	1.83
7-12	56.68	10.99	8.06	3.65	8.16	1.65	1.77	0.16	0.19	0.72	0.72	3.31
7-14	52.89	14.19	10.46	3.62	7.46	1.94	1.91	0.00	0.18	1.56	0.72	2.95
7-22	47.66	11.78	9.50	3.26	8.09	1.41	1.89	0.00	0.24	1.76	0.79	11.55
7-24	51.47	11.36	9.68	2.87	10.76	1.67	1.72	0.45	0.21	3.29	1.28	3.01
7-31	52.61	12.95	11.94	3.51	9.20	1.46	2.12	0.34	0.16	0.14	1.16	1.35
Average.	55.22	11.45	8.60	3.06	8.50	1.86	1.62	0.27	0.25	1.54	0.78	3.90
8-2	49.14	13.00	8.94	4.15	9.92	2.49	1.20	0.28	0.18	3.46	0.74	3.20
8-4	50.26	13.59	7.86	3.40	11.68	2.48	1.12	0.06	0.16	4.23	0.91	1.26
8-12	45.13	12.92	8.51	4.70	10.75	1.76	1.32	0.32	0.19	2.86	0.59	8.16
8-22	45.37	11.80	6.70	3.74	8.68	2.49	0.87	0.32	0.24	6.33	0.92	9.37
8-32	47.48	12.71	8.21	3.57	12.63	1.89	1.29	0.14	0.21	2.93	0.72	5.32
8-42	49.51	12.02	8.17	4.47	11.87	1.88	1.32	0.28	0.19	4.20	0.87	2.16
Average.	47.81	12.67	8.06	4.00	10.91	2.16	1.18	0.23	0.19	4.00	0.79	4.91
Rankama and Sahama (1950)												
Magmatic rocks;	59.40	15.35	8.37	3.45	5.08	3.12	0.74	0.12	0.27	0.10	0.03	-
Turekian and Wedepohl (1961).												
Deep sea sediments.												
Clays.	53.50	15.85	9.30	3.50	4.06	3.01	0.77	0.13	0.34	-	-	-
Carbonate.	6.87	3.77	1.29	0.67	43.70	0.35	0.12	0.13	0.09	-	-	-
Goldberg and Arrhenius (1958).												
Pelagic sample CAP 31BG, containing basaltic pyroclastics.	47.90	17.75	9.58	3.50	5.88	2.17	2.03	-	-	-	-	-

\- data not available.

Table 1.3 J.

Minor element data for Meteor samples.

Sample.	B.	Cr.	V.	Ni.	Ba.	Zr.	Sr.	Rb.	Cu.	Zn.
1-2	42	113	174	63	390	222	353	21	129	139
1-4	-	97	152	28	261	169	246	18	140	999
1-12	-	66	110	43	480	423	242	46	74	139
1-14	-	-	-	14	528	690	207	58	45	178
1-22	-	-	-	61	411	200	212	58	68	89
1-24	-	-	-	33	395	178	236	55	57	85
1-32	37	120	116	43	340	228	244	38	72	315
1-34	-	-	-	28	370	236	252	48	47	64
1-42	-	95	126	43	430	232	237	53	60	74
1-44	-	-	-	131	403	224	230	61	51	69
Average.	40	99	135	49	400	280	246	46	74	215
2-2	123	155	162	37	437	147	325	46	99	56
2-4	-	124	126	28	378	158	349	48	78	58
2-12	-	120	102	24	409	186	372	50	55	50
2-14	17	-	-	22	412	141	478	36	65	56
2-22	-	-	-	22	292	65	875	32	49	45
2-24	-	-	-	6	376	98	722	39	59	53
2-32	43	124	126	24	386	162	554	38	53	46
2-34	-	-	-	8	185	-	1297	9	67	26
2-42	-	84	-	9	184	3	1091	11	47	26
2-44	-	-	-	12	184	20	1069	13	46	57
Average.	61	121	129	19	324	98	713	28	62	47
6-2	60	150	142	78	360	175	284	75	89	107
6-4	-	-	180	-	314	216	383	37	89	58
6-12	-	148	168	61	360	223	290	56	65	117
6-14	63	131	140	157	292	175	301	28	115	51
6-22	-	-	-	89	240	161	295	43	115	100
6-24	133	140	145	32	272	200	262	24	103	50
Average.	85	142	155	83	306	190	292	43	96	80

All concentrations in parts per million.

Table 1.3J.

Minor element data for <u>Meteor</u> samples.

Sample.	B.	Cr.	V.	Ni.	Ba.	Zr.	Sr.	Rb.	Cu.	Zn.
7-2	28	77	96	39	400	210	251	50	72	73
7-4	-	82	86	25	395	268	216	57	51	67
7-12	-	137	206	52	330	246	248	40	141	109
7-14	155	105	160	50	336	202	218	42	106	125
7-22	-	-	-	61	370	215	230	22	153	158
7-24	-	-	-	39	511	223	275	27	99	140
7-31	-	88	168	52	520	194	206	23	162	124
Average.	91	98	143	45	408	222	234	37	112	113
8-2	137	140	164	86	330	161	242	86	100	126
8-4	54	-	-	34	375	173	288	42	112	58
8-12	-	-	-	86	290	129	287	52	112	113
8-22	-	140	145	80	390	167	243	98	81	122
8-32	85	156	152	85	310	164	300	55	110	111
8-42	-	159	182	88	350	167	339	56	105	110
Average.	92	148	176	76	340	160	283	65	103	106
Rankama and Sahama (1950). Magmatic rocks.										
	3	136	66	66	240	220	175	424	67	110
Turekian and Wedepohl (1961). Deep sea sediments.										
Clays.	230	90	120	225	2300	150	180	110	250	165
Carbonate.	55	11	20	30	190	20	2000	10	30	35
Goldberg and Arrhenius (1958). Pelagic sample CAP 31BG, containing basaltic pyroclastics.										
	120	110	230	190	1100	160	350	na.	640	na.

\- not determined.
na. not available.

CHAPTER 1.4

GEOCHEMISTRY

In this chapter, the distribution of both the major and minor elements within the sediments will be considered. Factor analytical studies made on the data attempt to draw the information together, facilitating interpretation of correlations between the different elements, and identification of the main controls of variance of the data.

MAJOR ELEMENT GEOCHEMISTRY

The distribution of the elements Si, Al, Fe, Mg, Ca, K, Ti, S, P. CO_2, C, H_2O will be discussed within, and between the cores, so that conclusions may be drawn as to their origin and location in the sediments.

Silica

The abundance of SiO_2, as determined by various workers, is listed and compared with the results obtained in the present study in Table 1.31. These SiO_2 values are similar to those of Turekian and Wedepohl (1961) for deep sea clays, although some dilution appears to have occurred, particularly in the sediments from west of the Iceland-Faeroes Rise, the result of the presence of authigenic and bioclastic material, such as organic debris, and precipitated carbonate. The higher silica values east of the Rise, seen in cores 1 and 7, are probably due to the presence of more detrital material in the sediment, some of which may be of Scandinavian origin. While two elements may show correlation they are not necessarily in the same mineral. In the core from station 2, there is a very distinct increase in carbonates with depth, so that the detrital fraction, clay minerals, and resistates such as quartz, must necessarily decrease. Good positive correlation between SiO_2 and K_2O will, therefore, be the result of a parallel decrease in the content of K_2O in illite, and of SiO_2 in clay minerals and detrital quartz.

SiO_2 is clearly present in a number of mineralogical phases: in the tectosilicates, such as quartz and feldspar; the phyllosilicates such as illite, montmorillonite, and possibly chlorite; volcanic glass and as amorphous silica in sponge spicules. Many lithic fragments appear to have been derived from a volcanic source, as shown by the presence of glass shards, Iceland being a possible source for these. The presence of strained quartz grains, microcline feldspar, and highly altered K feldspar suggest a metamorphic provenance. The prevailing water current system c.f. Worthington (1970) indicates that this source area is probably Scandinavia.

Alumina

Alumina is present in two dominant mineral groups, the clay minerals and the detrital feldspar; clays are dominant in the *Meteor* cores.

Correlation coefficients

Station	$Al_2O_3:Fe_2O_3$	$Al_2O_3:TiO_2$	$Al_2O_3:K_2O$
1	0.0720	-0.0935	0.4813
2	0.8891	0.9139	0.9854
6	0.5553	0.8196	-0.4752
7	0.8844	0.8479	-0.4374
8	0.5258	0.2894	0.1623

In all of the cores, with the exception of 1, there is a marked correlation between Al_2O_3 and Fe_2O_3. The close correlation between these constituents suggests their association in a common mineral phase, probably the hydrolysate fraction of the sediment. Since the volcanic shards and the detrital feldspar are common in the sediment from station1, it would seem possible that their presence may account for the low correlation coefficient between Al_2O_3 and Fe_2O_3.

The Al_2O_3:TiO_2 correlation coefficients are high positive except in cores 1 and 8. Goldberg and Arrhenius (1958) note that high TiO_2 values in Pacific sediments can be related to the presence of basaltic pyroclastics within the sediment. While the presence of such volcanic debris in core 1, is undisputed, the overall level of TiO_2 in this core is not any higher than that seen in core 7, where a much closer correlation between Al_2O_3 and TiO_2 is to be seen. The relatively low correlation coefficients may thus be a result of a higher proportion of detrital feldspar in the sediment at station 1 and 8. A qualitative examination of X-ray diffractograms obtained from the samples in these cores would lend support to this suggestion.

The Al_2O_3:K_2O correlation coefficients show a wide variation from core to core. It would be expected that there would be a good positive correlation between the two in view of their presence in both the clay minerals and feldspars. The low correlation coefficients observed in cores 1 and 8 may be due to the presence of volcanic debris and plagioclase feldspar, whose presence has been confirmed by microscope study. K_2O derived from pore water would also influence the correlation. The negative correlation observed in cores 6 and 7 may be due to variation in clay mineral species, with possibly more montmorillonite present than in the other cores, suggested by the good correlation between MgO and Al_2O_3.

In summary, the Al_2O_3 results obtained in this study occupy an intermediate level for deep sea sediments c.f. Landergren (1954), Turekian and Wedepohl (1961). In general, close correlation exists between Fe_2O_3:Al_2O_3 and TiO_2:Al_2O_3, which are mainly the results of the close association of these oxides with the hydrolysate, and detrital fractions of the sediment. Deviations, such as those seen in core 1, and to a less extent in core 8, are probably due to variations in the content of volcanic debris and feldspar in the sediment. The notable variation in the Al_2O_3:K_2O correlation coefficient is attributed to the presence of plagioclase feldspar in cores 1 and 8, while the low negative correlations observed in cores 6 and 7 may be due to the presence of volcanic debris. Areal variation in the distribution of the alumina is in part due to the dilution of the hydrolysate and clastic fractions of the sediment by authigenic and bioclastic $CaCO_3$ and opal.

Total Fe: as Fe_2O_3

Fe in the sediment will be present in a number of locations, the most important being clay minerals.

	Correlation coefficients
Station	Fe_2O_3:TiO_2
1	0.9676
2	0.9710
6	0.8114
7	0.9606
8	0.8244

In all of the cores, there is a close correlation between TiO_2 and Fe_2O_3. This relationship, and the Fe_2O_3:Al_2O_3 correlation is probably due to isomorphous substitution between Ti^{3+}, Al^{3+}, Fe^{3+} and possibly Mg^{2+} in either or both the clay minerals and volcanic glass. According to Grim (1968), in a well crystallised mica, Ti^{3+} may possibly enter octahedral positions in the crystal lattice. However, since there are a smaller number of Al^{3+} substituted for Si^{4+} ions in the lattice of illites than in a well crystallised mica, the charge deficiency on the whole lattice is less. This has marked effects on the amount of substitution possible, and is also one of the reasons for the generally small particle size in illites. Most illites are dioctahedral, but some may show replacement of the Al by Fe or Mg.

The high level of Ti is probably due to the presence of volcanic glass, observed in the coarse fraction of the sediment. From the correlation coefficients listed above, there is obviously marked coherence between Ti and Fe in these sediments. The relationships between Ti and Al has been dealt with earlier, when it was concluded that these elements would occur, together, predominantly in the volcanic debris. It seems possible that Fe is also present in the hydrolysate fraction of the sediment.

It must not be assumed, however, that all of the Fe is present in the illite lattice, since it is quite possible that some of it will be present in the octahedral layers of either or both chlorite and montmorillonite.

In summary, therefore, it would appear that the Fe content of the sediment is located partly in the hydrolysate fraction, and partly in the detrital volcanic glass seen in the cores, because of the close correlation observed with TiO_2 content of the sediment, and a less distinct correlation with Al_2O_3.

Major variation in total Fe from core to core is due to dilution by authigenic and bioclastic material such as calcareous organic fragments and biogenic opal. This dilution is particularly noticeable in core 2.

Magnesia

MgO will be distributed in a number of mineral phases, and possibly also in the pore water, although no analyses of the latter are available. Some Mg will also be present in the calcite substituting for Ca, as indicated by the small shift in the calcite $d_{(104)}$ spacing described above. Magnesia will also be present in the volcanic glass shards found in all of the stations and finally, and possibly the most important site, Mg will occur in the hydrolysate fraction of the sediments. It is an essential constituent of the members of the montmorillonite group of minerals, where it usually occupies an octahedral position in the lattice, and in the chlorite group, where it is present in the brucite layer. Both of these minerals are likely decomposition products of basic igneous material.

In considering which of the mineral phases have most influence in controlling the variance of Mg, it is of interest to consider the correlation coefficients shown below.

Correlation coefficients

Station	$MgO:Fe_2O_3$	$MgO:P_2O_5$	$MgO:Al_2O_3$	$MgO:CO_2$	$MgO:CaO$
1	0.6537	0.9439	-0.4357	0.6132	0.8069
2	0.9599	-0.7094	0.9067	-0.9327	-0.8583
6	0.5273	-0.7228	0.6423	-0.6084	-0.8121
7	0.7940	-0.9318	0.7606	-0.2917	-0.0399
8	0.4593	-0.0739	-0.2465	-0.3205	-0.1177

The strong correlation between MgO and Cao, CO_2 and P_2O_5 occurs only in station 1, where Mg^{2+} may be largely associated with the carbonate phase. A secondary relationship is, however, possible with the volcanic shards, as indicated by the close correlation with Fe. Negative correlation with Al_2O_3 is probably due to the relatively high detrital feldspar content in corel.

In cores, 2, 6, 7 and 8, MgO shows a positive correlation with Fe and in cores 2, 6 and 7 with Al_2O_3. The variance of MgO is thus probably dominated by the hydrolysate fraction and volcanic debris on these cores. Absence of a correlation with Al_2O_3 in core 8 again being attributable to the high feldspar content in that core.

Only in core 6, is there any correlation (0.4943) between MgO and total water. Dehydration of the hydrolysate minerals must have occurred, however, during the drying and grinding processes. During the grinding process which utilises a Tema swing mill, the steel grinding discs became too hot to handle after the 15 minutes grinding.

In summary, MgO in these cores appears to be present mainly in the hydrolysate fraction and volcanic debris of cores 2, 6, 7 and 8. In core 1, there is a relationship with carbonate, possibly also, volcanic debris. Areal variation in the content of MgO is largely influenced by variation in the amount and composition of the detrital fraction.

Lime

Ca is largely present in the authigenic fraction of the sediment as $CaCO_3$, although obviously some will also be present in the silicates, either in clays or in plagioclase feldspar. Plagioclase feldspar, apparently fresh and angular in shape, was noted in the coarse fraction of the sediment from all stations. Ca may also be present in clay mineral lattices; in montmorillonite minerals it would be present in intersheet positions as an exchangeable cation; in illites in interlayer positions proxying for K, and in chlorites possibly, in octahedral positions. Ca, however, is not an important constituent of clay minerals, a result of its relatively high ionic radius compared with Mg^{2+}, and Fe^{2+}.

	Correlation coefficients	
Station	$CaO:CO_2$	$CaO:P_2O_5$
1	0.5569	0.7143
2	0.8227	0.6697
6	0.3334	0.9175
7	0.3740	-0.2605
8	-0.6421	-0.4582

It is obvious that there is some degree of positive correlation between CaO, and CO_2 in cores 1,2, 6 and 7 and a distinct, but negative correlation in core 8. Correlation between CaO, and TiO_2 (0.7360) in core 8, suggests that the Ca may be present in volcanic glass. However, high feldspar contents are known for this core and are thus doubtless responsible for the negative correlation to CO_2.

There is a strong positive correlation between CaO, and P_2O_5 except in cores 7 and 8. This may result from the low concentration of P found in these cores, the average for core 7 being 0.11 percent and core 8, 0.08 percent.

In summary, CaO is the dominant authigenic constituent present in the sediment, as the carbonate. This carbonate is present both as organic debris, such as foraminiferal tests, and finely divided shell fragments. Some precipitated $CaCO_3$ may also be present. Ca also appears, as a minor constituent in phosphates, as suggested by the correlation between P_2O_5, CaO and CO_2 in the cores, as well as plagioclase feldspar and the hydrolysate fraction.

The sediment core collected at station 2, shows the highest content of $CaCO_3$, and was collected from the edge of the submarine channel between Faeroe Bank and Bill Baileys Bank. A strong northwestward flowing current, similar to that observed in the nearby Faeroe Bank Channel, may have influenced the process of sedimentation. There is a distinct increase in carbonate content with depth in this core. The inverse relationship between carbonate and the detrital fraction may indicate a stage, or extended period, when the supply of terrigenous material was either reduced or interrupted. This increase in carbonate content with depth, while seen in other stations, is not nearly so distinct as that at station 2.

Potash

K_2O in these sediments will be present in three possible locations; mainly in the hydrolysate fraction, in detrital feldspar, and in solution in the pore water in the sediment.

	Correlation coefficients	
Station	$Al_2O_3:K_2O$	$SiO_2:K_2O$
1	0.4813	0.9026
2	0.9854	0.9679
6	-0.4752	0.6159
7	-0.4374	0.7951
8	0.1623	0.2838

From the table above, K_2O shows but poor correlation with Al_2O_3, this may be the result of a number of factors. The presence of K derived from interstitial water would probably influence the analysis, and secondly, the presence and nature of the feldspar. The negative correlations discussed above have been attributed to dilution by volcanic debris. Some correlation would be expected between SiO_2 and K_2O through their association with the detrital minerals in the sediment.

Titania

The level of TiO_2 found in these sediments is obviously high, and seems to be related to the content of volcanic glass fragments. Goldberg and Arrhenius (1958) noted a similar relationship, the TiO_2 content of Pacific sediments being related to distance from the Hawaiian Islands. (ibid., p.189, Table 16.) Correns (1954) also comments on this relationship with regard to sediments collected from the Atlantic Ocean between West Africa and Brasil. Volcanic debris and TiO_2 are higher in stations 1 and 7 than in other stations, the low average TiO_2 content of station 2 being due to dilution of the sediment by authigenic and bioclastic carbonate. The difference in average TiO_2 content between stations 1 and 7 as compared with 6 and 8, is probably the result of the intervening Iceland-Faeroes Rise, which appears to have acted as a sediment dam, Coarser debris has thus probably settled out to the east of this dam, only the finer fragments carried along by bottom currents passing over the Rise.

Some of the Ti is probably contained in the hydrolysate fraction of the sediment. Arrhenius (1952) goes as far as to suggest that Ti content can be used as a measure of the total clay content of a sediment.

Sulphur

The average S content does not vary greatly between the cores, but the distribution within the cores fluctuates markedly, making comparison with other elements difficult. This fluctuation may well be the result of poor analytical precision in view of the low concentration of the element in the cores.

The presence of pyrite was noted in X-ray diffractograms although no quantitative assessment was made. Despite the lack of obvious correlation between Fe_2O_3 and S to be expected since the variance of Fe is dominated by other constituents, the sulphur in these sediments is probably present as pyrite.

Phosphorus

The average content of P_2O_5 shows a good deal of variation from core to core, being highest in cores 2, 6 and 7; the P_2O_5 is probably present as calcium phosphate. Rankama and Sahama (1950), and Turekian and Wedepohl (1961), provide average P values for sediments, noting that the content of this element is less in carbonate rich sediments. In the present study, this is not found to be the case.

Since P is an important constituent of cytoplasm, as tissue phosphate and phospho-proteins, it seems reasonable to suppose that sediment containing abundant organic debris should also contain relatively high P_2O_5. Abundant foraminiferal tests, and opal sponge spicules occur in the sediments, particularly in station 2, which has the highest average P_2O_5 content.

P_2O_5 shows a sympathetic relationship to carbonate (CaO) except in cores 7 and 8. Negative correlation between CaO, and P_2O_5, seen particularly in core 8, may be due to the association of Ca with silicates rather than carbonates, as discussed above.

Carbon

Inorganic carbon, i.e., carbon dioxide, is present as $CaCO_3$, which appears to be largely calcite, of either bioclastic or authigenic origin. Foraminiferal tests are the most common recognisable organic remains to be seen in the sediments, although it is quite possible that other organic debris is also present. The distribution of CO_2 listed above can be related to the distribution of calcite in the sediment.

Organic carbon shows correlation with CO_2 in core 8, (0.8069) but not with any other major element. In general, organic carbon is present in minor amounts in these sediments, and in some cases, was not detected. It seems reasonable to suppose that the organic carbon was derived, at least in part, from bioclastic debris.

Water

The results obtained for Total water may be subject to considerable error, due to sample preparation, as described earlier. The results are shown in Table 1.31, for reference.

MINOR ELEMENT GEOCHEMISTRY

In this section, the distribution of the following elements is considered: B, Cr, V, Ni, Ba, Zr, Sr, Rb, Cu and Zn. The chemical analyses are listed in Table 1.3J, together with relevant values from the literature for comparison.

Boron

The level of concentration of this element shows some variation between the cores, but in general, the values lie within the range for sediments obtained by earlier workers, as shown in Table 1.3J. It is obvious from Table 1.3J that B is present in higher concentration in argillaceous than calcareous sediments.

Boron is likely to occur in three main sites; in interstitial water, in the clay minerals, and possibly in detrital resistate minerals such as tourmaline. The hydrolysate fraction would be expected to be the principal site for B, since it dominates the three controls listed above. Harder (1961) has suggested illite to be the most important site for B in sediments, while Porrenga (1967) has shown that reduced crystallinity is likely to enhance the absorption of B in hydrolysate sediments. Qualitative X-ray diffractograms obtained on sub-samples, indicate illite to be the most common clay mineral, and of relatively low crystallinity compared with the Fithian illite. Some degradation may however, have resulted during the grinding process employed in sample preparation.

The relatively low content of B compared with other deep sea argillaceous sediments c.f.Turekian and Wedepohl (1961), Goldberg and Arrhenius (1958), results from dilution by carbonate of either bioclastic or authigenic character. The presence of volcanic debris, detrital feldspar, and quartz will also result in dilution. It is interesting to notice that the B values obtained by Thompson and Bowen (1969) for a coccolith ooze lie close to the values obtained in this study.

Chromium

There is clearly a higher concentration of Cr in cores from west of the Iceland-Faeroes Rise (Cores 2, 6 and 8). This is only slightly offsect by carbonate dilution in core 2, although only two sub-samples, 2-32 and 2-42, have been analysed, and the Cr values may not be truly representative of this core, Moderate positive correlation occurs between Cr and V in all cores. In cores 2, 7 and 8, Cr also shows correlation with Cu, Ni and TiO_2. The correlation between Cr and TiO_2 in core 7 is interesting, since relatively high concentrations of TiO_2 have been related to the volcanic debris discussed earlier in the section dealing with the major element geochemistry. If volcanic debris controlled the variance of Cr, a closer correlation between Cr and TiO_2 would be expected in station 1.

			Correlation coefficients		
Station	Cr:C	Cr:V	Cr:TiO_2	Cr:Cu	Cr:Ni
1	0.4728	0.4361	0.1464	0.2404	0.3020
2	0.8764	0.9362	0.8280	0.8372	0.9882
6	0.9008	0.4896	0.2503	-0.8283	-0.6357
7	0.5336	0.8540	0.5019	0.5336	0.5987
8	-0.1298	0.5334	0.7569	0.7493	0.6327

The negative correlation between Cr:Cu and Cr:Ni in core 6 may result from the presence of Cr in the hydrolysate fraction while the other elements occur in detrital volcanic debris. The content of Cr is distinctly higher west of the Rise, in contrast to TiO_2 which shows a distinct increase in sediments containing visible volcanic debris, from east of the Rise.

The relatively high contents of Cr west of the Iceland-Faeroes Rise are probably associated with the hydrolysate fraction of the sediment. The Cr may have been almost wholly derived from the breakdown of volcanic glass, in view of the relatively high level present in the sediments, and the apparent increase northwards. Goldberg and Arrhenius (1958) suggest that concentrations of Cr in pelagic sediments, greater than approximately 100 ppm. may be useful indicators of the presence of unaltered basaltic pyroclastics. The observed distribution does, however, pose some problems. The Cr content at stations 1 and 7, where volcanic debris is visibly present in the coarse fraction, is lower than that seen in stations 2, 6 and 8 where visible volcanic glass is not as common. Volcanic glass may be present in the cores west of the Rise, in the sub-microscopic fraction, after having been separated from the coarse fraction left on the eastern flank of the Rise during transportation by westward flowing currents. Alternatively, if the Cr is largely located in the hydrolysate fraction of the sediment, a higher proportion of clay minerals would be expected in the cores collected from west of the Rise.

Vanadium

Average V contents are somewhat higher than those reported in the literature, Table 1.3J, except by Goldberg and Arrhenius (1958). In general, higher average concentrations occur to the west of the Iceland-Faeroes Rise; there is a moderate to strong positive correlation with Cr. The V, in common with Cr, may be derived from basic volcanic debris, but probably occurs in the hydrolysate fraction. Landergren (1954) ascribed the distribution of V to volcanic debris in core 238 of the Swedish Deep Sea Expedition; the level was however, much lower than in the present study.

Nickel

The levels of Ni are relatively high in two of the stations from west of the Iceland-Faeroes Rise, while there is a decrease in the average content in the core from station 2. Apart from these variations, the level of concentration lies within the range suggested by earlier workers, shown in Table 1.3J.

Correlation coefficients

Station	Ni:TiO_2	Ni:Cu	Ni;C	Ni:Cr	Ni:Zn	Ni:Rb
1	-0.2329	-0.0638	0.8285	0.3020	-0.2840	0.2249
2	0.7207	0.6335	0.0265	0.9882	0.5339	0.7278
6	-0.2066	0.4803	-0.3400	-0.6357	-0.2443	-0.1520
7	0.8287	0.9075	0.3260	0.5987	0.7621	-0.7275
8	0.3030	-0.2563	-0.4889	0.6327	0.9420	0.4255

Ni, in general, shows but poor correlation with TiO_2, and hence probably to volcanic debris. An exception is station 7, where in view of the good correlation with TiO_2, and negative correlation with Rb, an association with volcanic debris is suggested. The correlation data suggest that Ni is related to either the hydrolysate or detrital fractions, but the correlation with the elements Cu, Cr and Rb. In some cores, there is obviously a similarity between the distribution of Ni, Cr and V which may indicate a common derivation from the breakdown of volcanic debris mentioned above.

In summary, Ni, in general, is present in higher concentration west of the Iceland-Faeroes Rise. Levels of concentration are lower in station 2, because of the dilution effect by carbonate. The Ni appears to be present either in volcanic debris or in the hydrolysate fraction. In view of the poor correlation between Ni and TiO_2 the hydrolysate fraction may be the more important site, except possibly in station 7.

Barium

The results shown in Table 1.3J are in agreement with those of earlier workers. The level of concentration is higher east of the Iceland-Faeroes Rise in cores 1 and 7, than in cores 2, 6 and 8.

			Correlation coefficients		
Station	Ba:Zr	Ba:Rb	Ba:Zn	Ba:TiO_2	Ba:CaO
1	0.7842	0.6406	-0.6723	-0.3718	-0.8588
2	0.9330	0.9484	0.6589	0.8597	-0.9332
6	0.4905	0.7060	0.4573	-0.6893	-0.4234
7	-0.3057	-0.4691	0.1707	0.1732	0.8331
8	0.7599	0.3562	-0.3267	-0.8036	-0.3943

The higher level of concentration of Ba in the cores east of the Rise may result from the higher concentration of detrital material in these cores. The correlation between Ba and Zr, except in core 7, might support this.

Ba most commonly substitutes for K in feldspar in igneous rocks, and is removed from sea water during the deposition of hydrolysate minerals where it will substitute for K in intersheet positions. Rankama and Sahama (1950) have suggested that near shore sediments would be enriched in Ba relative to those accumulating in the deeper regions, but Turekian and Johnson (1966), conclude that deep sea sediments are relatively enriched in Ba, and suggest barite as a possible site for Ba. They further conclude that high Ba containing water does not necessarily overly Ba enriched sediments, and that vulcanism may be the possible primary source of Ba.

The presence of feldspar in the sediments of the present study, together with its distribution suggest that most of the Ba is present in the detrital (resistate) phase, as opposed to the hydrolysate fraction. The good correlation between Ba, Rb, Zn and TiO_2 in core 2, reflect parallel decreases in hydrolysates and resistates by dilution with carbonate. The correlation between Ba and CaO in core 7, must have resulted from the sympathetic increase of carbonate and detrital material without a sympathetic increase in Zr, as expected.

Zirconium

The results of the analysis for this element are shown in Table 1.3J. The higher level of Zr east of the Rise is probably attributable to detrital zircon, possibly of Scandinavian origin.

There is generally good correlation with Ba, which supports the suggestion that most of the Ba is located in detrital feldspar, as discussed above.

Strontium

This element, is on average, lower in stations 1 and 7 than in 2, 6 and 8, the highest average concentration is in station2. Correlation between Sr and CaO is high in cores 1, 2 and 8 but insignificant in 6 and 7.

	Correlation coefficients
Station	Sr:CaO
1	0.6830
2	0.9662
6	-0.3854
7	0.4863
8	0.6018

Most of the Sr is probably present in the carbonates, the poor correlations seen in stations 6 and 7, being possibly due to the lower average content of carbonate in these cores. Calcite is the dominant carbonate mineral in the <u>Meteor</u> cores and the dominant constituent in the sediment from station2.

The suggestion of Rankama and Sahama (1950) that Sr is present as strontianite, in association with calcite, may be valid although no distinct Sr minerals have been detected in the present work. The possible diadochic replacement of Ca^{2+} by Sr^{2+} in plagioclase or of Sr associated with hydrolysates must not be ruled out, but it is assumed that this would be of only minor importance in the cores under consideration.

Rubidium

No distinct differences are to be seen in the level of concentration of the element between the stations east and west of the Iceland-Faeroes Rise. No marked correlation between Rb and the other elements is to be seen consistently in the sediments, and thus it is difficult to draw definite conclusions as to the exact locations of the element in the sediments. It seems probable that Rb is mainly associated with the hydrolysate fraction.

Copper

While the values obtained in the present study lie within the range observed by previous workers, it is interesting to note a distinct increase in Cu content northwards.

	Correlation coefficients			
Station	Cu:TiO_2	Cu: CaO	Cu:Ni	Cu:Zn
1	0.8384	0.8170	-0.0638	0.7094
2	0.6224	-0.5270	0.6335	0.3248
6	0.4156	0.5160	0.4803	-0.5317
7	0.8934	0.1374	0.9075	0.7422
8	0.8237	0.8322	-0.2563	-0.5035

The good correlation between Cu and CaO seen in cores 1, 6 and 8 is an association which hasbeen noted before in both Pacific pelagic sediments by Revelle et. al. (1955), and in the Atlantic Ocean by Turekian and Imbrie (1966). Revelle et. al (op. cit.) suggest that the correlation is due to biogenic Cu associated with the soft parts of organisms, or their excreta, accumulating in the sediment at a rate in general proportional to that ofthe bioclastic material. This seems in reasonable agreement with the correlation coefficients seen for stations 6 and 8, where there is abundant bioclastic debris, but not for station 2, where both the levels of Cu and the correlations with CaO are low.

The increase in Cu content northwards may represent an association with volcanic debris originating in Iceland. Recommended values noted by Rankama and Sahama (1950) indicate a distinctly higher concentration in basic magmatic rocks, in contrast to acid types. Sediments containing, or derived from, basic volcanic debris would thus be expected to show a higher concentration of Cu. Some of the combined Cu may pass into solution in the pore water of the sediment and be either absorbed ultimately on one of the clay minerals, or under favourable conditions, be precipitated in sulphides.

The lowest average Cu content seen in core 2, is the result of dilution of the hydrolysate fraction of the sediment, probably the main site of Cu^{2+} ions, by carbonate.

Zinc

Slightly higher Zn contents are shown by stations 1 and 8, in comparison to 2 and 6. The range of concentration, however, lies within that suggested by earlier workers. There is in general a slight overall increase in concentration northwards. which would suggest the possible influence of volcanic debris, notably present in cores 1 and 7. Station 2 shows the lowest average Zn content due to dilution of the detrital fraction by $CaCO_3$.

To conclude this section on the geochemistry of the minor and major elements, it is considered relevant to include a comparison and discussion of the distribution of some minor elements in stations 1 and 7 with the conclusions of Angino (1966). The reason for this is to discover if the minor element distribution in these cores qualify them as glacial marine sediments, as suggested in Chapter 1.2 of this thesis, after a comparison of the

Table 1.4A.

A comparison of elemental ratios obtained for the cores from Stations 1 and 7, with the limits suggested by Angino (1966) as being indicative of particular sedimentary environments.

	After Angino, (1966).			Present work.	
Ratio.	Deep Sea Clay.	Carbonate.	Glacial Marine.	Station 1.	Station 7.
Cu/Al.	0.30×10^{-2}	0.15×10^{-2}	0.20×10^{-2}	0.12×10^{-2}	0.18×10^{-2}
V /Al	0.14×10^{-2}	0.10×10^{-2}	0.30×10^{-2}	0.23×10^{-2}	0.23×10^{-2}
Cu/Fe	0.40×10^{-2}	0.046×10^{-2}	0.40×10^{-2}	0.15×10^{-2}	0.18×10^{-2}
Cr/Al	1.07×10^{-3}	0.55×10^{-3}	1.20×10^{-3}	0.17×10^{-2}	0.16×10^{-2}
Ni/Al	2.70×10^{-3}	1.50×10^{-3}	0.50×10^{-3}	0.80×10^{-3}	0.70×10^{-3}
Fe/Al	0.77	0.45	0.51	0.86	0.99
Ti/Al	0.55×10^{-1}	0.38×10^{-1}	0.49×10^{-1}	1.4×10^{-1}	1.6×10^{-1}
Cr/V	0.75	0.55	0.45	0.73	0.69
Fe/Ti	14.00	11.70	10.50	6.09	6.21

lithology of the cores with those of Holtedahl (1955, 1959).

Unfortunately, it is not possible to use all the criteria suggested by Angino (op.cit.) because of a lack of data, but 9 ratios out of a possible 14 have been used. This comparison is shown in Table 1.4A.

It is obvious that while some of the ratios lie within the range observed by Angino (op.cit.) such as Cu/Al, V/Al, Ni/Al and Fe/Ti, others do not. These include the ratios Cu/Fe, Cr/Al, Fe/Al, Ti/Al, Cr/V. The influence of volcanic debris would obviously affect all of these ratios and result in divergence from the results of Angino (op.cit.). In any case, the variation between sediment types listed by Angino does not appear to be very conclusive.

FACTOR ANALYSIS

The major and minor element analyses of the *Meteor* cores were processed using a Factor Analysis program. The statistical basis of the technique was published by Karl Pearson in 1901, and developed by Charles Spearman over a period of forty years, mainly in psychometric studies. The result of this work by Spearman and subsequently by other workers, was the development of the procedure known as Factor Analysis. This has been made use of in the past few years by a number of workers in the geological field; Spencer et. al. (1967), Spencer (1966), Turekian and Imbrie (1966), in geochemical interpretation; Imbrie and van Andel (1964) on heavy mineral data; and Khaleelee (1969), on geochemical prospecting.

The basic principles of Factor Analysis are described by Cattell (1965), and have been summarised by Spencer (1966), Reeves and Saadi (1970). In Factor Analysis, data must be provided for every element in each sub-sample. This means that elements such as B, Cr and V for which analyses are only available for selected horizons cannot be used. The distribution of 19 variables in 39 sub-samples from the Meteor cores was examined by this multivariate technique; the variables being SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, K_2O, TiO_2, S, P_2O_5, CO_2, C, H_2O, Ni, Ba, Zr, Sr, Rb, Cu and Zn. Since the distribution of most elements is better approximated by a lognormal rather than a normal distribution, the logarithm of concentration of each element is used to form the correlation matrix for Factor Analysis.

From the principal factor pattern obtained, given in Table 1.4C, it is obvious that there are 9 dominant factors, accounting for 96 per cent of the variance of the original data, including all factors which account for more than 2 percent of the variance. A list of the eigenvalues and cumulative percent of total variance explained, is given in Table 1.4B.

The promax oblique factor matrix, K min 8, is given in Table 1.4D and Factor scores are plotted in FIGURE 1.41. The latter are of particular value in areal studies, and, as will be shown later, show distinct changes east and west of the Iceland-Faeroes Rise.

It is obvious from Table 1.4D, that the dominant factors are 3, 7, 8 and 9. The remaining factors account for the variance of only one element in four instances, factors 1, 4, 5 and 6, while factor 2 is chiefly concerned with the variance of Zn but has an opposed Ba loading. The opposed loadings on the four dominant factors are shown below.

TABLE 1.4B

Eigenvalues	Cumulative percent of total variance
8.990	47.319
3.256	64.458
1.621	72.994
1.055	79.448
0.941	84.402
0.773	88.474
0.639	91.840
0.432	94.116
0.397	96.206
0.261	
0.179	
0.137	
0.109	
0.076	
0.059	
0.028	
0.022	
0.010	
0.007	
18.999	

TABLE 1.4C

Principal Factor Matrix

	1	2	3	4	5	6	7	8	9
SiO_2									0.92
Al_2O_3			-0.40						0.78
Fe_2O_3								0.47	0.82
MgO							0.40	0.59	0.63
CaO									-0.87
K_2O						0.40	0.38	-0.59	0.51
TiO_2								0.41	0.85
S					-0.67			0.59	
P_2O_5	0.45					0.34			-0.68
CO_2							0.33		-0.84
C				-0.74	0.28			0.45	0.31
H_2O					0.41	-0.67	0.51		
Ni			0.42				0.38	0.30	0.67
Ba		-0.39						-0.44	0.69
Zr							-0.43	-0.43	0.63
Sr									-0.94
Rb							0.54	-0.41	0.64
Cu								0.76	0.47
Zn		0.37				-0.34		0.38	0.64

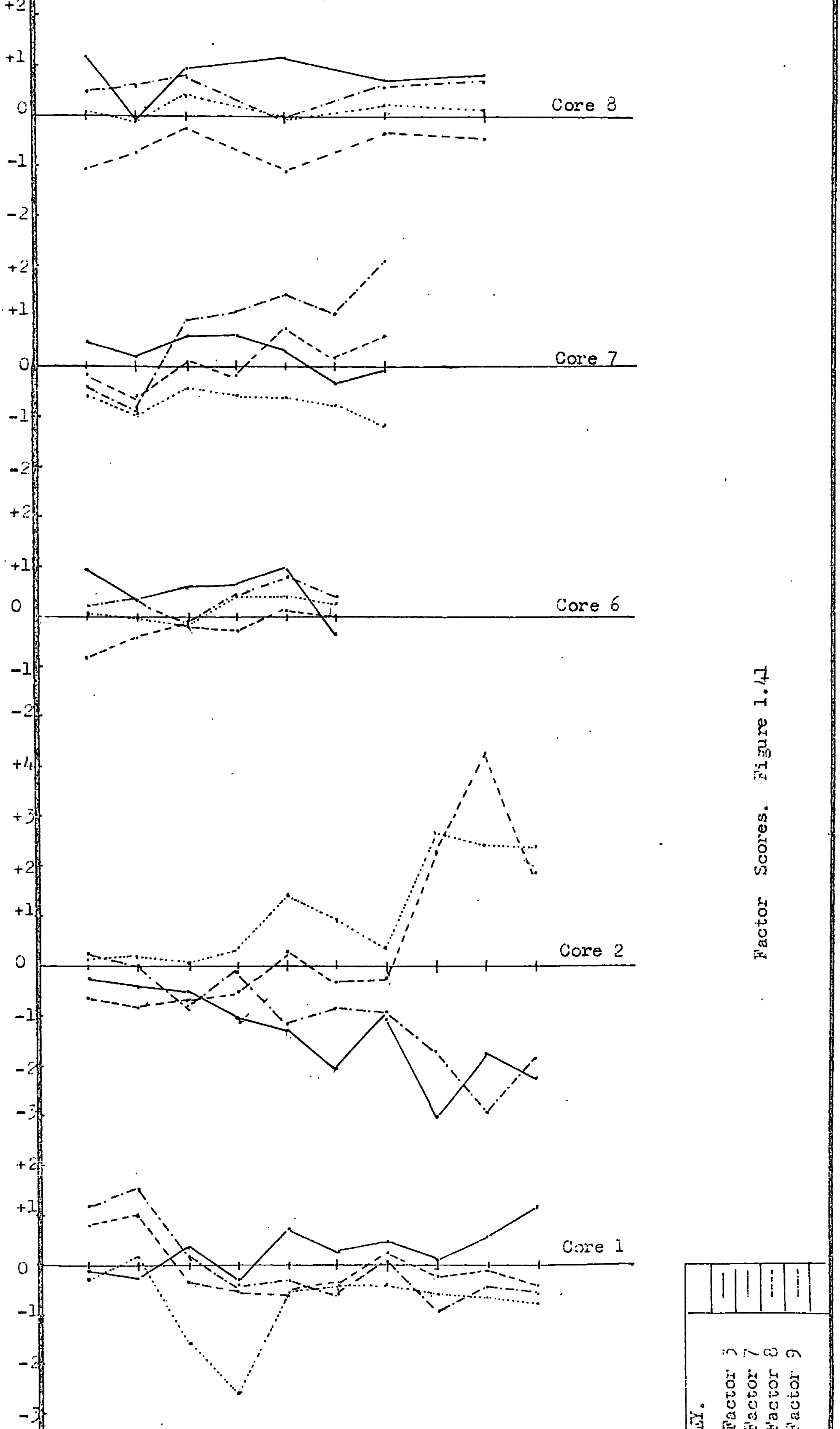
Factors less than 0.30 omitted

TABLE 1.4D

	1	2	3	4	5	6	7	8	9
SiO_2							-0.44	-0.34	
Al_2O_3			-0.33					-0.84	0.40
Fe_2O_3									0.79
MgO			0.39				0.37		0.67
CaO			-0.36				0.75		
K_2O								-1.07	
TiO_2									0.60
S					-1.08				
P_2O_5	1.42								
CO_2							0.37		
C				-1.09					
H_2O						-1.04			
Ni			1.07						0.38
Ba		-0.41					-1.11		
Zr							-1.31		
Sr			-0.42				0.40		
Rb			0.40					-0.60	-0.44
Cu									1.17
Zn		1.11							

K min = 8.

Factors less than 0.30 omitted



Factor Scores. Figure 1.41

	Factor 3	Factor 7	Factor 8	Factor 9
+	MgO, Ni, Rb	MgO, CaO, CO_2, Sr.		Al_2O_3, TiO_2 Fe_2O_3, MgO.
-	Al_2O_3, CaO Sr.	SiO_2,Ba, Zr.	SiO_2, Al_2O_3, K_2O, Rb.	Rb

Factor 7

This is the most distinct, and most important factor, with MgO, CaO CO_2 and Sr loadings, opposed by SiO_2, Ba and Zr. FIGURE 1.41 clearly shows that there is a distinct systematic variation in the scores for this factor between the cores east and west of the Iceland-Faeroes Rise. This factor represents a balance between SiO_2, Ba and Zr, the detrital content of the sediment, and the authigenic and bioclastic fraction represented by CaO, MgO, CO_2 and Sr. In chapter 1.3, it was noted that quartz is present in higher concentration in the two stations east of the Rise. When weight percent quartz is plotted against the scores for this factor, a relationship approximately linear emerges. This is shown in FIGURE 1.42, and would support the suggestion that the negative loading represents the detrital fraction. Ba, as discussed earlier, is able to proxy for K^+ in feldspar, which is a relatively important constituent of the sediment east of the Rise. The association CaO, MgO, CO_2 and Sr is a common one and clearly represents carbonate, as discussed above.

Factor 8

This factor has loadings of SiO_2, Al_2O_3, K_2O and Rb and would appear to represent clay minerals, probably illite. FIGURE 1.41 indicates that the highest scores for this factor are shown for stations 2, 6 and 8. If the higher scores had been in stations 1 and 7 the factor could have represented K feldspar. Although higher scores occur west of the Iceland-Faeroes Rise, the factor scores in all the cores,

Figure 1.42

Scores for Factor 7 plotted against Weight percent Quartz.

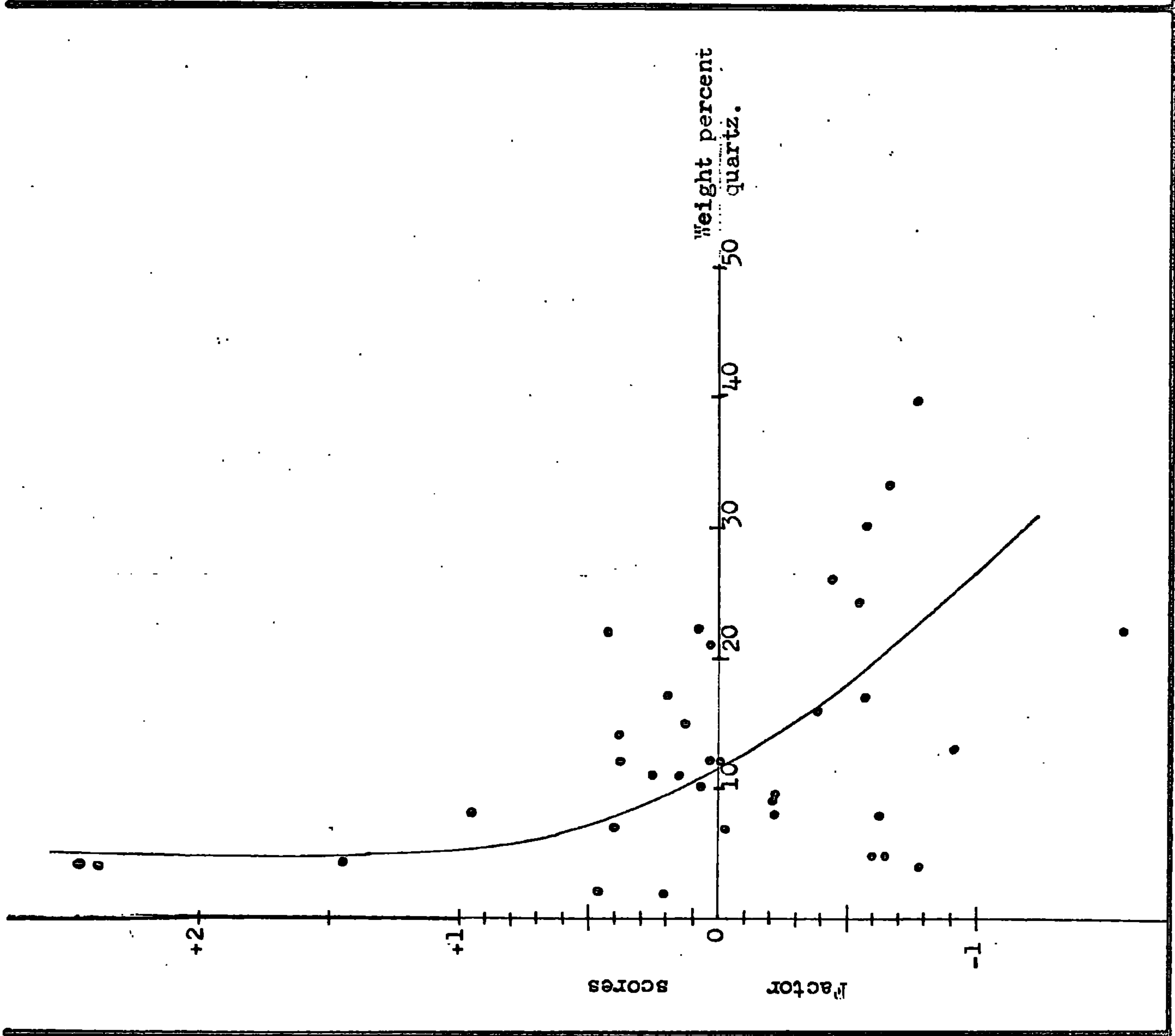


TABLE 1.4E

Factor correlation matrix

	1	2	3	4	5	6	7	8	9
1	1.00	-0.61	-0.68	0.32	-0.32	0.01	0.81	0.69	-0.54
2		1.00	0.67	-0.47	0.20	0.11	-0.58	-0.34	0.72
3			1.00	-0.41	0.23	-0.01	-0.63	-0.58	0.55
4				1.00	-0.21	-0.13	0.34	0.16	-0.54
5					1.00	0.26	-0.56	-0.22	0.17
6						1.00	-0.24	0.10	0.13
7							1.00	0.58	-0.51
8								1.00	-0.36
9									1.00

since illite is possibly the most common constituent in these sediments.

Factor 9

In this factor, Al_2O_3, Fe_2O_3, MgO, TiO_2, Ni and Cu are opposed by Rb, and the factor is believed to represent detrital volcanic debris. Some systematic variation is visible about the Iceland-Faeroes Rise, as shown in FIGURE 1.41, with distinctly higher scores in cores 1 and 7, than in cores from west of the Rise. Factor scores increase from stations 1 and 2, to 6, 7 and 8. The low scores of station 2 are not entirely due to its southerly position relative to other stations but also result from its high carbonate content. The possible association of Ni, TiO_2 and Cu with volcanic debris has been discussed above, together with the possible relationship between Cu and Ni and the hydrolysate fraction. Clearly the volcanic glass would have been formed at temperatures of the order of 1000°C, and hence would be metastable in the marine environment, breaking down to form clay minerals, probably chloritic or montmorillonitic in character. The increase in factor scores northwards, and eastwards, suggests that Icelandic provenance influences this factor.

Factor 3

On this factor, Mg, Ni and Rb are opposed by Al_2O_3, CaO and Sr, possibly suggesting an opposed clay-carbonate factor. A consideration of FIGURE 1.41 indicates that the Mg, Ni and Rb side of this factor is dominant in all cores, except 2, with generally higher scores in stations 6 and 8 compared with station 1. This would suggest a relationship with the hydrolysate rather than resistate fraction of the sediment. The significance of the Al_2O_3 loading with CaO and Sr is not clear.

Factor 1

This has a loading for P_2O_5 only and may result from the generally low level of concentration of the oxide, and low analytical precision.

Factor 2

On this factor, Zn is loaded against Ba. In the discussion earlier, Zn was considered to be present mainly in the hydrolysate fraction of the sediment, with some Ba being present in the detrital feldspar.

Factor 4

Carbon scores on this factor. Again the low concentration of this element makes correlation difficult with other elements and introduces the possibility of low precision influencing the results.

Factor 5

The element S scores on this factor, and as mentioned in the discussion on the element, low analytical precision would be expected because of the low concentration found in the Meteor cores.

Factor 6

Total water scores on this factor, and as mentioned earlier, analyses of this are believed to be suspect, as a result of the drying and grinding process used in the sample preparation.

In summary, 4 dominant factors emerge from a consideration of the distribution of 19 chemical variables in the Meteor cores. These include carbonate, detrital material, clays and volcanic debris. Trends are to be seen when the Factor scores are compared between cores. When the detrital phase is compared with the carbonate, it plays a dominant role in station 1 and 7, but only a minor role in stations 2, 6 and 8.

Two factors attributable to the clays emerge, one K bearing, the other Mg bearing, with both showing greater importance in stations 2, 6 and 8 than in 1 and 7. Volcanic debris and/or their alteration products have higher scores in stations 6, 7 and 8 than in 1 and 2, representing a northwards increase. It is of interest to note the importance of using only good analyses in Factor analytical studies, as shown in the discussion on factors 1, 4,5, and 6.

CONCLUSIONS

1. The Iceland-Faeroes Rise has acted as a sediment barrier, or dam, for relatively coarse detrital material, some of which having been derived from a source area which includes some metamorphic terrain.
2. True marine sedimentation, i.e., precipitation of carbonate sediment, becomes important in the stations to the west of the Rise.
3. Iceland has overprinted the sediments by the introduction of volcanic glass debris. The greater proportion of unaltered debris in the two cores from east of the Iceland-Faeroes Rise may be the result of the prevailing westerly winds.
4. The bottom currents flowing over the Iceland-Faeroes Rise may have carried over either the fine fraction of the volcanic debris, or its alteration products, into the west of the area.
5. A comparison of the results on the cores obtained at stations 1 and 7, with the results of Angino (1966) are inconclusive since the trace element ratios used by Angino (op.cit.) have been influenced by the presence of volcanic debris.

SECTION 2

GEOCHEMICAL STUDIES OF SEDIMENTS
FROM
THE GULF OF PARIA, VENEZUELA.

CHAPTER 2.1

Introduction

The gulf of Paria is a shallow, land locked basin off the N.E. coast of South America. The Gulf is bordered to the north by the mountains of the Peninsula of Paria, and the Northern Range of Trinidad; the northern coastline is steep, rocky and deeply indented. The eastern side of the Gulf is marked by low cliffs and long beaches which border the hilly country of Central and Southern Trinidad, only one important stream occurs here, the Caroni River. In the south and west, the Gulf is bordered by extensive mud flats and estuaries, forming part of the delta of the Orinoco river. The Gulf is connected to the Atlantic Ocean by a long channel, the Serpents Mouth, and to the Caribbean by a deep, island studded trough of structured origin the Dragons Mouth. The latter is separated from the deepest part of the Gulf by a sill at 27m., and from the Caribbean by a sill at 95m.

Bottom relief of the Gulf is very gentle, with a maximum depth of approximately 40m., except for a relatively deep trough and narrow channel in the western part, and the rugged relief of the Serpents Mouth and Dragons Mouth. Widespread shallows exist in the western part, around S.W. Trinidad and in the N.E. corner. The floor of the Gulf is covered predominantly by very fine mud, while a sandy platform surrounds S.W. Trinidad, with outcrops of rock around the Soldado Rock, and the Serpents Mouth.

The Peninsula and Northern Range mentioned earlier, are the eastwards continuation of the Venezuelan Coast Range, consisting of low and medium grade metamorphic rocks of late Jurassic and Cretaceous age. The Central and Southern ranges of Trinidad are made up of

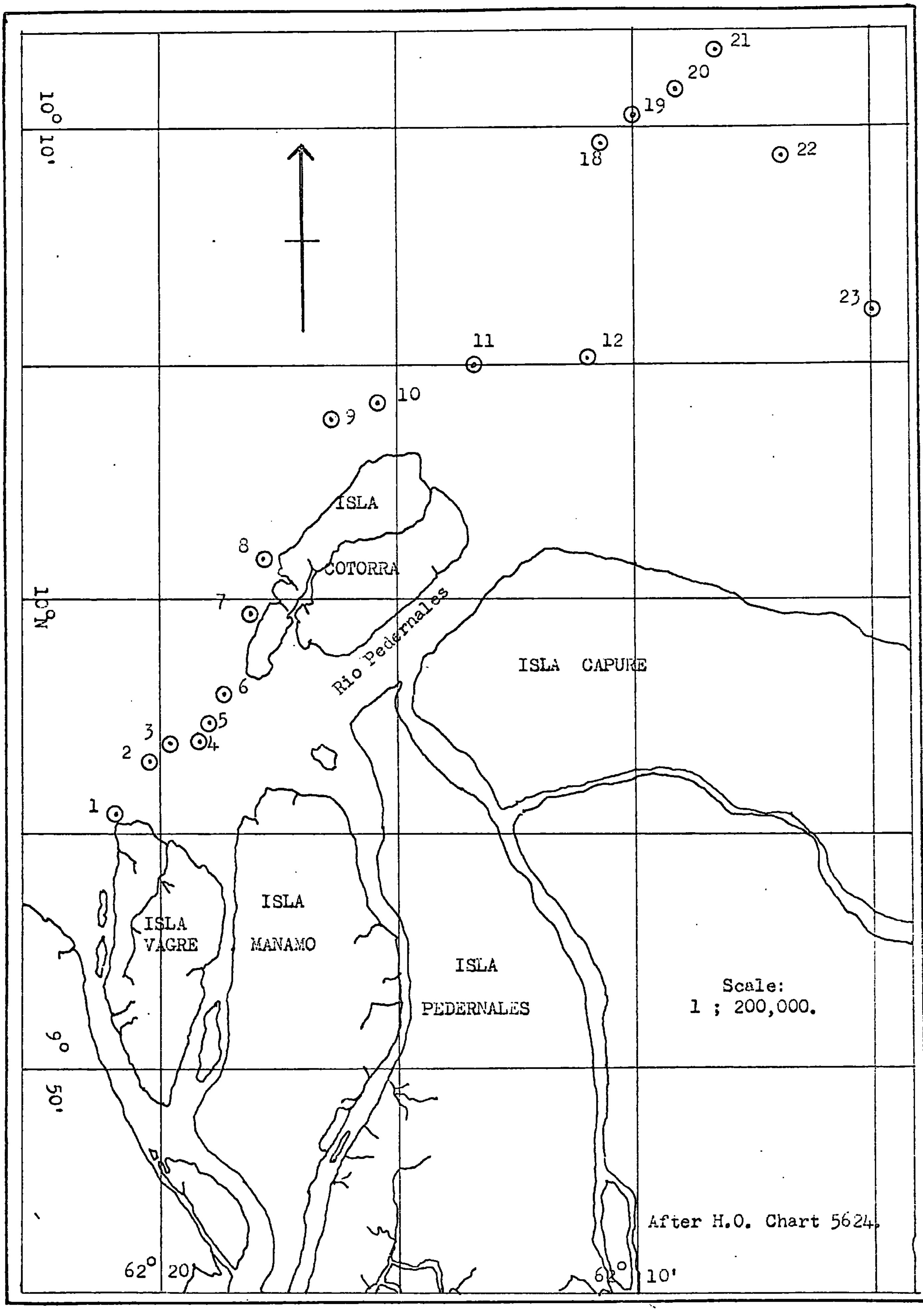
Tertiary sediments with complex faulting and numerous diapiric structures these are considered to be the eastward extension of the Interior Range of Venezuela. This trend can be observed to continue from S.W. Trinidad over the Soldado Rock area to the Pedernales and Guanipa sub-surface structures in the northern Orinoco Delta. Between the Central and Northern Ranges of Trinidad is a broad synclinal trough with a large thickness of late Cenozoic sediment. The central and northern portions of the Gulf are generally considered to be westward extensions of this depression.

The Gulf of Paria has been the scene and subject of considerable research during the last twenty years. The first, and possibly the most detailed, published study of the Gulf was that of van Andel and Postma (1954), based on material collected by the Orinoco Shelf Expedition during 1952-53. Nota (1958) continued with a discussion of the sediments of the Northern Guiana shelf carried out during the latter part of the Expedition in 1953. Both of these studies were primarily of a sedimentological and micropalaeontological nature, but geochemical studies on material collected by van Andel and Postma (1954) were subsequently made by Hirst (1958, 1962a, b.).

When Woods Hole Oceanographic Institution organised Cruise 35 Equalant, plans were drawn to collect a series of gravity cores from the Boca Vagre in the S.W. portion of the Gulf. The location of these stations was decided after a consideration of the results of Hirst (1962a, b.) which indicated a distinct change in the nature of the sediments accumulating there, particularly with reference to the dominant type of clay mineral. Besides the collection of the suite of cores, Chain Cruise Equalant was also concerned with the structure of the sediments which was investigated by acoustic reflection methods. (van Andel and Sachs, 1964)

The cores collected in a traverse from the Boca Vagre into the western entrance of the Serpents Mouth, should, according to Hirst (1962a,b.) cross the boundary between a sediment in which the dominant clay constituent

Figure. 2.11
Sample locations in Boca Vagre, Gulf of Paria.



was illite, to one where montmorillonite is dominant. The core stations are indicated in FIGURE 2.11, after U.S. Hydrographic Office chart 5624.

Exact details of the gravity coring equipment are not available, but it is believed to have been a free corer of the type described by Moore (1961), using plastic liners. The complete cores received at Durham in 1967, although sealed in plastic liners, were in a thoroughly dry state. As a result of the drying out process, some colour changes had resulted, in all probability, reflecting chemical changes due to oxidation. In some of the cores, particularly those collected out into the Gulf, the process of drying had resulted in noticeable shrinkage. Unfortunately, no detailed logs of the cores, on collection, are available, and only very brief descriptions were made when the cores were opened in Durham. These will be mentioned in the next chapter, where the mineralogy of the samples will be considered.

It is of interest to mention a review by van Andel (1967) on the Orinoco Delta, and also the work of Seiglie (1968) on the foraminiferal assemblages of the Gulf of Cariaco, Eastern Venezuela and their relationships to the high C content in sediments, and polluted waters.

The object of the present study was to study the mineralogy and geochemistry of the cores, and see what variations are present; commenting on their significance; use will also be made of Factor Analysis. A comparison of the results of Hirst (1962a, b,) is also to be made, particularly with regard to the minor and major element geochemistry.

CHAPTER 2.2

MINERALOGY

Sub-sampling scheme

Sub-samples ,between 0.07 and 0.10m in length,were taken from the dry cores at selected horizons after first being removed from the plastic liners. Some cores, numbers 18, 19 and 20 had had the top 0.035m removed beforehand for foraminiferal work at Woods Hole Oceanographic Institution. Sub-sampling was carried out uniformly, so that the whole of the core would be sampled for geochemical and mineralogical studies. Separate sub-samples were removed from each core for grain size analysis, usually the 0.08m section between 0.18 and 0.26m depth in the core, except in core 4, where this had to be taken from between 0.34 and 0.42m. Actual lengths of cores together with horizons of the sub-samples and their sample numbers are shown in Table 2.2A. The same sub-samples were analysed for both the mineralogy and geochemistry, after being subject to similar grinding times as the Meteor cores, i.e., 15 minutes. No microscopical examination has been made on the samples in the present study.

/ m.

Grain size analysis

This was carried out on selected horizons from each core, as mentioned earlier. The analytical method will not be elaborated here as this has already been adequately documented elsewhere, in Milner (1962), and BS 1377 (1961).

The samples were first of all subject to pipette analysis when the content of material less than 0.06×10^{-6}m. in diameter was determined. The coarse fraction was then dry sieved using B.S. sieves with a mechanical shaker.

$\times 10^{-6}$

TABLE 2.2A

Lengths of cores collected from the Gulf of Paria.

Chain Cruise, 35, Equalant May, 1963.

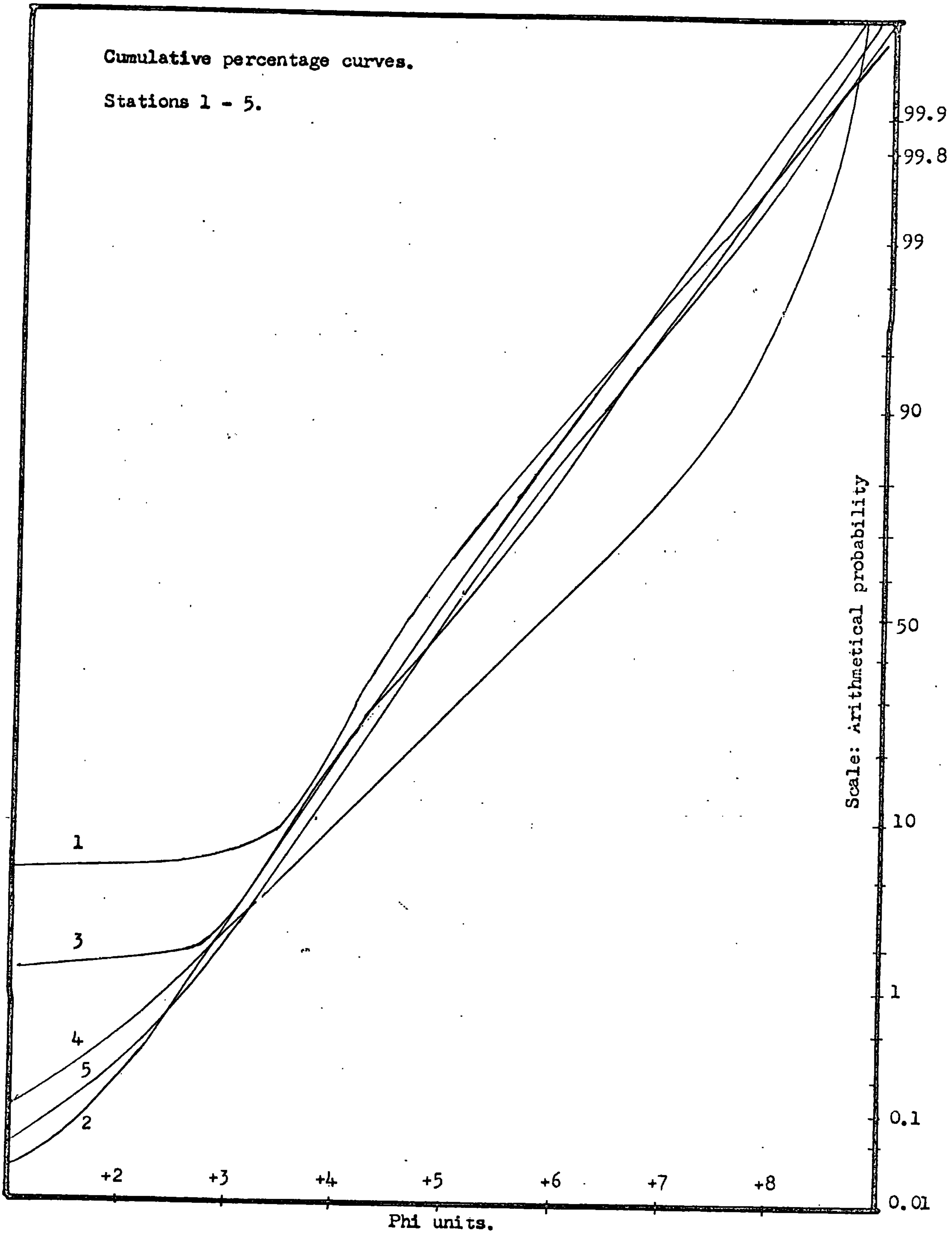
Core Station	Length	Notes
1	0.56m	
2	0.68	
3	0.64	
4	0.60	Cores 1 - 12 collected from launch.
5	0.70	Cores 18 - 23 collected from R.V. *Chain*
6	0.90	
7	0.64	
8	0.40	
9	0.50	
10	0.23	
11	0.66	
12	0.08	
18	1.02	Top 0.035m used in foram studies.
19	1.00	Top 0.035m used in foram studies.
20	1.00	Top 0.035m used in foram studies.
21	1.10	Note. Top of cores 18, 19 and 20 was taken at the 0.035m mark.
22	0.80	
23	1.01	All foram studies mentioned were carried out at Woods Hole Oceanographic Institution, U.S.A.

The size grades, in microns (10^{-6}m.) were then recalculated as phi units, or negative logarithms to the base 2, after Krumbein (1936). Cumulative percentage curves were then constructed for each of the samples using phi units as the grade scale: these are presented in FIGURE 2.21, from these curves, data such as the 1st and 3rd quartile, and median grain size are obtained; these parameters have been used by Doeglas (1968) to classify environments of deposition. Normally, however, these data are used to calculate statistical measures such as sorting coefficients, skewness, and kurtosis, as described in Inman (1952), Folk and Ward (1958). Another approach to the interpretation of grain size distribution curves of sediments is that of Passega (1957), and Bull (1962), who proposed the use of C - M textural patterns. A C - M diagram is a logarithmic plot of the 1 percentile grain size (C), and the median size (M) of the sediment, which produces patterns characteristic of distinct environments.

Frequency distribution curves obtained for the samples indicate the polymodal character of the sediments, a feature noted earlier by van Andel and Postma (1954), with a marked concentration of material with grain size finer than 0.015 x 10^{-3}m. A possible cause of the apparent polymodal character would be the mixing of coarser and finer strata within the sediment prior to analysis, as suggested by Pettijohn (1957) p.38, 39. This seems quite reasonable explanation in the present study, since, firstly the sediment cores were collected in the Boca Vagre, which according to H. O. Chart 5624 shows marked tidal fluctuations and secondly the relatively large size of the samples analysed (0.08m).

A number of parameters obtained from cumulative percentage curves have been proposed by various authors over the past

Figure 2.21



Cumulative percentage curves.

Stations 1 - 5.

Figure 2.21 (continued.)

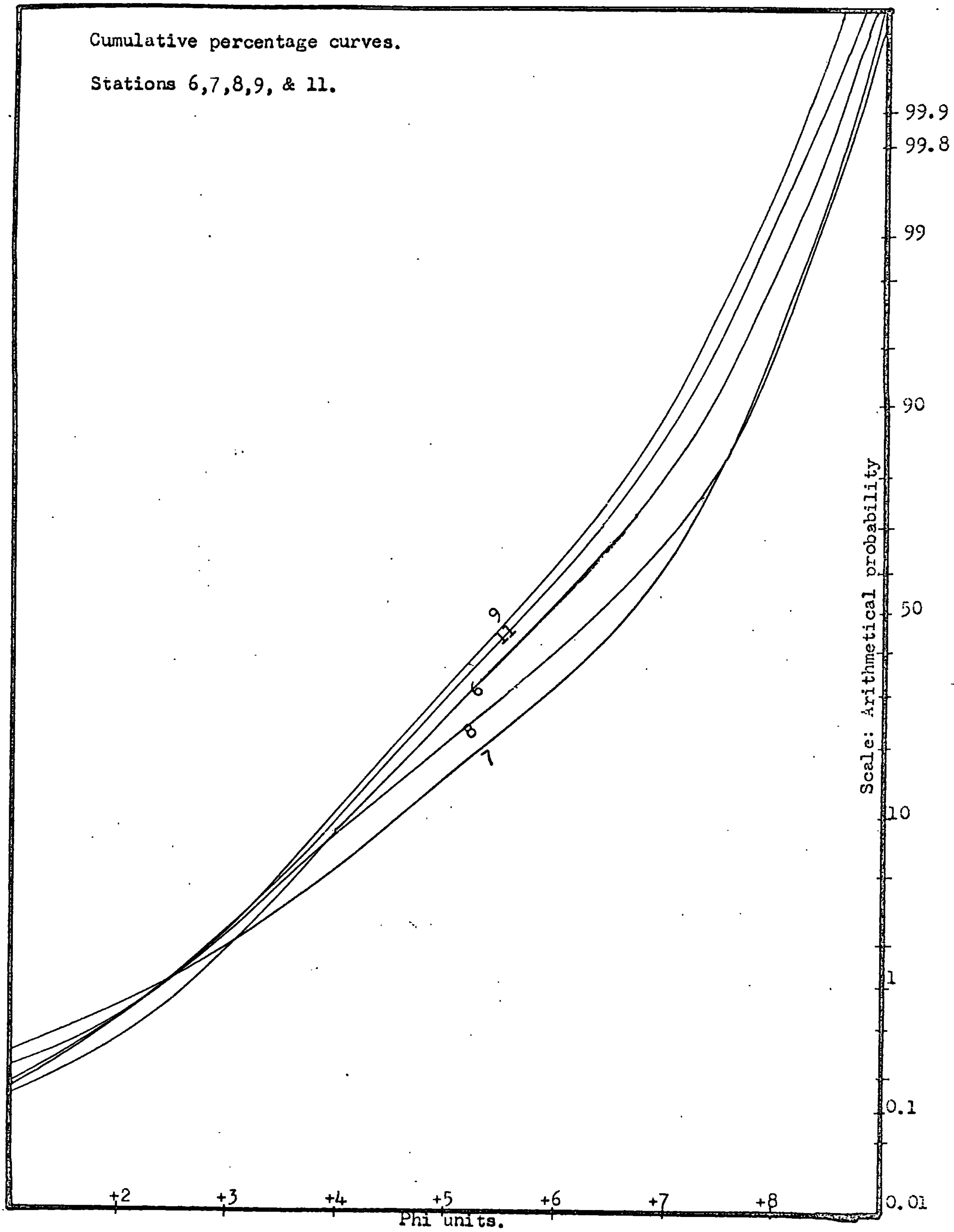
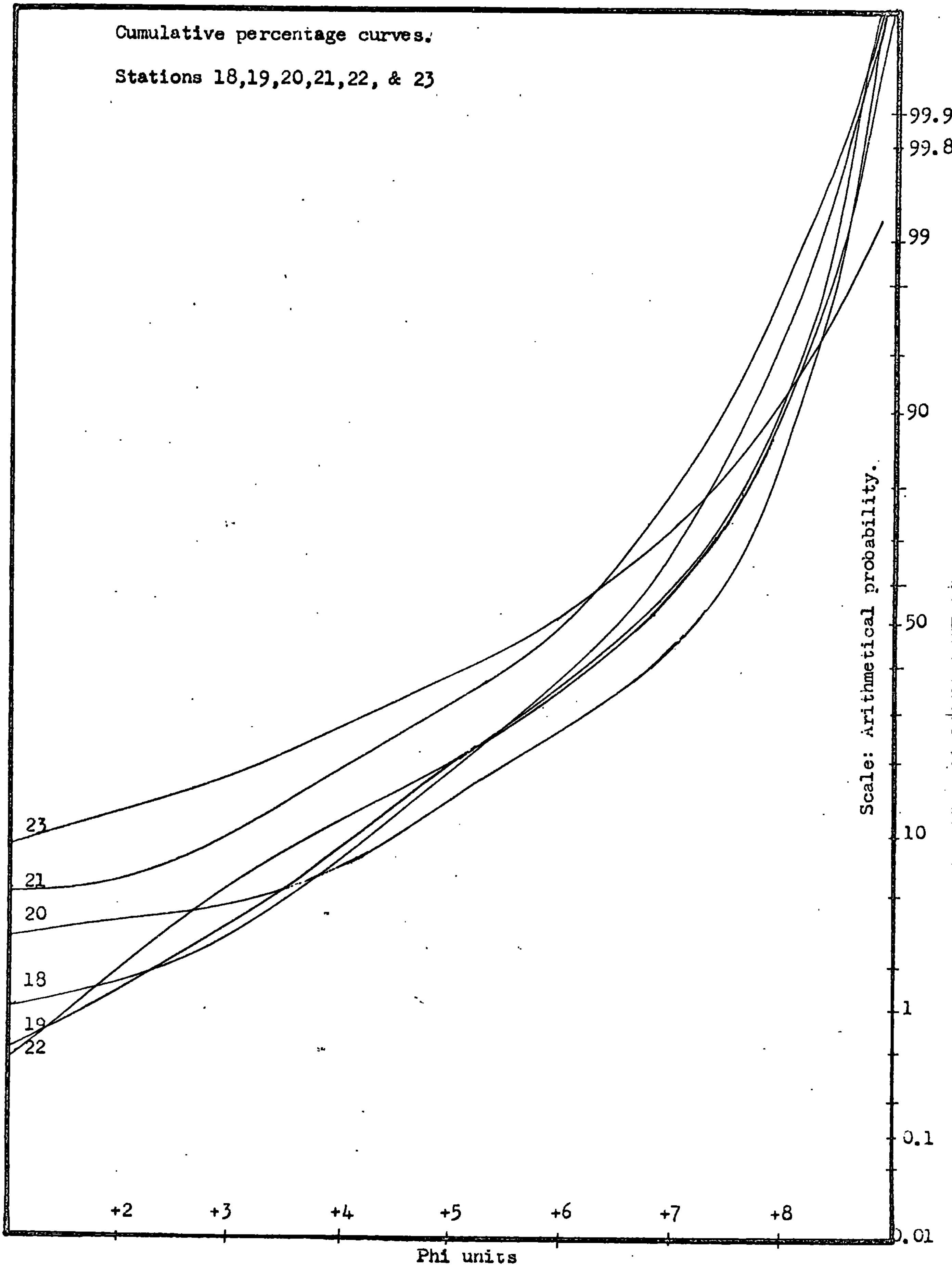


Figure 2.21 (continued.)



fifty years; Trask (1932, in: Pettijohn 1957. p. 37.), Inman (1952), Folk and Ward (1957). In the present work the parameters defined by Folk and Ward (1957) are used since they are probably more representative, as more points are taken from the curve thus representing more accurately the properties of the sediment. The cumulative percentage curves are presented in FIGURE 2.21.

NS

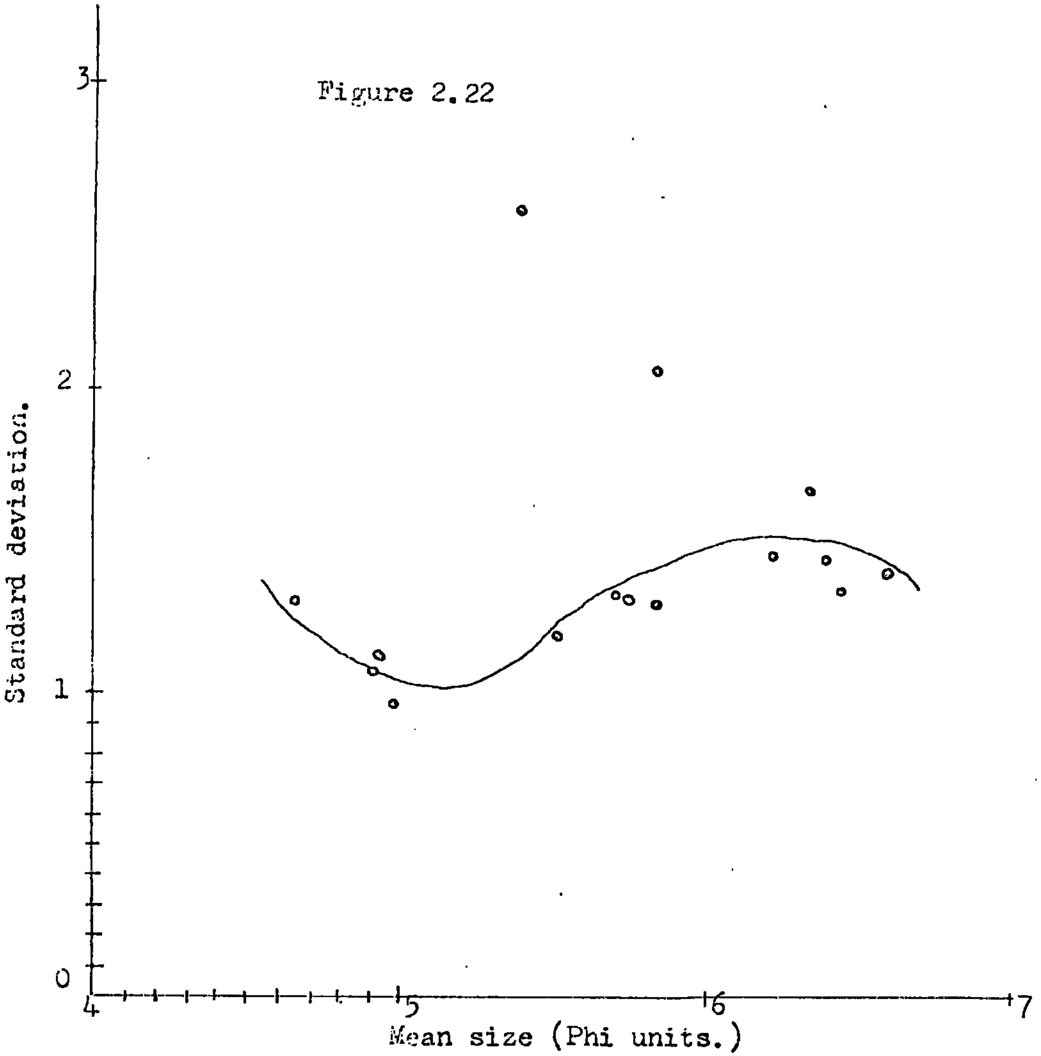
Folk and Ward (op. cit.) studied the interrelation of the 4 size parameters, mean size, skewness, standard deviation, and kurtosis. They found in their study of the sediments of the Brazos River Bar, that mean size plotted against standard deviation, results in a scatter trend with the shape of a broadened M. This relationship was also observed in the present study as shown in FIGURE 2.22. These workers (ibid.) also observed that with a small range of grain size, a V or inverted V, shaped trend is produced. Such a V shape is to be seen in FIGURE 2.23, suggesting a restricted range of grain size within the samples analysed. This is probably reasonable because of the relatively minor area of the Orinoco delta sampled.

When kurtosis and mean size are plotted as shown in FIGURE 2.23, the scatter observed is distinctly similar to the results of Folk and Ward (1957). The scatter pattern for these samples is restricted probably due to the small area sampled.

The relationships derived by plotting mean size against skewness, and standard deviation against skewness are unclear, possibly due to in part the restricted lateral range of the samples on which the present study is based. The plot of kurtosis against skewness, FIGURE 2.24, shows a distribution which correlates with that expected for a normal curve, according to Folk and Ward (1958. p.21). The spread of points is probably due to the apparently poor sorting in the sediment.

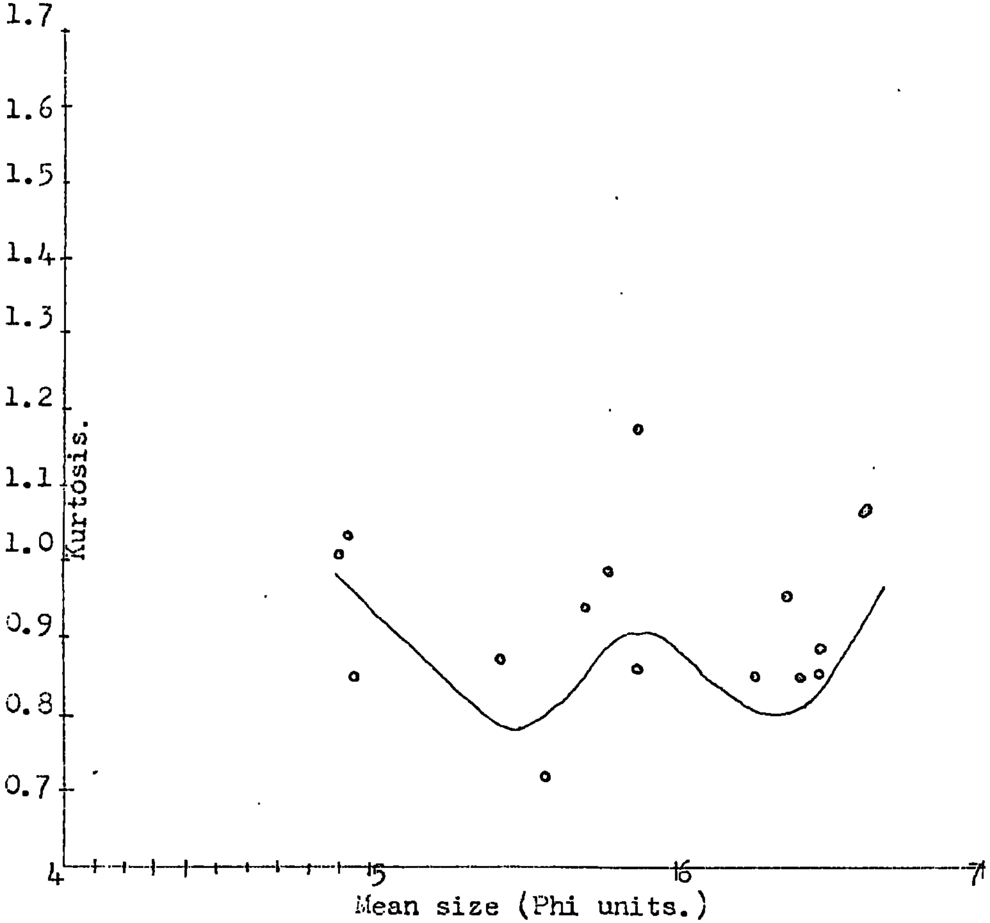
In conclusion, it seems that while some of the statistical measures obtained for the sediments agree with the results of Folk and

Figure 2.22



cf. Folk and Ward (1957. p.17, Fig. 10)

Figure 2.23



cf. Folk and Ward (1957. p.20. Fig. 13.)

Ward (1958), others do not. This may be due to error in the analytical method, or because a comparison between the Brazos River Bar and the Boca Vagre is not really valid.

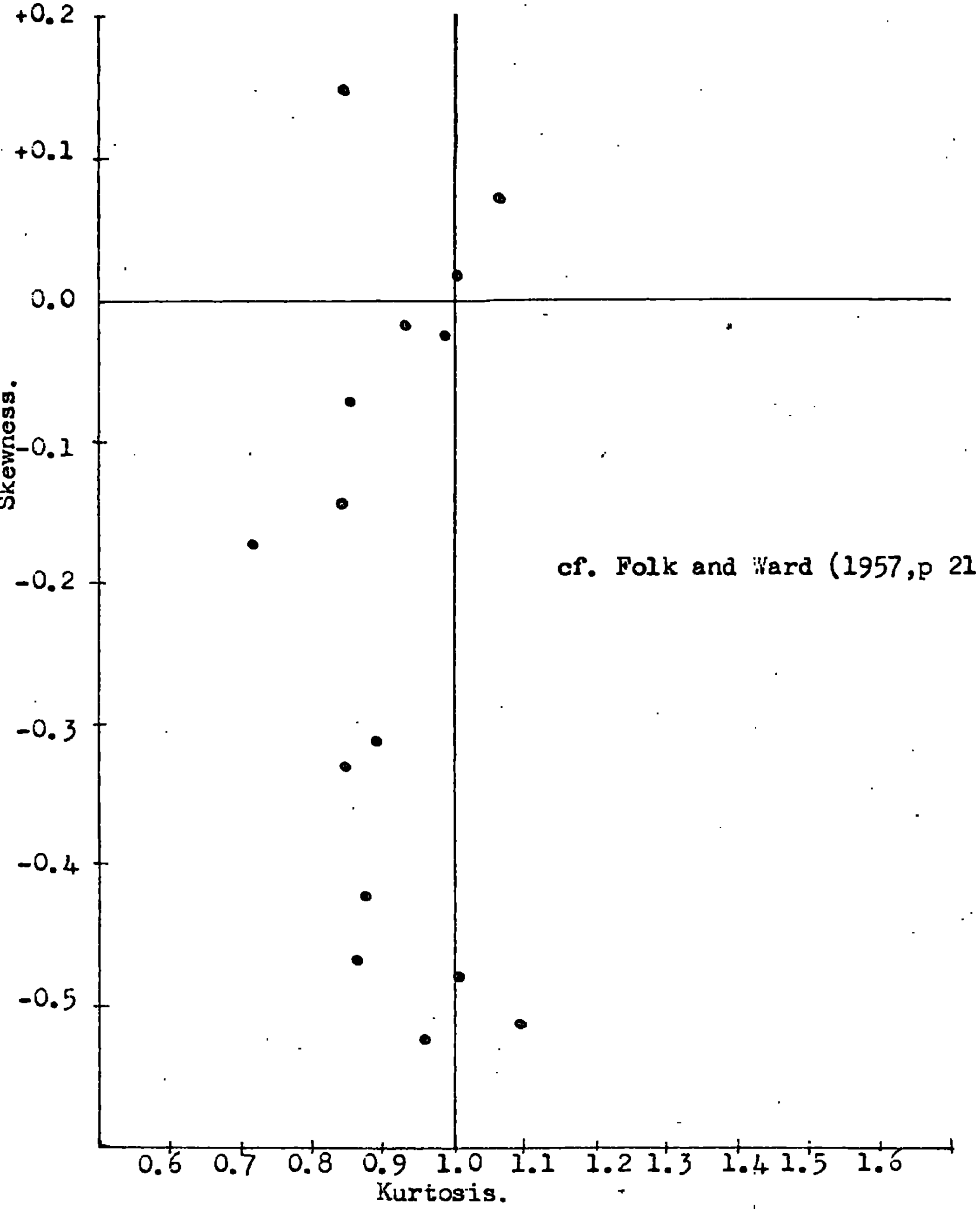
Cumulative percentage curves plotted for samples 1 - 20 are comparable to the results of Fisk et.al. (1954) for samples collected from natural levees on the Mississippi delta. The natural levees are apparently one of the more distinctive groups of sediments in the deltaic plain, and consist of well bedded unfossiliferous clay-silt, and silty-clay laid down in seasonal floods. There seems to be a similarity in the habitat of the samples from the Boca Vagre, since the cores of the present study were collected in channels lying between tidal flats.

Doeglas (1968) uses the indices Q_1, Md, and Q_3, to distinguish between river, marine and loess deposits. These indices are plotted in FIGURE 2.25. The range covered is restricted, compared with the results of Doeglas (1968. p.88, 89) but there is some similarity with data from estuarine sand and clay deposits in the Polder Kruiningen. This suggestion seems reasonable, since the conditions of deposition in the Boca Vagre are essentially estuarine, with sluggish and relatively shallow water conditions.

The theoretical basis of the C - M diagram mentioned earlier, is that the loads of fine and coarse sediments are largely independent of each other, and that parameters such as sorting coefficients and skewness, being measurements of the total sediment, do not express the true character of deposition. In several environments, according to Passega (op.cit.) the coarse fraction of the sediment is more representative of the environment of deposition than the fine fraction. In the C - M diagram, the coarse and fine fraction of a sediment are thus treated separately, and the coarse fraction represented preferentially.

In the C - M diagram, the only limit on which points can fall

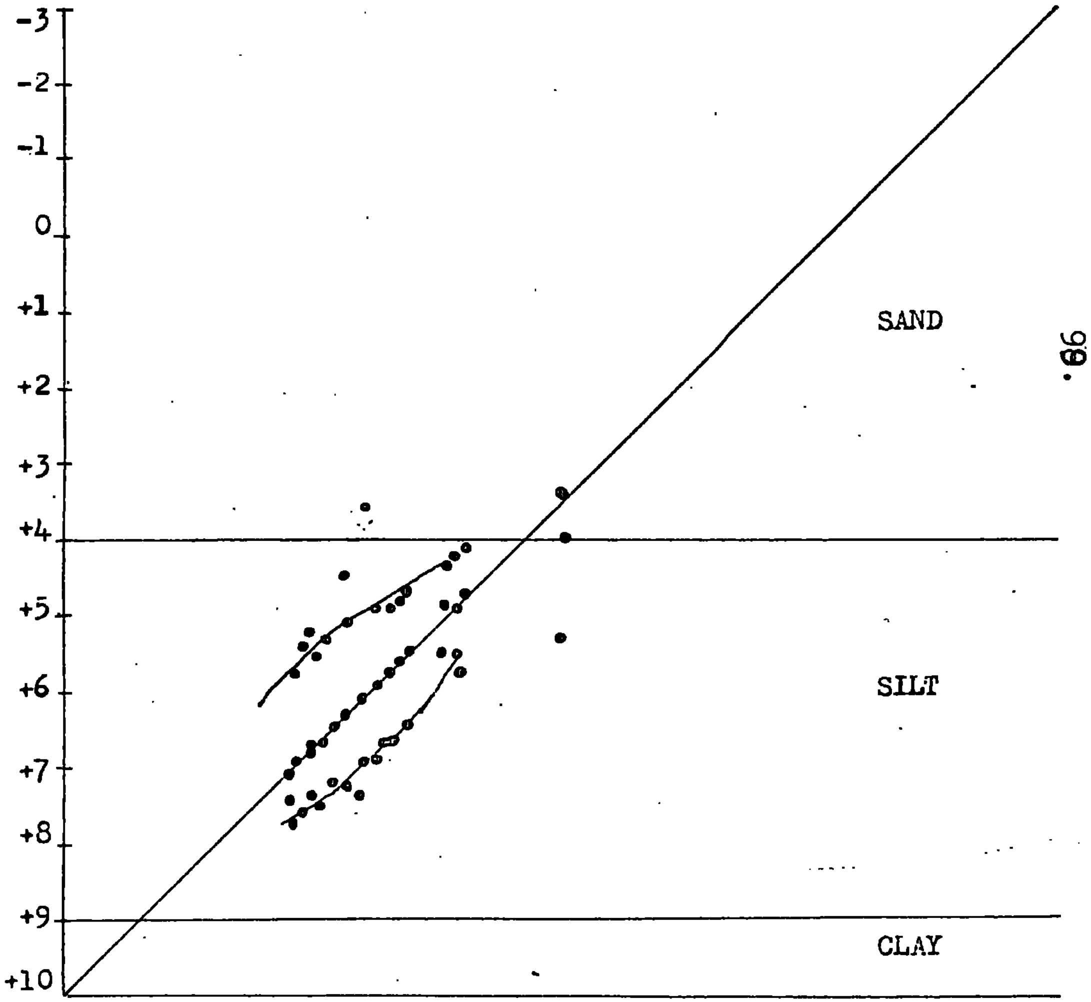
Figure 2.24



cf. Folk and Ward (1957,p 21.)

Figure 2.25

Q_1MdQ_3 Diagram after: Doeglas (1963)



is the C - M, where samples have the median approximately equal to the coarsest grain size. There are a number of problems encountered with the use of the 1 percentile measure. Inman, (1952) p. 128 shows a graph relating percentile to relative standard error, where 1 percentile values show a significant margin of error. Shepard (In: Passega 1957) has suggested that the value of C may be in error, where non-terrigenous matter such as shell debris is present in the sediment. When results of the present study are plotted on a C - M diagram, good agreement is reached with the results of Passega (1957) for a quiet water environment.

In summary, it appears there is a correlation between the results of this study, and those of earlier workers studying similar environments, namely Fisk et.al.(1954). Using the approach of Doeglas (1968) the results show a pattern to be expected in a delta channel such as the Boca Vagre. The C - M diagram indicates quiet water conditions.

X-ray diffraction studies

In the Boca Vagre samples, a relatively rapid method was required to identify, and give a quantitative measure of the minerals present. Peak diffracted intensity was used for simplicity and while it is possible that this is not as reliable a measure of concentration as peak area, results obtained in the present study justified its adoption.

The theoretical aspects of X-ray diffraction have already been considered in Chapter 1.2 and will not be further developed here. The method used was a modification of that described by Kaye et. al. (1968). The peak intensity of the following reflections was used in the determination.

Mineral	d spacing x 10^{-10}m.	Goniometer position (Cu K alpha radiation)
Total Clay	4.5	20^{o}
Quartz	4.26	20.86^{o}
Feldspar	3.10	28.00^{o}
Calcite	3.03	29.40^{o}

Total clay consisted of a mixture of 65 percent illite, 10 percent montmorillonite and 25 percent kaolinite. Fithian illite, as supplied by the Illinois Geological Survey, was used, together with Supreme kaolinite, supplied by a firm English Clays Lovering, Pochin and Co., Ltd, St. Austell, and a smectite, locality unknown, from the Mineralogy Collection of the Department of Geology, Durham University. Quartz was obtained by crushing clear Brazilian rock crystals to pass 200 mesh (B.S.) bolting cloth. Feldspar present in the samples was identified as being plagioclase, from a study of X-ray diffractograms, so that a relatively uncontaminated sample of andesine was obtained from the Mineralogy collection for use in the preparation of standards. A sample of Iceland Spar, ground to pass a 200 mesh (B.S.) was used as the calcite standard, [illegible] Pyrite, locality unknown, was added to the standards to allow for the presence of this mineral c.f. van Andel and Postma (1954) p. 161 Fig. 76.

Range of standards		correlation coefficients for Calibration curves.
Quartz	10 - 70 percent	0.9870
Total clay	10 - 70 percent	0.9823
Feldspar	2 - 30 percent	0.9468
Calcite	2 - 30 percent	0.9163
Pyrite	5 percent	

There are a number of differences between the method used by Kaye et. al. (1968), and that employed in the present work. The peak position was found manually, and intensity estimated by counting for a fixed time; Kaye et. al. (op. cit.) used diffractograms to measure peak intensity directly. Kaye et. al (op. cit) used the quartz 101 reflection at 3.34×10^{-10}m but because of interference by an illite reflection also located at 3.34×10^{-10}m. the quartz 100 reflection at 4.26×10^{-10}m was used. Kaye et al. (op. cit.) used standard cavity mounts, as described in Klug and Alexander (1954 p.300, 301.). For the present work, however, low precision was achieved from the use of these mounts, so that a Philips rotating specimen holder PW 1064 was subsequently used, resulting in much improved precision.

All standards were analysed, using 4 separate mounts which were run 4 times on both the peak and background positions. Mounts of the unknowns were run in a similar manner, the X-ray diffractometer and associated electronics being kept running continuously throughout the determinations. The results of the analysis are given in Table 2.2B at the end of the chapter.

The results of the X-ray diffraction analysis of the samples indicates a distinct, but gradual, change in the amount of quartz and clay out into the Gulf from the Boca Vagre., with little variation in the feldspar content. Calcite was found to be below the detection limit of the method, and in fact the level of carbonate generally, in these samples was found to be low.

In summary, the grain size distribution of the samples indicates a quiet water environment with some tidal fluctuations. The apparent polymodal nature of the sediments may be the result of the mixing of thin laminae of the sediment. Modal analyses by X-ray diffraction indicates an increase in clay content, in agreement with the results of the grain size analysis, accompanied by a decrease in the content of quartz, i.e., detrital material, into the Gulf. These trends are to be expected at the mouth of a large river such as the Orinoco.

Table 2.2B.

Modal Analysis by X-ray diffraction.

Sample.	1S1	1S2	1S3	2S1	2S2	2S3	3S1	3S2	3S3	4S1	4S2	4S3	5S1	5S2	5S3	6S1	6S2	6S3	6S4	7S1	7S2	7S3	8S1	8S2	9S1	9S2	10S1
Quartz.	22%	30%	nd.	23%	28%	37%	26%	31%	42%	43%	40%	38%	39%	39%	38%	28%	27%	31%	34%	29%	22%	28%	35%	24%	38%	34%	35%
Total clay.	77%	69%	nd.	76%	70%	62%	72%	67%	56%	56%	57%	58%	58%	58%	58%	70%	70%	65%	64%	68%	75%	70%	63%	73%	58%	62%	61%
Feldspar.	1%	1%	nd.	1%	2%	1%	2%	2%	2%	2%	3%	4%	3%	4%	4%	3%	3%	3%	3%	3%	2%	3%	2%	3%	4%	4%	4%

Sample.	11S1	11S2	11S3	12S	18S1	18S2	18S3	18S4	19S1	19S2	19S3	19S4	20S1	20S2	20S3	20S4	21S1	21S2	21S3	21S4	21S5	21S6
Quartz.	30%	38%	35%	31%	24%	26%	21%	21%	20%	18%	17%	22%	15%	14%	15%	18%	15%	13%	18%	16%	17%	16%
Total clay.	67%	59%	62%	65%	74%	74%	77%	77%	77%	79%	83%	75%	82%	83%	83%	79%	83%	84%	80%	82%	79%	82%
Feldspar.	3%	3%	3%	3%	2%	2%	3%	2%	2%	3%	2%	2%	2%	2%	2%	2%	2%	2%	3%	2%	2%	2%

Sample.	21S7	21S8	21S9	21S10	22S1	22S2	22S3	23S1	23S2	23S3	23S4
Quartz.	17%	16%	17%	18%	16%	16%	21%	14%	15%	13%	14%
Total clay.	81%	81%	81%	80%	81%	81%	77%	85%	82%	85%	84%
Feldspar.	2%	2%	2%	3%	2%	2%	1%	2%	3%	2%	2%

Note: All results expressed in terms of Weight percent.

Operating conditions for Philips PW 1o51

X-ray diffractometer.
Cu. anode. Tube rating: 1Kw.
Operating power: 40Kv. 20 ma.
Machine settings: Counter 32.
No discrimination.
Counting time 16 secs.
Sample mount: Philips PW 1064 rotating.

CHAPTER 2.3

CHEMICAL ANALYSIS

Analysis for carbon, carbonate, and total water.

The techniques used in analysis for carbon and total water were identical to those described in Chapter 1.3.

The concentration of carbonate was low, around 0.5 wt percent, so that the method of determination of CO_2 described by Shapiro and Brannock (1955b) was used. In this method, carbon dioxide is determined by measuring the volume of gas evolved, when a powdered sample is heated with acid in an oil filled tube with fitted side arm. This method was found to give satisfactory precision, and the results of the analyses are shown in Table 2.3D at the end of this chapter.

X-ray Emission Spectrography

This method was used for the analysis of both light elements in major amounts, and relatively heavy elements in minor amounts. A general discussion with references on the method is given in Chapter 1.3.

Major element analysis

The sub-samples were analysed for the elements Si, Al, Mg, Fe, Ca, K, Ti, S and P. The operating conditions for the spectrograph and associated electronics were essentially the same as in the analysis of the *Meteor* cores, details of which have been given in Chapter 1.3. Unreliable Na analyses were obtained once again due to the restricted range of the standards and low analytical precision. Only minor trouble was encountered from the formation of a film of salt on the bricquette surface after being pelletised, compared with that observed when dealing with the Meteor samples. The sedimentary standards described in Chapter 1.3 were again used, and an identical procedure was followed in the preparation of the samples for major element analysis, and in the reduction of the intensity data into weight percent oxides. The results of the analyses are given in Table 2.3D at the end of this chapter.

Minor element analysis

The minor elements Ba, Zr, Sr, Rb, Zn, Cu and Ni were determined by X-ray spectrography using a technique identical to that described for the Meteor cores in Chapter 1.3. Details of the standards are given in Table 1.3D, in the first half of this thesis.

Analysis for B, Cr, V and Ba was undertaken, on selected sub-samples, by Optical Emission Spectrography, following details and procedure identical to that given in Chapter 1.3. Again Ba was analysed by this method as a means of checking the results obtained by X-ray Emission Spectrography, these comparative results are given in Table 2.3B, and details of the precision for B, Ba, V and Cr in Table 2.C. The minor element analyses are listed in Tables 2.3E at the end of this chapter.

Additional data, supplied by Woods Hole Oceanographic Institution, include salinity and pH values for some of the stations. These data are listed in Table 2.3A, for reference.

TABLE 2.3A

Salinity and pH results obtained by R.V. Chain in Boca Vagre, Gulf of Paria, May 2nd, 1963.

Salinities from R.V. Chain approaching bar, off Isla Cotorra.

	Depth
31 0/00	8.23m
28 0/00	5.50m
26 0/00	4.88m

Salinities from launch: West of Isla Cotorra, crossing bar.

25 0/00	4.57m
23 0/00	3.66m
19 0/00	4.57m

Salinities from launch: beginning of channel, north and west of Isla Cotorra.

12.8 0/00	5.50m

Stations: salinities (0/00) versus depth.

Station	1	2	3	4	5	6	7	8	9	10
Surface	4.8	5.5	7.8	10.5	11.0	11.5	24.0	25.0.	25.0	26.0
1.525m		6.5	11.0							
				19.0	21.0				26.0	
3.05 m	6.3					23.0		25.0		
4.57 m.		7.0	15.0						26.0	
				24.0	22.0					
6.10 m	10.0					20.0				
								27.0		
7.62 m.		11.8							26.0	
9.15 m.	18. 0					24.0				

Water squeezed from sediment
14.5 12.5 15.0

Station 3 pH vs depth.

Surface	8.0
1.83m	7.8
4.88m	8.0
Water squeezed from sediment	7.15

TABLE 2.3B

A comparison of Ba analyses by Optical Emission, and X-ray Emission Spectrography

Sample No.	X-ray Emission Spectrography	Optical Emission Spectrography
1S1	400 ppm	330 ppm
2S1	410	255
3S1	380	485
4S1	370	432
5S1	400	360
6S1	380	390
7S1	350	320
8S1	330	330
9S1	350	340
10S1	380	360
11S1	370	320
12S	360	285
18S1	410	360
19S1	410	375
20S1	390	430
21S1	460	350
22S1	310	500
23S1	410	315

Details of the precision of Ba analyses by both methods are given in Chapter 1 - 3.

TABLE 2.3C

Precision for analysis for B, Cr, V and Ba by Optical Emission Spectrography

B Sample No. 20S1

Average content = 56 ppm

No of repeat determinations = 5

Standard deviation = ± 4.82 ppm

Relative deviation = 8.6 percent.

Ba, V and Cr

Sample No. 21S1	Ba	V	Cr
No of determinations	5	5	5
Average content =	361 ppm	123ppm	97 ppm
Standard deviation =	± 45 ppm	± 16 ppm	±8 ppm
Relative deviation	12.5 per cent	13 per cent	8.25 per cent

Precision of analyses by X-ray Emission Spectrography are presented in Chapter 1.3.

Table 2.3D

Major element data with depth of sub-samples.

Sample.	Depth. m.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	S	P_2O_5	CO_2	C	H_2O
1S1	0.0 - 0.09	58.17	18.58	6.28	1.77	0.12	2.35	0.91	0.52	0.11	0.18	1.00	8.49
1S2	0.26 - 0.35	60.39	17.54	6.03	1.75	0.17	2.23	0.85	0.38	0.12	0.35	0.58	8.11
1S3	0.53 - 0.58	62.67	17.21	6.13	1.61	0.10	2.21	0.90	0.29	0.10	0.38	0.88	6.00
2S1	0.0 - 0.10	59.41	18.39	6.22	1.58	0.11	2.42	0.93	0.31	0.12	0.15	1.34	7.49
2S2	0.27 - 0.35	60.50	17.50	5.86	1.54	0.08	2.28	0.88	0.44	0.12	0.18	0.81	8.32
2S3	0.53 - 0.61	67.32	13.59	5.09	1.25	0.10	1.75	0.68	0.93	0.07	0.26	1.22	6.20
3S1	0.0 - 0.12	60.93	16.90	5.63	1.27	0.07	2.26	0.90	0.32	0.12	0.24	1.55	8.27
3S2	0.28 - 0.37	61.91	17.13	5.51	1.26	0.05	2.25	0.88	0.49	0.08	0.22	1.11	7.59
3S3	0.55 - 0.64	70.05	13.48	4.13	1.02	0.05	1.80	0.73	0.32	0.10	0.18	0.90	5.74
4S1	0.0 - 0.10	68.19	14.74	4.55	1.09	0.04	1.96	0.82	0.25	0.10	0.14	0.86	5.73
4S2	0.26 - 0.34	67.43	15.24	4.71	1.16	0.05	2.11	0.89	0.29	0.10	0.11	0.19	5.19
4S3	0.53 - 0.60	66.71	16.00	4.74	0.51	0.05	2.05	0.87	0.29	0.11	0.14	1.56	5.46
5S1	0.0 - 0.10	66.61	14.99	4.74	1.15	0.11	1.94	0.80	0.27	0.12	0.17	0.86	6.75
5S2	0.29 - 0.38	67.61	15.44	4.91	1.16	0.13	1.99	0.82	0.21	0.11	0.15	0.39	5.57
5S3	0.56 - 0.64	68.69	14.27	4.50	1.18	0.14	1.89	0.79	0.24	0.10	0.15	0.55	6.02
6S1	0.0 - 0.12	60.77	18.61	6.03	1.56	0.11	2.31	0.91	0.22	0.14	0.12	1.30	6.42
6S2	0.28 - 0.38	60.55	19.26	5.80	1.39	0.08	2.35	0.92	0.16	0.14	0.15	1.15	6.56
6S3	0.55 - 0.64	59.68	18.70	5.90	1.42	0.10	2.26	0.92	0.25	0.14	0.15	1.28	7.70
6S4	0.80 - 0.90	61.17	18.32	5.82	1.54	0.12	2.26	0.90	0.29	0.14	0.17	1.07	6.67
7S1	0.0 - 0.13	61.87	15.94	5.70	1.57	0.15	2.09	0.84	0.35	0.14	0.10	1.64	8.05
7S2	0.29 - 0.39	60.71	19.54	6.63	1.50	0.10	2.46	0.97	0.09	0.15	0.18	1.41	4.71
7S3	0.56 - 0.64	59.17	17.64	5.94	1.51	0.14	2.16	0.85	0.15	0.15	0.15	1.23	9.43
8S1	0.0 - 0.12	63.61	15.07	5.45	1.59	0.14	2.01	0.78	0.20	0.14	0.15	2.26	7.05
8S2	0.29 - 0.40	58.93	17.96	6.67	1.54	0.02	2.37	0.96	0.61	0.13	0.15	1.22	7.75
9S1	0.0 - 0.13	64.61	15.20	5.48	1.72	0.17	2.14	0.80	0.42	0.13	0.18	1.96	5.58
9S2	0.31 - 0.40	61.96	15.09	5.03	1.44	0.12	1.99	0.78	0.25	0.13	0.15	1.26	10.28
10S1	0.0 - 0.07	63.87	17.68	5.79	1.54	0.08	2.41	0.87	0.28	0.13	0.16	1.28	4.34
11S1	0.0 - 0.14	59.63	18.32	6.06	1.59	0.05	2.35	0.91	0.48	0.15	0.15	1.35	7.38
11S2	0.31 - 0.40	61.86	16.00	5.21	1.35	0.08	2.10	0.82	0.53	0.12	0.14	0.74	9.50
11S3	0.57 - 0.65	61.22	16.82	5.63	1.60	0.10	2.18	0.84	0.78	0.11	0.17	1.10	7.91
12S	0.0 - 0.08	63.15	16.56	5.56	2.66	0.06	2.19	0.82	0.27	0.12	0.15	1.25	5.66

Table 2.3D (continued.)

Sample.	Depth. m.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	S	P_2O_5	CO_2	C	H_2O
18S1	0.05 - 0.12	58.06	18.80	6.26	1.50	0.24	2.64	0.91	0.03	0.07	0.18	1.87	7.84
18S2	0.31 - 0.38	53.12	18.33	6.31	1.55	0.15	2.44	0.85	0.11	0.07	0.17	1.19	14.18
18S3	0.56 - 0.66	57.01	20.08	6.96	1.67	0.20	2.80	0.96	0.06	0.06	0.23	1.41	6.95
18S4	0.80 - 0.89	53.83	18.51	7.25	1.83	0.03	2.46	0.89	0.43	0.14	0.23	1.37	11.27
19S1	0.06 - 0.15	54.94	20.34	6.87	1.75	0.27	2,76	0.92	0.06	0.07	0.23	1.28	8.93
19S2	0.33 - 0.42	51.82	19.11	6.17	1.90	0.14	2.36	0.80	0.42	0.14	0.22	1.07	14.41
19S3	0.59 - 0.69	52.36	19.36	7.46	2.00	0.07	2.57	0.91	0.44	0.12	0.27	3.09	9.64
19S4	0.85 - 0.97	52.82	19.58	6.58	2.05	0.14	2.44	0.84	0.42	0.58	0.15	1.23	11.71
20S1	0.05 - 0.13	53.19	19.97	6.79	1.92	0.27	2.70	0.88	0.03	0.07	0.20	1.13	11.32
20S2	0.32 - 0.41	54.94	19.96	6.97	1.79	0.31	2.74	0.89	0.07	0.07	0.23	1.02	9.45
20S3	0.66 - 0.74	51.19	19.37	6.70	2.13	1.13	2.42	0.81	0.46	0.14	0.81	0.99	12.41
20S4	0.82 - 0.91	55.03	19.49	6.62	2.27	0.42	2.58	0.87	0.61	0.11	0.25	0.95	9.31
21S1	0.0 - 0.10	52.60	19.22	6.55	1.84	0.42	2.56	0.82	0.00	0.06	0.22	1.18	13.03
21S2	0.26 - 0.30	51.30	20.17	6.99	1.92	0.55	2.68	0.86	0.07	0.08	0.44	1.07	12.32
21S3	0.30 - 0.40	52.60	20.15	7.20	1.97	1.21	2.74	0.87	0.23	0.07	0.55	1.07	9.79
21S4	0.40 - 0.50	51.75	18.98	6.43	1.99	0.90	2.51	0.81	0.29	0.07	0.57	0.95	13.23
21S5	0.50 - 0.60	52.50	19.87	6.60	1.93	0.73	2.65	0.86	0.28	0.07	0.39	0.82	11.75
21S6	0.60 - 0.70	53.94	19.79	6.67	1.94	0.48	2.71	0.88	0.21	0.06	0.21	0.79	10.77
21S7	0.70 - 0.80	53.09	19.75	6.69	2.27	0.45	2.57	0.86	0.56	0.12	0.28	0.86	11.02
21S8	0.80 - 0.90	54.36	19.89	6.91	2.29	0.31	2.58	0.87	0.55	0.11	0.20	1.00	9.42
21S9	0.90 - 1.00	53.84	19.07	6.33	2.24	0.32	2.40	0.82	0.66	0.11	0.18	1.13	11.46
21S10	1.00 - 1.10	57.54	19.43	6.83	2.34	0.33	2.60	0.88	0.63	0.11	0.22	1.03	6.53
22S1	0.0 - 0.17	49.82	18.11	7.61	2.53	3.83	2.35	0.78	0.55	0.16	3.08	0.80	8.87
22S2	0.35 - 0.44	55.51	20.24	6.74	2.29	0.25	2.66	0.88	0.50	0.11	0.27	0.77	8.28
22S3	0.60 - 0.69	55.25	19.73	6.76	2.33	0.22	2.67	0.88	1.46	0.52	0.18	0.81	7.66
23S1	0.05 - 0.12	53.19	19.97	7.06	2.36	0.90	2.59	0.84	0.35	0.13	0.77	0.96	9.37
23S2	0.31 - 0.38	52.86	20.70	7.37	2.14	1.05	2.85	0.91	0.11	0.06	0.97	0.58	8.81
23S3	0.56 - 0.65	53.71	20.87	7.37	2.71	0.46	2.30	0.89	0.45	0.11	0.35	0.85	7.91
23S4	0.89 - 0.95	53.93	21.00	7.17	2.07	0.60	2.90	0.90	0.18	0.06	0.40	0.58	8.64

Table 2.3D (continued.)

Comparative results from literature.

Rankama and Sahama (1950).	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	S	P_2O_5	CO_2	C	H_2O
Magmatic rocks.	59.40	15.35	8.37	3.45	5.08	3.12	0.74	0.12	0.27	0.10	0.03	na.
Hirst (1962 a.) Average of 3 samples from Boca Vagre.	na.	5.43	2.71	0.40	0.43	0.89	0.40	na.	0.05	0.14	na.	3.74
Average of 12 clays.	55.90	15.40	6.01	2.20	0.71	1.89	0.78	na.	0.14	1.44	na.	10.10

All analyses in terms of Weight Percentages.

na. data not available.

Table 2.3E.

Minor element data.

Sample.	Ba.	Ni.	Zr.	Sr.	Rb.	Cu.	Zn.	Cr.	V.	B.
1S1	400	59	279	109	107	39	157	85	86.	75.
1S2	380	53	352	104	99	34	129	-	-	-
1S3	380	55	310	104	105	41	138	-	-	-
2S1	410	59	311	109	113	29	158	81	81	32
2S2	390	56	357	99	108	36	131	-	-	-
2S3	300	41	330	81	80	24	100	-	-	-
3S1	380	57	367	103	104	27	138	97	92	58
3S2	370	51	371	98	99	34	122	-	-	-
3S3	310	41	492	72	75	29	94	-	-	-
4S1	370	46	684	84	88	27	105	82	-	65
4S2	370	47	673	83	86	27	111	-	-	-
4S3	360	55	807	86	88	29	113	-	-	-
5S1	400	44	459	86	84	32	111	55	-	49
5S2	390	47	423	81	87	34	114	-	-	-
5S3	370	43	436	82	85	27	106	-	-	-
6S1	380	55	392	106	106	32	137	75	94	168
6S2	400	55	405	103	107	36	134	-	-	-
6S3	380	55	375	104	108	34	137	-	-	-
6S4	370	52	470	96	96	36	128	-	-	-
7S1	350	52	410	103	94	32	129	47	24	130
7S2	430	57	328	110	111	34	144	-	-	-
7S3	380	55	372	106	100	32	132	-	-	-
8S1	330	47	384	94	85	34	128	140	114	100
8S2	400	56	346	105	107	17	139	-	-	-
9S1	350	48	366	96	82	27	120	55	-	108
9S2	370	50	392	93	95	32	120	-	-	-
10S1	380	50	334	94	98	34	126	82	-	55
11S1	370	57	304	100	103	39	147	102	106	63
11S2	350	50	385	92	92	32	121	-	-	-
11S3	350	51	360	99	98	36	127	-	-	-
12S	360	53	335	103	100	43	132	41	-	100

Table 2.3E (Continued.)

Sample.	Ba.	Ni.	Zr.	Sr.	Rb.	Cu.	Zn,	Cr.	V.	B.
18S1	410	61	254	106	109	36	147	97	124	58
18S2	410	57	229	106	113	34	152	-	-	-
18S3	440	59	240	109	116	34	151	-	-	-
18S4	400	61	238	110	116	48	156	-	-	-
19S1	410	61	222	116	119	36	159	96	128	100
19S2	420	62	234	112	120	39	156	-	-	-
19S3	440	63	211	118	126	50	162	-	-	-
19S4	410	66	217	120	123	36	163	-	-	-
20S1	390	61	208	116	120	48	162	107	158	63
20S2	440	65	190	117	125	39	169	-	-	-
20S3	390	63	194	143	125	41	170	-	-	-
20S4	420	65	232	123	123	46	153	-	-	-
21S1	460	65	191	124	124	77	180	112	100	70
21S2	390	71	188	123	120	34	173	-	-	-
21S3	400	67	210	140	120	46	162	-	-	-
21S4	430	65	238	134	117	36	159	-	-	-
21S5	410	65	229	123	117	43	163	-	-	-
21S6	420	59	209	121	122	46	161	-	-	-
21S7	430	55	207	126	122	50	163	-	-	-
21S8	420	57	207	120	120	46	162	-	-	-
21S9	410	57	239	119	117	48	154	-	-	-
21S10	390	56	230	118	117	39	158	-	-	-
22S1	310	55	188	223	110	43	172	97	108	90
22S2	430	59	222	118	121	48	163	-	-	-
22S3	390	55	236	113	113	39	159	-	-	-
23S1	410	56	200	159	122	43	170	94	120	41
23S2	410	59	185	154	125	39	176	-	-	-
23S3	440	60	171	131	128	48	178	-	-	-
23S4	390	65	197	131	127	46	175	-	-	-

Table 2.3E. (continued.)

Comparative results from literature.

Rankama and Sahama (1950).	Ba.	Ni.	Zr.	Sr.	Rb.	Cu.	Zn.	Cr.	V.	B.
Magmatic rocks.	240	66	220	175	424	67	110	136	66	3
Hirst (1962 b.)										
Average of 3 samples from Boca Vagre.	173	17	436	35	41	5.8	na.	27	49	51
Average of 12 clays.	376	31	169	184	146	23	na.	75	86	82

All analyses in terms of parts per million.

- not determined.
na. not available.

CHAPTER 2.4

In this chapter, the distribution of both the major and minor elements within the sediments will be considered. Factor analytical studies made of the data attempt to draw the information together, facilitating interpretation of correlations between the different elements and identification of the main controls of variance of the data.

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The distribution of the elements Si, Al, Fe, Mg, Ca, K, Ti, S, P. CO_2, C and H_2O will be discussed within and between the cores, so that conclusions may be drawn as to their origin and location in the sediments.

Silica

The distribution of this element is shown in Table 2.3D and the content of quartz in the samples is given in Table 2.2B. It is obvious that the results of the present study occupy an intermediate position between the results obtained by Hirst (1962a) for delta sands and clays. The decrease in quartz and silica out into the Gulf results from the fall in amount of detrital SiO_2 present in the sediments. SiO_2 will be present in two main locations in these sediments; in tectosilicates such as quartz and feldspar; in phyllosilicates, either illite, montmorillonite or kaolinite.

Of these, detrital quartz and the clay minerals are the most important, as shown in Table 2.2B. The core samples of the present study were collected from the part of the Gulf of Paria where, according to van Andel and Postma (1954), Orinoco sands are accumulating. These consist of, typically, small honey coloured quartz grains, having a coating of Fe, and are probably derived from the Llanos. (ibid. p.75). In stations 18 - 23, the content of SiO_2 is approximately 10 wt percent lower than at the stations further inshore. A similar decrease in the weight percent quartz is also apparent. The decrease results from a reduction in the resistate fraction with a concurrent increase in the content of hydrolysate minerals. A slight increase in carbonate, in the form of shell debris is also apparent in the offshore sediments. Whole, small pelecypod valves, and an occasional scaphopod have been found in some of the samples from stations 21 & 23. Hirst (1962a) p.318. suggested that free silica in the Gulf samples would be in the form of finely divided quartz. As will be shown later, the distribution of the element Zr correlates with SiO_2 in the samples, so that a relationship between these elements and the resistate fraction seems probable. If silica were being precipitated from solution, then as the salinity increases, precipitation would be expected to increase. Comparison of the results in Tables 2.2B and 2.3D show that this is not the case.

In summary, a decrease in both the total silica, and quartz is to be seen outwards from the Boca Vagre. The silica probably occurs largely in detrital quartz and the hydrolysate fraction. The free silica in the sediment appears to be detrital quartz, , as suggested by earlier workers, rather than precipitated SiO_2.

Alumina

The content of this oxide is listed in Table 2.3D where it will be seen that the results of the present study are higher than those of Hirst (1962a). Alumina is an important constituent in the samples studied, being present in two mineral phases, in the detrital fraction of the sediment, i.e., the clay minerals and the feldspar.

	Correlation coefficients			
	Al_2O_3:Fe_2O_3	Al_2O_3:MgO	Al_2O_3:K_2O	Al_2O_3:TiO_2
Stations 1-12, 18,19, 20, 22 & 23	0.8858	0.6458	0.9488	0.6790
Station 21	0.8342	-0.1496	0.8273	0.7700

As will be noted, in the table above, the data from all stations has been plotted together, with the exception of station 21. The reason for this is the uniformity in appearance between cores, and also the small number of sub-samples taken from each core.

From the correlation coefficients listed above, it is obvious that there is a close correlation between Al_2O_3, Fe_2O_3,K_2O and TiO_2. The low negative correlation between Al_2O_3 and MgO in station 21 is surprising since the results of Factor Analysis, discussed below, indicate that montmorillonitic clays are relatively abundant in the hydrolysate fraction in station 21, and a correlation might thus be expected between MgO and Al_2O_3. The good correlation between Fe_2O_3 and Al_2O_3 is due to their presence in the hydrolysate fraction of the sediment. Although all the Fe in the sediment is recorded as Fe_2O_3, it is obvious that some of the element will be in the divalent state, some of which would be oxidised when the sediments dried out, after collection. Replacement of some of the Al in octahedral positions in the illite lattice by Fe^{2+}, and Fe^{3+} can occur, while in montmorillonite minerals, Fe may also enter into the octahedral positions.

The close correlation between K_2O and Al_2O_3 results from their association in the hydrolysate fraction of the sediment, particularly in illite. Some K_2O may also be present in detrital feldspar, but as this appears to be predominantly plagioclase, this will be minor.

The close correlation between Al_2O_3 and TiO_2 is due to their relationship with the hydrolysate fraction of the sediment where Ti^{3+} may substitute for Al^{3+} in the octahedral positions of the mica lattice.

In summary, it is suggested that the major portion of the alumina in these sediments is located in the hydrolysate fraction of the sediment. Some will also be present in detrital feldspar, but will be of only minor importance. There is an overall increase in Al_2O_3 out into the Gulf, which reflects a parallel increase in total clay as discussed in chapter 2.2.

Total Fe, as Fe_2O_3

The level of concentration of Fe shown in Table 2.3 is intermediate to that found by Hirst (1962a) for delta sands and clays. This element shows a slight increase into the Gulf, as with Al_2O_3, the increase being particularly apparent between stations 12 and 18. This fact, together with the close correlation with Al_2O_3 noted, earlier, suggests a close relationship with the hydrolysate fraction. Fe can occur in both illite and montmorillonite lattices, where it wouldoccupy octahedral lattice positions.

Fe_2O_3/Al_2O_3 ratio	Fe_2O_3/Al_2O_3 ratio	
Present work	Hirst (1962a)	
(Average for uppermost sample)	Average 12 clays.	Boca Vagre sands.
0.34	0.39	0.50

The relatively constant Fe_2O_3/Al_2O_3 ratio observed, suggests that the two elements are associated in the same minerals in the cores. It will be noted the ratio of these oxides is lower than that obtained by Hirst (1962a) for delta clays and sands.

Some Fe may also be present as a coating on sand grains and as a constituent of the heavy mineral fraction in such minerals as garnet, hornblende and pyroxene, c.f. van Andel and Postma (1954 o.75, Map III). Heavy minerals however, are only of very minor importance.

Correlation coefficients

	Fe_2O_3:S	Fe_2O_3:TiO_2
Station 1 - 12, 18, 19, 20, 22 and 23	0.0770	0.5027
Station 21	-0.3508	0.7138

The poor correlation between Fe_2O_3 and S suggest that this correlation is masked by the dominance of other Fe bearing minerals present in the hydrolysate fraction. Some pyrite has been detected in X-ray diffractograms.

In summary, the bulk of Fe in the sediment appears to be associated with the hydrolysate fraction of the sediment there being a sympathetic increase in total Fe and total clay. The close correlation between Fe_2O_3 and Al_2O_3, Fe_2O_3 and TiO_2 substantiates this association.

Magnesia

The average level of concentration shown in Table 2.33 lies between the results Hirst (1962a) obtained for sands and clays. There is a marked increase in MgO out into the Gulf, the increase being most distinct between stations 12 and 18. In view of the good correlation between MgO and Al_2O_3, the bulk of magnesia is probably located in the hydrolysate fraction of the sediment. Montmorillonite would probably be the site of most Mg, the element being present in octahedral sites within the lattice. It is unfortunate that no detailed shipboard logs are available for the cores, since it may have been possible to recognise the clay facies described in van Andel and Postma (op. cit.). The only information regarding the appearance of the wet sediment is on the six cores 18 - 23. At the time of collection a distinct colour change was observed in a seaward direction from grey to distinctly green in a distance of about a mile. (Pers. comm. Nicholls to Hirst 1963). On this evidence, it would appear that the present cores belong to the greenish mud facies of van Andel and Postma (1954), as indicated in Fig. 65, p. 136, ibid.

MgO/Al_2O_3 ratio present work	MgO/Al_2O_3 Hirst (1962a)	
	Average;12 clays.	Boca Vagre sands(3).
0.10	0.14	0.07

Both the ration Fe_2O_3/Al_2O_3 and the MgO/Al_2O_3 are relatively constant in the top sub-samples, with only a marginal increase in stations 20 - 23; these values lie within the range observed by Hirst (1962a). The increase noticed in outer stations may be due to the presence of some Mg in the calcite lattice of bioclastic debris present in these cores, or more likely, to a relative increase in the proportion of montmorillonite in the sediment.

In summary, it seems that the bulk of the Mg is present in the hydroloysate fraction of the sediment, suggested by the constant MgO/Al_2O_3 ratio, and the close correlation in most of the samples between MgO and Al_2O_3. The slight increase in MgO content out into the Gulf, together with a similar one for Fe_2O_3, Al_2O_3 and total clay, further substantiates the relationship with the hydrolysate fraction. The relatively constant MgO/Al_2O_3 ratio suggests that the MgO would be incorporated in the clay lattice at source rather than during diagenesis. The suite of samples considered in the present study has been collected where the sedimentation rate, according to van Andel and Postma (1954) show an abrupt change from 1 m./century to 0.5 - 1.0m/century. This would in part result from a decrease in the amount of detrital material being carried by the water currents, as shown by the decrease in quartz content. Obviously as the rate of sedimentation decreased, if the Mg or Fe were incorporated into the hydrolysate fraction after flocculation, a distinct increase in the MgO/Al_2O_3 ratio would result. Since this does not occur, it would appear that the bulk of the Mg was incorporated during the original weathering process.

Lime, CaO

The level of concentration of CaO is shown in Table 2.3D, there is a slight increase out into the Gulf, particularly noticeable between stations 12 and 18.

	Correlation coefficients	
	$CaO:CO_2$	$CaO:P_2O_5$
Stations 1 - 12, 18, 19 20, 22 and 23	0.9854	0.0076
Station 21	0.9044	-0.5401

In view of the close correlation between CaO and CO_2, it would seem probable that the bulk of the Ca in the sediments is located in the carbonate fraction. A point of disagreement with the results of van Andel and Postma (1954) arises over the carbonate content of stations 1 - 8 collected to the south west of the Isla Cotorra. These workers state that carbonate is entirely absent from the sediments of the Boca Vagre (ibid., pp 99 - 100). In the present study, this has been found not to be the case, Van Andel and Postma (op. cit.) further state that no detrital carbonate is being introduced by the rivers. This may well be the case, since bioclastic fragments, including bivalve shells were noticed in the sediment from stations 21 - 23. Further evidence given by van Andel and Postma (1954, p.114, 115. Fig. 59) indicates that a suite of cores on which the present study is based, crosses the boundary between a shallow fresh to brackish water, mud bottom regime, and a shallow marine shelly basement type. It would thus appear quite possible that the increase in carbonate noted in the stations out into the Gulf is the direct result of their containing bioclastic debris. It is of interest to note that on the basis of a qualitative X-ray diffraction study on the sub-samples, that in none of the samples has either calcite or aragonite been found. This would suggest that in view of the chemical analyses for CaO and CO_2, that the carbonate minerals present are below the detection limit for X-ray diffraction.

The poor correlation observed between CaO and P_2O_5 may be due in part to the low concentration of P_2O_5 observed in the cores and also to the fact that the variance of CaO is dominated by carbonate. It is of interest to note that the concentration of P_2O_5 found in the present study lies within the values obtained by Hirst (1962a) for the sands and clays. Van Andel and Postma (1954) do not report apatite in the results of the heavy mineral analyses, but as Hirst (op. cit.) has already commented (ibid. p.330) the amount of apatite required to account for the observed P_2O_5 would be small.

Plagioclase feldspar is also a possible, though minor, site for Ca as only a low concentration of feldspar was found; Table 2.2B. Calcium could also be present in intersheet positions in montmorillonite though it would be excluded from octahedral positions because of its relatively large ionic radius.

In summary, the principal site for Ca in the sediments is in the carbonate minerals, bioclastic debris being the most important source of these. Some Ca will also be present in the detrital feldspar, possibly in calcium phosphate, and to a small extent as an exchangeable ion in montmorillonite.

Potash

The level of concentration of K_2O is uniform from core to core, only a slight increase is noticeable between cores 12 and 18. Table 2.3D shows that the average concentration of K_2O in the present study is higher than values obtained by Hirst (1962a) p.321)

	Correlation coefficients $Al_2O_3:K_2O$
Stations 1 - 12, 18, 19 20, 22 and 23	0.9488
Station 21	0.8273

K_2O/Al_2O_3 ratio	K_2O/Al_2O_3 ratio	
	Hirst (1962a)	
Present work	Average 12 clays.	Boca Vagre sands(3).
0.13	0.12	0.16

In view of the close correlation between K_2O and Al_2O_3 in all of the samples, together with the increase noted in Al_2O_3, K_2O and total clay, it is suggested that the bulk of the potash in these sediments is located in the hydrolysate fraction, most probably in the illite lattice. Van Andel and Postma (1954 pp.78,79) provide semi-quantitative data on the composition of the hydrolysate fraction of some sediment samples. They conclude that illite is the dominant clay species in the Gulf, particularly in the approaches to the Rio Pedernales. These authors also note an increase in the contents of montmorillonite from the Boca Vagre into the Gulf proper, although the dominant clay species is still illite. Although, according to Van Andel and Postma (1954) there should be a relative increase in montmorillonite compared with illite in the Gulf stations 18 - 23 it is obvious from the present study that there is also a decrease in the resistate fraction, namely quartz. The increase in K_2O content could thus be explained by an overall increase in clay, and thus illite because of the constant value obtained for the K_2O/Al_2O_3 ratio.

It is possible that some K may be present in the detrital feldspar noted in the sediment, but as no microscopical examination has been carried out on the sub-samples, this must be pure conjecture. Some K may also have been derived from interstitial water in the sediment; this, however, must have been of only minor importance, since according to

Rankama and Sahama (1950 p.432) the content of K salts is greater in river than sea water, so that the amount of K contributed to the sediments by this source would decrease in stations 1 - 21, as shown by the increase in salinity listed in Tables 2.3A in the last chapter.

In summary, the principal site for the potash in these sediments is illite.

Titania

This oxide shows little fluctuation between stations, and if anything, is at a slightly higher level of concentration than that noted by Hirst (1962a p.319) In view of the lack of variation in the content of this oxide, and the close correlation between Al_2O_3 and TiO_2, it is suggested that the bulk of TiO_2 in these sediments is associated with the hydrolysate fraction of the sediment.

	Correlation coefficients $Al_2O_3:TiO_2$
Stations 1 - 12, 18, 19 20, 22 and 23.	0.6790
Station 21	0.7700

Van Andel and Postma (1954 p.68 Table 2) give the heavy mineral composition of some of the samples. These show that Ti bearing minerals such as anatase and rutile are present in only small concentrations. Unless these minerals are present in finely divided state in association with the hydrolysate fraction of the sediment as suggested by Goldschmidt (1954 p.419) it would appear Ti is present within the clay lattice as Ti^{4+}. Arrhenius (1952) concludes that Ti may be used as a measure of the hydrolysate fraction of the sediment in pelagic sediments from the Pacific Ocean. The lack of variation in TiO_2 with the sedimentation rate also suggests a relationship with the hydrolysate fraction and also suggests that the

Ti was incorporated at source rather than during deposition of the clay minerals.

Sulphur

The concentration of S fluctuates between cores but remains relatively constant throughout the length of traverse into the Gulf. Hirst (1962a) does not give analyses for this element, but Rankama and Sahama (1950 p.752) suggest an average S content for shales of 0.26 percent. Pyrite has been identified by qualitative X-ray diffraction in the sediments from some of the stations, and thus despite the lack of correlation between Fe_2O_3 and S, it would seem, therefore, that the sulphur is mainly present as the sulphide. The lack of correlation is probably due to the fact that the variance of Fe is dominated by the hydrolysate fraction. The pyrite observed in the samples may possibly be precipitated in situ, thus accounting for the low average S content out into the Gulf, where van Andel and Postma (1954.p.159) recorded a distinct change in sedimentation rate.

	Correlation coefficients Fe_2O_3:S
Stations 1 - 12, 18, 19, 20, 22 and 23.	0.0770
Station 21	-0.3508

Phosphorus

There is a slight decrease in P out into the Gulf, the values lying within the range observed by Hirst (1962a).

	Correlation coefficients $CaO:P_2O_5$
Stations 1 - 12, 18, 19, 20, 22 and 23	0.0076
Station 21	-0.5401

Lack of correlation to CaO observed undoubtedly results from the fact that the variance of CaO is dominated by carbonate. Van Andel and Postma (1954) do not report the presence of detrital apaitee in these sediments, but a detrital source may be responsible, as suggested by Hirst (1962a p.239). This would be in agreement with the results obtained in the present study, with slightly higher P_2O_5 values in stations 1 - 12.

In summary, a slight decrease in P_2O_5 is observed in the relatively off shore stations, a detrital source may be responsible for the distribution, in view of the similar decrease in quartz and Zr.

Carbon

The organic and inorganic carbon concentration will be discussed together. As will be noticed in Table 2.3D, the level of concentration of CO_2 lies within that observed by Hirst (1962a p.317). There is a slight increase in carbonate out into the Gulf, with a noticeable change between stations 12 and 18, as discussed above. The level of concentration of organic carbon is relatively constant, with no marked trends between stations.

	Correlation coefficients $CaO:CO_2$
Stations 1 - 12, 18, 19 20, 22 and 23	0.9854
Station 21	0.9044

The slight decrease in organic carbon in offshore stations would be expected if the major portion of the C were of terrestial origin. This is likely as the source area includes the densely forested Isla Vagra, Manamo, and Pedernales.

Water

Once again, total water was determined on all samples, and these results are tabulated in Table 2.3D, in view of the method used in grinding these samples, any results may be subject to error, as suggested in Chapter 1.4, when the major element geochemistry of the Meteor cores was considered.

MINOR ELEMENT GEOCHEMISTRY

The distribution of the elements B, Cr, V, Ni, Ba, Zr, Sr, Rb, Cu and Zn within the cores is discussed. The analyses for these samples are given in Table 2.3E at the end of the last chapter, together with a selection of values from the literature.

Boron

Only the top sub-samples from each core were analysed for this element. The concentration shows some fluctuation between the cores, but is within the range noted by Hirst (1962b). The B content of stations 6&9 is the highest, apart from isolated stations such as 12 and 19.

B may be expected to occupy three sites in the sediment; in the hydrolysate fraction, in the heavy minerals such as tourmaline, and possibly with organic carbon. In view of the low content of carbon, this latter control would appear to be of very minor importance.

Correlation coefficients

B:Clay	B:salinity
-0.1742	0.3605

Many workers, for example Landergren (1945), Fredrikson and Reynolds (1960), Walker and Price (1963), and Walker (1968) have proposed the use of the B content in clays as a palaeosalinity indicator, basing their proposals on the assumption that absorbed B increases with the salinity of the overlying waters. Other workers in this field, however, have cast doubts on the validity of the B-salinity relationship, notably Curtis (1964), Spears (1965) and Hirst (1962b., 1968). No discussion of this aspect of B geochemistry will be given in the present study in view of the restricted data on B content and salinity available.

In view of the lack of correlation between B and total clay, the ratios B/Al_2O_3 and B/K_2O have been considered, these results being shown in Table 2.4A. Out into the Gulf, K_2O and Al_2O_3 show a slight increase, to be expected, in view of the increase in total clay. If B is wholly associated with the latter, B/Al_2O_3 and B/K_2O should be relatively constant from station to station. Any fluctuation in these ratios would thus be the result of some additional control of the distribution of B. Both ratios show some fluctuation, in particular in stations 1 - 12 compared with stations 18 - 23, suggesting that some external control is influencing sedimentation in this part of the delta.

According to van Andel and Postma (1954 p.171 Fig.78) the area where cores 1 - 12 were collected is located on the delta front, where strong tidal influences, and a rate of deposition of 1 m./century is evident (p.159, Fig.75 ibid). Cores 18 - 23, on the other hand, were collected from the southern edge of the central gulf, with moderate depth, less tidal fluctuation, and a sedimentation rate of between 0.5 and 1.0m/century. Mixing of waters of differing salinity is feasible in the tidal area occupied by stations 1 - 12.

An increase in B content is noted in part of the delta between stations 6 and 7, where there is a change in salinity. It is suggested that this is the result of the mixing of the brackish waters of the Rio Pedernales with the more saline waters of the Gulf. An increase in total clay in the sediment is also noted, this may have resulted from an increase in the amount of clay particles flocculating in the zone of mixing due to rapidly changing salinity. The slightly higher B content in stations 1 - 12 on the delta may also be partly attributed to the tourmaline content of the heavy mineral fraction although this contribution must be small. While no correlation is evident between B and total clay, it is suggested that the hydrolysate fraction is the site of B in these sediments because of the fact that the mineralogy of these samples is dominated by the mineral illite,

TABLE 2.4A

Sub-sample	Total clay wt percent	B ppm	Al_2O_3 Wt per cent	K_2O Wt per cent	B/Al_2O_3 ratio $\times 10^{-3}$	B/K_2O ratio $\times 10^{-2}$
1S1	77	75	18.58	2.35	0.404	0.319
2S1	76	32	18.39	2.42	0.174	0.132
3S1	72	58	16.90	2.26	0.343	0.257
4S1	56	65	14.74	1.96	0.440	0.332
5S1	58	49	14.99	1.94	0.327	0.252
6S1	70	168	18.61	2.31	0.903	0.727
7S1	68	130	15.94	2.09	0.815	0.622
8S1	63	100	15.07	2.01	0.663	0.497
9S1	58	108	15.20	2.14	0.710	0.505
10S1	61	55	17.68	2.41	0.310	0.229
11S1	67	63	18.32	2.35	0.344	0.268
12S	65	100	16.56	2.19	0.603	0.456
18S1	74	58	18.80	2.64	0.308	0.220
19S1	77	100	20.34	2.76	0.491	0.363
20S1	82	63	19.97	2.70	0.315	0.233
21S1	83	70	19.22	2.56	0.365	0.273
22S1	81	90	18.11	2.35	0.497	0.383
23S1	85	41	19.97	2.51	0.205	0.158

and to a less extent, montmorillonite. The former is suggested by Harder (1961) to be the usual site of B in sediments. The relatively low B values for stations 18 - 23 are contrary to expectation, since they would be expected to be higher than those observed in stations 1 - 12 on the basis of an increase in hydrolysate fraction, and a decrease in the rate of sedimentation. Hirst (1962b), Harder (1963) have suggested that B contents would increase with a decrease in sedimentation rate. The B results are thus somewhat inconclusive and difficult to explain.

Chromium

This element has been determined in the surface samples only, the results of which are shown in Table 2.3E together with representative values from the literature. It is obvious that most of the analyses fall within the range observed by Hirst (1962b). The level of Cr concentration does not show much variation between the various stations but in stations 18 - 23 it is relatively constant.

Cr may be present in the sediments in two possible locations, in the hydrolysate fraction, or in the heavy minerals. The heavy fraction would, as Hirst (1962b p.1158) has pointed out, only contribute a small amount of the element. This implies, of course, that the hydrolysate fraction must control most of the variance of Cr, despite the low correlation between Cr and total clay (0.4215). Froehlich (1960) has discussed the geochemistry of Cr, and has suggested that micas and clays are the most important sites for the element in sediments.

In view of the poor correlation between clay and Cr, the ratios Cr/MgO, Cr/Al_2O_3 and Cr/Fe_2O_3 have been considered. If the Cr content were wholly in association with the hydrolysate fraction, then if this were to increase, so would the Cr content, and in effect the

TABLE 2.4B

Sub Sample	Cr ppm	MgO Wt.%	Al_2O_3 wt.%	Fe_2O_3 wt.%	Cr/MgO x 10^{-2}	Cr/Al_2O_3 x 10^{-3}	Cr/Fe_2O_3 x 10^{-2}
1S1	85	1.77	18.58	6.28	0.48	0.46	0.14
2S1	81	1.58	18.39	6.22	0.51	0.44	0.13
3S1	97	1.27	16.90	5.63	0.76	0.58	0.17
4S1	82	1.09	14.74	4.55	0.75	0.56	0.18
5S1	55	1.15	14.99	4.74	0.48	0.37	0.12
6S1	75	1.56	18.61	6.03	0.48	0.40	0.12
7S1	47	1.57	15.94	5.70	0.30	0.29	0.08
8S1	140	1.59	15.07	5.45	0.88	0.93	0.26
9S1	55	1.72	15.20	5.48	0.32	0.36	0.10
10S1	82	1.54	17.68	5.79	0.53	0.46	0.14
11S1	102	1.59	18.32	6.06	0.64	0.56	0.17
12S	41	2.66	16.56	5.56	0.15	0.25	0.07
18S1	97	1.50	18.80	6.26	0.65	0.52	0.16
19S1	96	1.75	20.34	6.87	0.55	0.47	0.14
20S1	107	1.92	19.97	6.79	0.56	0.54	0.16
21S1	112	1.84	19.22	6.55	0.61	0.58	0.17
22S1	97	2.52	18.11	7.61	0.39	0.54	0.13
23S1	94	2.36	19.97	7.17	0.40	0.47	0.13

ratio of the two would remain constant. As has been discussed in the relevant sections on the major element geochemistry, the oxides Al_2O_3, Fe_2O_3 and MgO are mainly associated with the hydrolysate fraction. The results shown in Table 2.4B indicate that Cr/Fe_2O_3 and Cr/Al_2O_3 show little fluctuation between stations. However, in the Cr/MgO ratio more fluctuation is evident, particularly in stations 1 - 12.

Hirst (1962b p.1158) has discussed the conditions whereby Cr would be expected to be more abundant in the illite structure on the basis of the physico-chemical conditions of formation. An increase in montmorillonite as noted by van Andel and Postma (1954 p.78) would thus result in a decrease in Cr. Factor analytical studies, discussed later in the chapter, indicate that the montmorillonite: illite ratio is probably relatively constant, thus an overall increase in the hydrolysate fraction would not affect the Cr/MgO ratio.

In summary, it would appear that Cr is associated largely with the hydrolysate fraction of the sediment, in view of the constant Cr/Al_2O_3 and Cr/Fe_2O_3 ratios, despite the poor correlation between Cr and total clay. The fluctuation in stations 1 - 12 may be the result of the tidal influences suggested in the discussion on B, but in this case, no clear relationship is apparent.

Vanadium

This element has been determined in only the uppermost sub-sample in each core, and the analyses are given in Table 2.3E. A slight increase in the V content occurs in the stations out in the Gulf.

This element could be expected to be associated with three possible phases: the hydrolysate minerals, organic C or Fe_2O_3. An association with the latter would only be expected in an oxidising environment such as on the Soldado and Erin Moruga platforms, or in the north and north western Gulf. c.f.van Andel and Postma (1954 Map lV).

Correlation coefficients

V:Clay	V:C
0.3967	-0.1360

The absence of a correlation with organic C may be attributed to the low levels of C and to the fact that the variance of V is dominated by other controls. No obvious close correlation is evident between V and total clay, and consequently the ratios V/Al_2O_3, V/Fe_2O_3 and V/MgO have been considered; they are shown in Table 2.4C. It is obvious that these ratios fluctuate, but apart from being more constant in stations 18 - 23, no marked changes are obvious, particularly in the ratios V/Al_2O_3 or V/Fe_2O_3. Average V/MgO ratios are also similar in stations 1 - 12 and stations 18 - 23. Hirst (1962b p.1160) suggested that montmorillonite is a relatively more important site for V than illite. The Factor analytical results indicate a relatively constant montmorillonite:illite ratio, and thus the increase in V content noted in stations 18 - 23 would be the result of an increase in total clay. This is supported by a lack of trends in the V/Al_2O_3, V/Fe_2O_3 or V/MgO ratios. In view of the lack of trends in the ratios, together with the marked change in salinity visible between stations 6 and 7, and the change in sedimentation rate reported in van Andel and Postma (1954) between stations 12 and 18, it would appear that the bulk of V is of a detrital nature, in that it is located in the clays, having been incorporated during the processes of weathering at source.

In conclusion, it is suggested that V is largely associated with the hydrolysate fraction in the sediment. The slight increase in V content in stations 18 - 23 would thus be explained by the increase in

TABLE 2.4C

Sample	V ppm	Al_2O_3 wt.%	Fe_2O_3 wt.%	MgO wt.%	V/Al_2O_3 $\times 10^{-3}$	V/Fe_2O_3 $\times 10^{-2}$	V/MgO $\times 10^{-2}$
1S1	86	18.58	6.28	1.77	0.46	0.14	0.49
2S1	81	18.39	6.22	1.58	0.44	0.13	0.51
3S1	92	16.90	5.63	1.27	0.55	0.16	0.73
6S1	94	18.61	6.03	1.56	0.51	0.16	0.60
7S1	24	15.94	5.70	1.57	0.15	0.04	0.15
8S1	114	15.07	5.45	1.59	0.76	0.21	0.72
11S1	106	18.32	6.06	1.59	0.58	0.18	0.67
18S1	124	18.80	6.26	1.50	0.66	0.20	0.83
19S1	128	20.34	6.87	1.75	0.63	0.19	0.73
20S1	158	19.97	6.79	1.92	0.79	0.23	0.82
21S1	100	19.22	6.55	1.84	0.52	0.15	0.55
22S1	108	18.11	7.61	2.52	0.60	0.14	0.43
23S1	120	19.97	7.17	2.36	0.60	0.17	0.51

total clay, noted earlier in Chapter 2.2.

Nickel

Nickel shows a slight increase in concentration out into the Gulf; the levels are higher than those recorded by Hirst (1962b).

Correlation coefficients

	Ni:C	Ni/Clay	Ni:Rb
Stations 1 - 12, 18, 19 20, 22 and 23	0.1647	0.8600	0.9262
Station 21	0.2395	0.3879	0.0456

The correlation coefficients given above suggest that an association between Ni and the organic C is of only minor importance, and that the variance of Ni is dominated by an association with the hydrolysate fraction of the sediment. The absence of significant correlation between Ni and organic C would be expected in view of the relatively low concentration of the latter in these sediments. In view of the increase in content of the hydrolysate minerals in the sediment away from the shoreline in the Boca Vagre, noted by van Andel and Postma (1954 p.78, Fig 33) some change in the level of concentration of Ni might be expected. A possible change in concentration might result from a close association between Ni and Mg in montmorillonite. However, octahedral sites in illites are also probable sites for Ni.

A slight increase in concentration of Ni, of the order of 10 ppm in stations 18 - 23 relative 1 - 12 can be explained in terms of an increase in total clay. Besides location in the hydrolysate fraction, some Ni will also be present in minerals of the heavy fraction, such as epidote, hornblende and pyroxene, where it will proxy for Mg in the crystal lattice.

Barium

The level of Ba shows a distinct increase between the sub-samples of stations 1 - 12 and those of stations 18 - 23. In general, the range of concentration is approximately similar to that observed by Hirst (1962b).

	Correlation coefficients		
	Ba:quartz	Ba:Al_2O_3	Ba:Clay
Stations 1 - 12, 18, 19 20, 22 and 23	-0.6539	0.7436	0.6474
Station 21	-0.1684	-0.4748	0.2877

A consideration of the correlation coefficients shown above indicates that the variance of Ba is dominated by its relationship with the hydrolysate fraction rather than with the detrital resistate fraction of the sediment. Some Ba would also be expected to be located in detrital feldspar, where it could substitute for K; this, however, would be of only minor importance in the present study because of the generally low content of detrital feldspar present. The negative correlation noted for the sub-samples of core 21 is somewhat unusual and cannot be explained by the presently available data.

Van Andel and Postma (1954 Fig 74 p.159) give rates of sedimentation for the area and their values show that the boundary between the areas where sediment is accumulating at a rate of 1m./century and 0.5 to 1m/century lies approximately between stations 12 and 18. If the sedimentation rate influences the Ba content of sediments, i.e., by sorption, or if all of the Ba is not in association with the hydrolysate fraction of the sediment, variation in the Ba/Al_2O_3, Ba/Clay and Ba/MgO ratios would result. These ratios given in Table 2.4D show no such fluctuations, so that it is reasonable to suggest that the Ba content is independent of the rate of

TABLE 2.4D

AVERAGE CONTENTS

Station	Ba ppm	Clay Wt.%	Al_2O_3 Wt.%	MgO Wt.%	Ba/Clay x 10^{-3}	Ba/Al_2O_3 x 10^{-2}	Ba/MgO x 10^{-1}
1	386	73	17.77	1.71	0.529	0.217	0.225
2	366	69	16.49	1.46	0.530	0.221	0.250
3	350	65	15.84	1.18	0.538	0.220	0.296
4	370	57	15.66	0.92	0.649	0.236	0.402
5	386	58	14.90	1.16	0.665	0.259	0.332
6	382	67	18.72	1.47	0.570	0.204	0.259
7	386	71	17.71	1.14	0.543	0.217	0.338
8	365	68	16.51	1.56	0.536	0.221	0.365
9	360	60	15.14	1.58	0.600	0.237	0.227
10	380	61	17.68	1.54	0.622	0.214	0.246
11	356	62	17.04	1.51	0.574	0.208	0.236
12	360	65	16.56	2.66	0.553	0.217	0.135
18	415	74	18.93	1.63	0.560	0.219	0.254
19	420	78	19.59	1.92	0.538	0.214	0.218
20	410	81	19.69	2.02	0.506	0.208	0.202
21	416	81	19.63	2.07	0.513	0.211	0.200
22	376	79	19.36	2.38	0.475	0.194	0.157
23	410	84	20.36	2.32	0.488	0.201	0.176

sedimentation, and salinity changes and so has been introduced to the sediment combined in the clay lattice, i.e., it is of detrital origin.

It is interesting to note that Factor Analytical studies discussed later in this chapter, suggest an association between Ba and montmorillonite, which is in turn supported by higher Ba contents of off shore samples. In montmorillonite absorbed Ba could probably occupy intersheet positions, in illite, the element could proxy for K.

Zirconium

The level of concentration of Zr shows a gradual decrease out into the Gulf, with a distinct decrease between stations 12 and 18. The results of the present study lie within the range observed by Hirst (1962b).

	Correlation coefficients Zr:Quartz
Stations 1-12, 18, 19, 20, 22 and 23.	0.8244
Station 21	0.6315

The close correlation between Zr and quartz suggests that the variance of Zr is dominated by an association with the detrital resistate fraction in the sediment. Zircon has been noted by van Andel and Postma (1954 Map III) in the Boca Vagre area. These authors suggest that the boundary of their 0 - zircon province runs NW - SE, due north of the Isla Cotorra; this would lie approximately betweenstations 12 and 18. To the north of this boundary minerals other than zircon are dominant in the heavy fraction. It would seem reasonable to suggest that the bulk of Zr in the samples is present in the mineral zircon, which is very stable and resistant to both mechanical and chemical weathering. The decrease in Zr content into the Gulf would thus be expected as a result of the decrease in relative amounts of coarser detrital material with a drop in the velocity of the sediment bearing current. The change noted may also have been influenced by the confluence of bottom currents flowing westwards through the Serpents Mouth with the sediment bearing currents from the Boca Vagre. This could result in the deposition of most of the coarser sediment load, so that only finer clay particles are carried into the Gulf.

Strontium

The level of concentration of Sr also shows a distinct change between cores 12 and 18. In stations 1 - 12 little fluctuation is noticeable, but between cores 18 and 23, a slight increase is noticeable. The level of concentration observed in the present study lies within that observed by Hirst (1962b).

	Correlation coefficients $Sr:CO_2$
Stations 1 - 12, 18, 19, 20, 22 and 23	0.8504
Station 21	0.8439

In view of the close correlation with CO_2, it is obvious that the variance of Sr is dominated by its association with the carbonate phase of the sediment. Shell debris, such as mollusc shells, was observed in some of the cores. The shells are aragonitic and thus likely to be important sites for Sr, which can substitute for Ca in the crystal lattice of this mineral. For a discussion and bibliography on the Sr content of calcareous skeletons, see: Dodd(1967). According to Noll (1934), aragonite can contain up to 4 weight percent Sr. Sr^{2+} may also be present, as a result of diadochic replacement of Ca^{2+} in plagioclase feldspar, or in the hydrolysate fraction.

In summary, it is suggested that most of the Sr is present in aragonite of bioclastic origin, a result of diadochic substitution for Ca^{2+}.

Rubidium

The level of concentration of Rb is relatively constant in cores 1 - 12, but there is a distinct increase between cores 12 and 18, resulting in higher levels in cores 18 - 23. The concentration found in the present work agrees with the range observed by Hirst (1962b).

	Correlation coefficients	
	Rb:Clay	Rb:K_2O
Stations 1 - 12, 18, 19, 20, 22 and 23.	0.9391	0.9036
Station 21	0.5020	0.3113

The correlation coefficients indicate an obvious close correllation with the hydrolysate fraction of the sediment. Some Rb may also be present in feldspar, but this will be of minor importance in view of the fact that most of the feldspar would appear to be plagioclase.

Copper

The level of concentration of Cu shows increase with distance from the shore line, particularly distinct between stations 12 and 18. On the whole, a higher level of concentration has been found in the present study than by Hirst (1962b).

	Correlation coefficients	
	Cu:Clay	Cu:C
Stations 1 - 12, 18, 19 20, 22 and 23.	0.6140	0.0287
Station 21	0.1714	0.3744

From these correlation coefficients it would appear that in most of the sub-samples, Cu is associated with the hydrolysate fraction of the sediment. The reason for the poor correlation between Cu and organic C may be the relatively low concentration of the latter. In stations 18 - 23, the higher concentration of Cu correlates with an increase in total clay. Factor analytical studies, discussed later, suggest an association between Cu and montmorillonite; this is contrary to the Cu-illite relationship originally suggested by Hirst (1962b) for these sediments, but in agreement with the factor analysis of Spencer et.al.(1968).

In summary, it would appear that the variance of Cu in these sediments is dominated by its association with the hydrolysate fraction of the sediment, particularly with montmorillonite. Organic carbon may also be a possible associate, but only low correlation is shown. A distinct increase is noted in the level of concentration in stations 18 - 23 compared with 1 - 12. This is the result of an increase in the hydrolysate fraction of the sediment.

Zinc

The concentration of this element shows a noticeable increase in level between stations 12 and 18. Hirst (1962b) does not give analyses for Zn, so that no comparative data is available. The results lie within the range given for shales by Rankama and Sahama (1950 p.713).

	Correlation coefficients	
	Zn:C	Zn:Clay
Stations 1 - 12, 18, 19, 20, 22 and 23	0.0542	0.9428
Station 21	0.3376	0.6145

The variance of Zn is clearly dominated by its association in the hydrolysate fraction. The relatively high concentration of the element, noted in cores 18 - 23, is probably the result of an increase in the hydrolysate fraction and is independent of the sedimentation rate.

FACTOR ANALYSIS

The major and minor element analyses of the cores from the Gulf of Paria were processed using the Factor Analysis program previously used for the Meteor cores. The data obtained by Hirst (1962a, b.) has also been processed by a similar method, the results obtained being described by Spencer, Degens and Kulbicki (1968).

Since data must be provided for each sub-sample, the B, Cr, and V analyses have been omitted as they were only determined for selected horizons. The distribution of 19 variables in 60 sub-samples from 18 stations was examined by this multivariate technique; the variables used were SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, K_2O, TiO_2, S, P_2O_5, CO_2, C, H_2O, Ni, Ba, Zr, Sr, Rb, Cu, Zn.

From the Principal Factor Matrix, shown in Table 2.4F, 7 factors emerge which account for 95 percent of the variance in the original data. These include all factors which account for at least 1.5 percent of the variance. A list of the eigenvalues and cumulative percentage of total variance explained is given in Table 2.4E. From the Principal Factor Matrix, it is clear that the major part of the variance of the data is explicable in terms of sorting in the sediments. The bi-polar SiO_2, Zr versus clay constituent, Factor 7, dominates the factor pattern and in this respect is in close agreement with the results of Spencer et. al. (1968).

The promax oblique factor matrix, K min=8, is given in Table 2.4G. Factor scores are of particular interest in areal studies, since changes can be observed in the factor scores between stations; for example between stations 12 and 18, as discussed later.

It is obvious from Table 1.4G that the dominant factors are 2, 3, 6 and 7. The remaining factors accounting for the variance of

TABLE 2.4E

Eigenvalues	Cumulative percent of total variance
10.939	57.576
2.185	69.079
1.583	77.412
1.169	83.566
0.829	87.929
0.644	91.321
0.478	93.839
0.304	95.440
0.247	
0.193	
0.120	
0.101	
0.051	
0.048	
0.034	
0.030	
0.019	
0.011	
0.007	
18.999	

TABLE 2.4F

Principal Factor Matrix

	1	2	3	4	5	6	7
SiO_2							-0.95
Al_2O_3						0.26	0.92
Fe_2O_3							0.94
MgO	-0.25	-0.25			0.26	-0.25	0.79
CaO						-0.54	0.70
K_2O							0.92
TiO_2				-0.37		0.76	0.40
S	-0.33	0.25			0.76	-0.26	
P_2O_5	0.39		0.29		0.82		
CO_2			-0.33			-0.63	0.58
C			-0.47	0.77		0.29	
H_2O		0.47	0.28	0.39			0.67
Ni						0.25	0.88
Ba			0.27			0.50	0.68
Zr							-0.91
Sr						-0.31	0.88
Rb							0.96
Cu		-0.41	0.30				0.71
Zn							0.98

Factors less than 0.25 omitted

TABLE 2.4G

Promax Oblique Pattern Matrix K min = 8

	1	2	3	4	5	6	7
SiO_2			-0.63			0.29	
Al_2O_3							0.94
Fe_2O_3						-0.31	0.57
MgO	-0.26	-1.20					
CaO						-1.02	-0.33
K_2O							0.90
TiO_2		0.50	0.63				1.76
S	-0.96	0.26					
P_2O_5					0.96		
CO_2		0.34				-1.46	
C				1.13			
H_2O		0.29	1.67				-0.47
Ni		0.37	0.51				0.69
Ba		-0.26	0.31			0.67	0.90
Zr		0.66					
Sr						-0.98	
Rb			0.26				0.63
Cu	0.29	-1.51					-0.25
Zn							0.47

Factors less than 0.25 omitted

TABLE 2.4H

Correlation between Factors

	1	2	3	4	5	6	7
1.	1.00	0.16	-0.07	-0.14	-0.40	0.26	-0.10
2.		1.00	-0.87	-0.45	0.03	0.84	-0.81
3			1.00	0.48	-0.05	-0.79	0.81
4				1.00	0.14	-0.41	0.49
5					1.00	0.04	-0.02
6						1.00	-0.70
7							1.00

only one element in two cases, Factor 4 and 5, while Factor 1 is concerned with the variance of MgO, and S, with an opposed Cu loading.

The loadings on the four dominant factors are shown below:

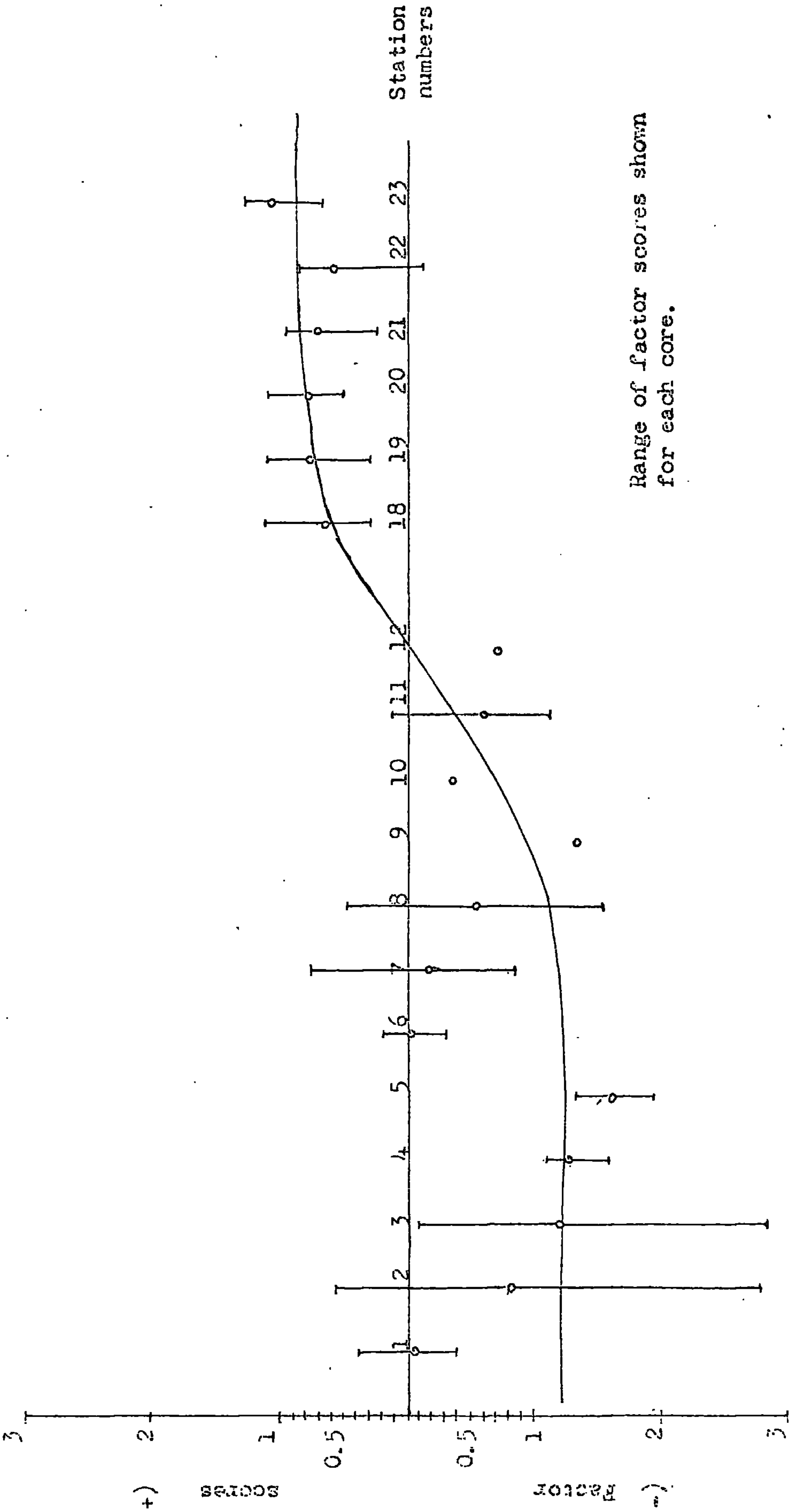
Factor 2	Factor 3	Factor 6	Factor 7
TiO_2, S, CO_2	H_2O, Ni,	SiO_2, Ba.	Al_2O_3, Fe_2O_3,
+ H_2O, Ni, Zr.	Ba, Rb.		K_2O, TiO_2
			Zn, Rb, Ba, Ni.
MgO, Ba	SiO_2, TiO_2,	Sr, CO_2	CaO, H_2O,
Cu		CaO,Fe_2O_3	Cu

Factor 7

Factor 7 is the most distinct and important factor with CaO, Cu and H_2O loadings opposed by Al_2O_3, Fe_2O_3, K_2O, TiO_2, Zn, Rb, Ba and Ni. From Figure 2.41, it is obvious that scores with negative loadings predominate in stations 1 - 12, after which positive loadings are predominant. A linear relationship is shown in Figure 2.42, when the factor scores are plotted against weight percent total clay. This, together with the range of constituents involved, suggests that the positive loadings on Factor 7 represent the hydrolysate fraction of the sediment. The negative loading on this factor of Cu, CaO, may be explained in terms of a relationship with feldspar in the detrital resistate fraction. It will be noted in Figure 2.41 that the negative loading is predominantly in stations 1 - 12, which would be in agreement with this suggestion. The H_2O loading in this factor may be explained in terms of analytical error, as discussed earlier in the section on major element geochemistry. It would thus appear that Factor 7 represents clay minerals bipolar with the detrital resistate fraction. Figure 2.43 shows a low correlation between median diameter and factor scorer. This is probably due to the restricted range of

Figure 2.41

FACTOR 7.



Range of factor scores shown for each core.

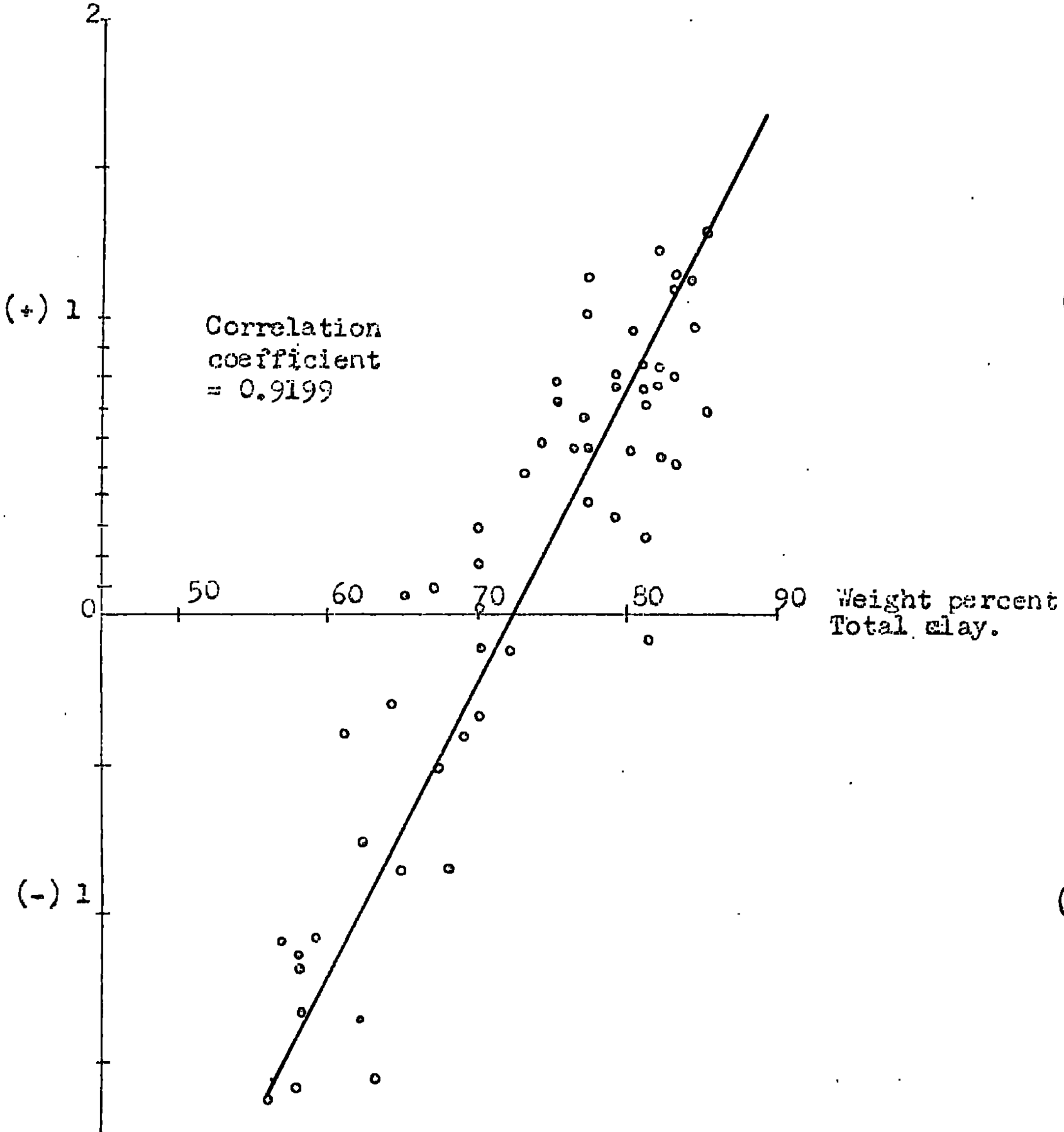


Figure 2.42. Scores for factor 7 plotted against weight percent total clay.

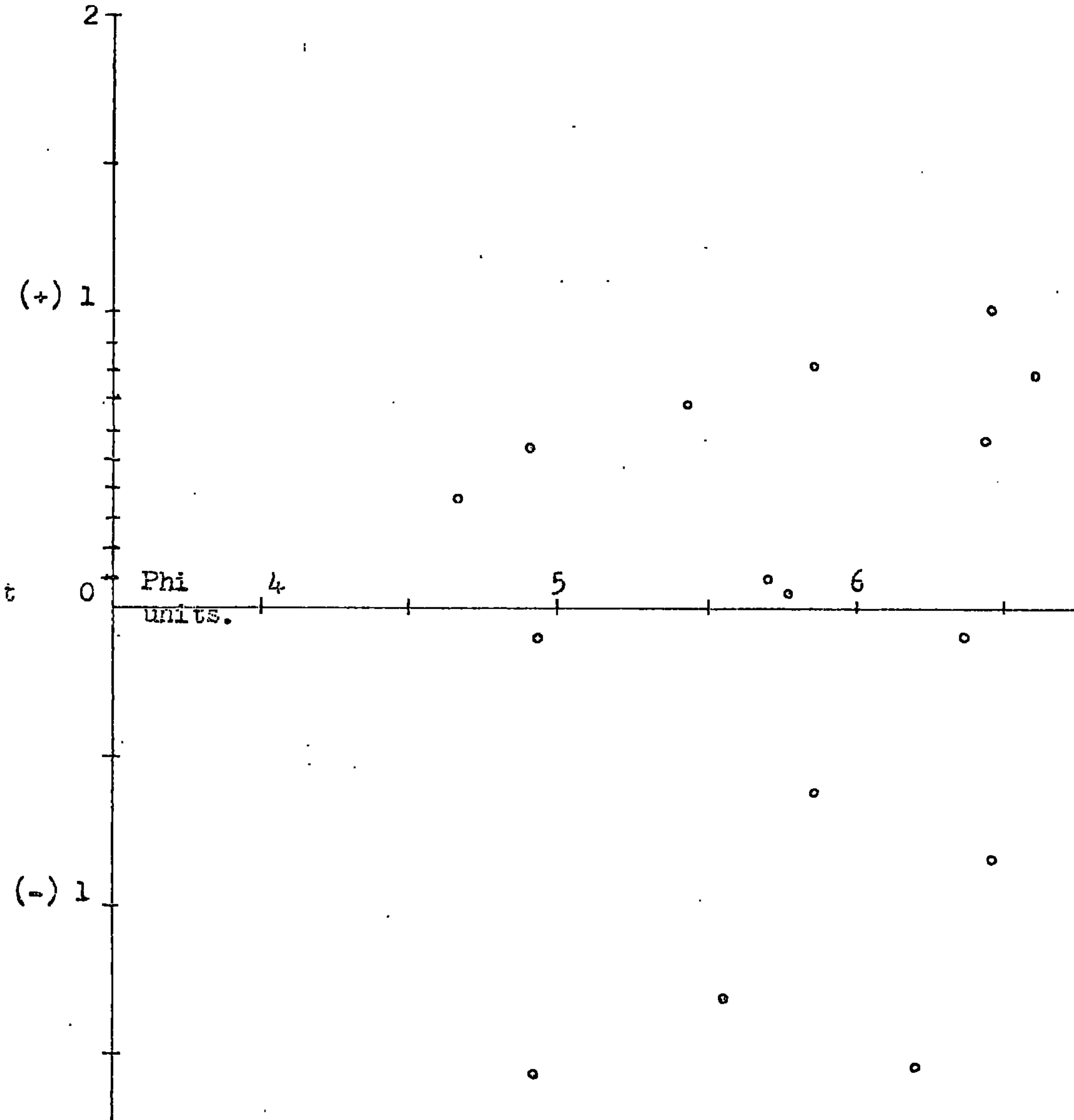


Figure 2.43. Scores for factor 7 plotted against Median diameter expressed in phi units.

grain size within the suite of cores, since Spencer et. al.(1968. p.991 Fig. 6.) show a relationship between geochemical data, derived by Hirst (1962a,b.) and grain size data from van Andel and Postma (1954). The samples examined by these workers had a greater range of grain size than those of the present study and included sands and silts. The strong loading for K_2O and the absence of an MgO loading, which could be expected for montmorillonite suggests that this represents illite. Figure 2.41 shows the plot of factor scores, the trend towards high positive loadings in stations 18 - 23 being explained in terms of an overall increase in the hydrolysate fraction.

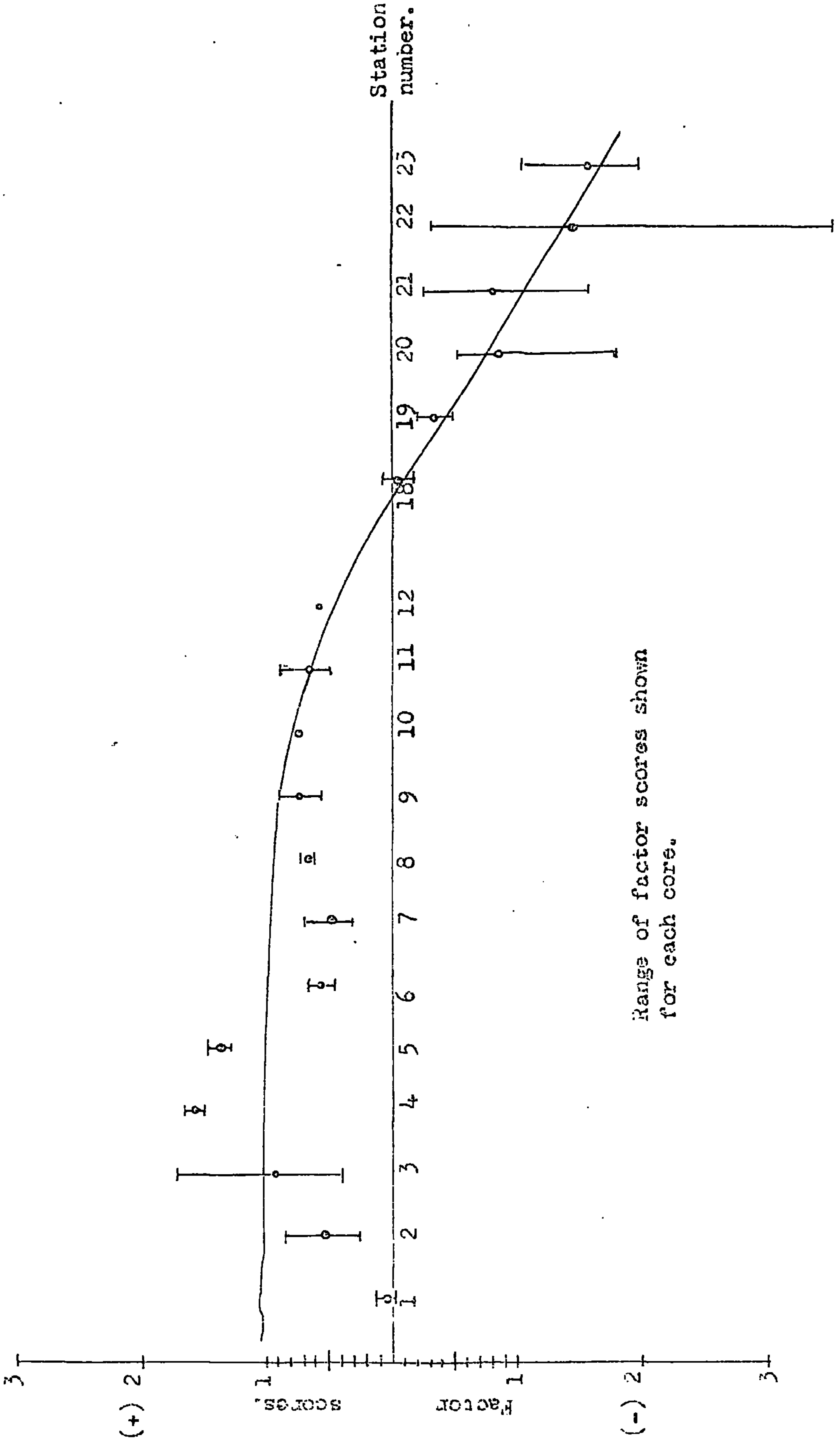
In Table 2.4H, correlation between the factors are listed. It is interesting to note strong negative correlations between Factor 7, 2 and 6 and a strong positive correlation with 3. These are to be expected in view of the fact that the hydrolysate loading on Factor 7 is resolved into Montmorillonite and illite respectively factors 2 and 3. The minor detrital loading on factor 6, and the suggested feldspar loading on factor 7 might contribute to the strong correlation between these two factors, but, more important, the correlation indicates that a relative increase in the hydrolysate fraction is accompanied by relatively high bioclastic carbonate, both resulting from a decrease in sedimention rate.

Factor 6

Factor 6 has SiO_2 and Ba loaded against Sr, CO_2, CaO and Fe_2O_3; Figure 2.44 shows a distinct break in factor scores between stations 12 and 18. Sr, CaO, CO_2 and Fe_2O_3, which dominate this factor, represent the carbonate fraction, where Sr may proxy for Ca in the mineral aragonite which is present in shell debris. The presence of Fe_2O_3 on this factor is a little unexpected, but may represent an

Figure 2.44

FACTOR 6.



Range of factor scores shown for each core.

association with shell debris. The negative loadings for Ba and SiO_2 will represent the detrital fraction, i.e., non-carbonate material, but it will be noted that this loading is relatively insignificant compared with the positive carbonate loadings. Since the carbonate content is higher in off shore samples there will naturally be a bias towards detrital constituents in the opposed loadings. The negative correlations between factor 6 and factors 3,7, strongly suggest that the Ba loading on this factor represents detrital Ba associated with relatively resistant minerals such as feldspar, rather than Ba associated with the hydrolysate fraction.

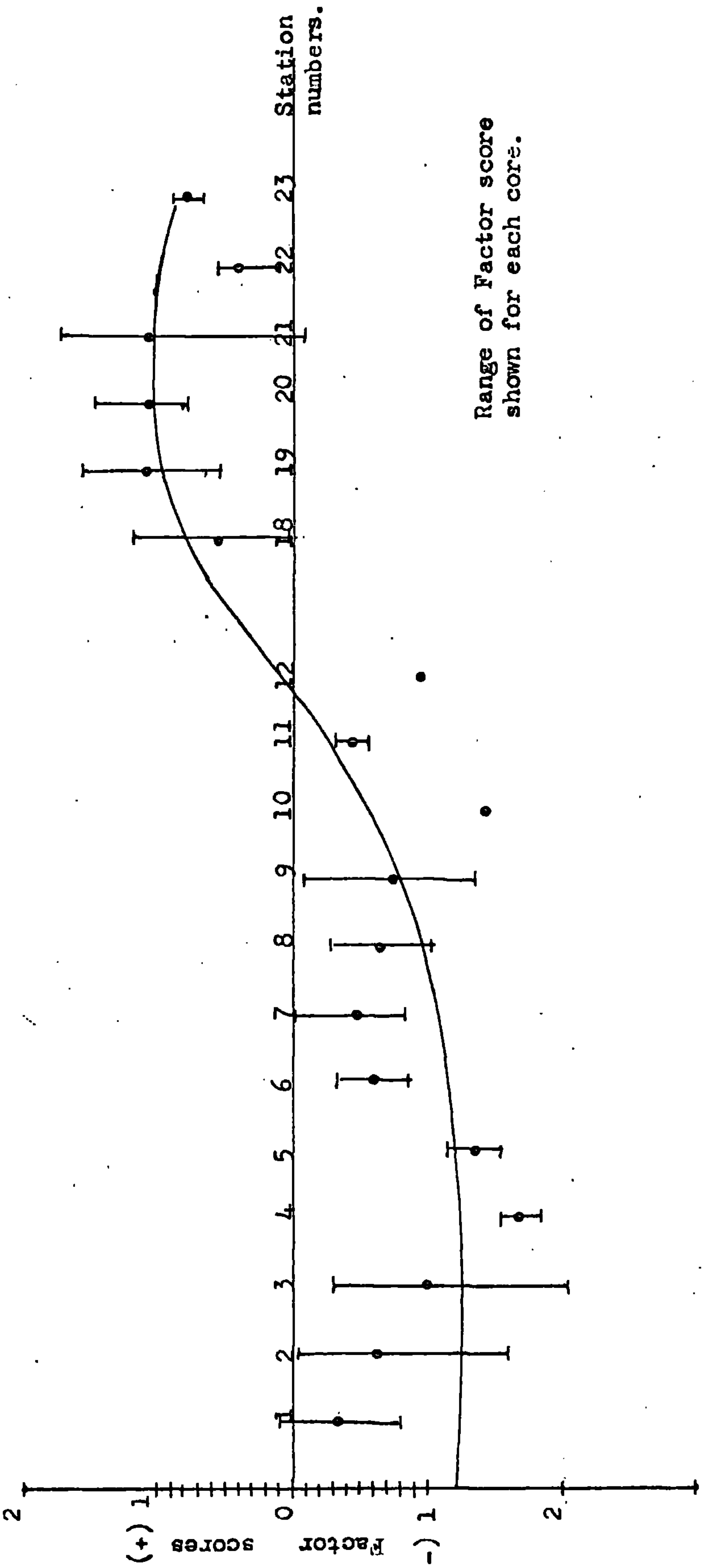
The noticeable break from positive to negative scores between stations 12 and 18 may be explained in terms of a change in the rate of sedimentation. Van Andel and Postma (1954 p.159. Fig. 75) place a boundary between the areas of higher rates of sedimentation (1.m./century) on the delta, and the lower rates of the Gulf proper (0.5 - 1.00m century) This boundary does in fact lie between stations 12 and 18. If the rate of sedimentation i.e., rate of accumulation of terrigenous material decreases, then authigenic bioclastic material, such as shell debris, introduced from the Gulf, or through the Serpents Mouth, would proportionally increase. This factor is one which is to some extent pH dependent since the change noted in the factor scores in Figure 2.44., coincides with a change in the pH of the surface sediment from pH 6.5 - 7.1, to 7.1 - 7.5 cf. van Andel and Postma (1954 p.96. Figure 43).

Factor 3

In this factor, positive loadings for H_2O, Ni, Ba and Rb are bipolar with SiO_2 and TiO_2; Fig. 2.45 again shows a distinct change in the factor scores between station 12 and 18. The factor may be explained in terms of clay versus detrital components, since Ni, Ba, Rb and H_2O would be present in the hydrolysate fraction. This suggestion is supported by the correlation between Factors 3 and 7 shown in Table 2.4H. In all

Figure 2.45

FACTOR 3



Range of Factor score shown for each core.

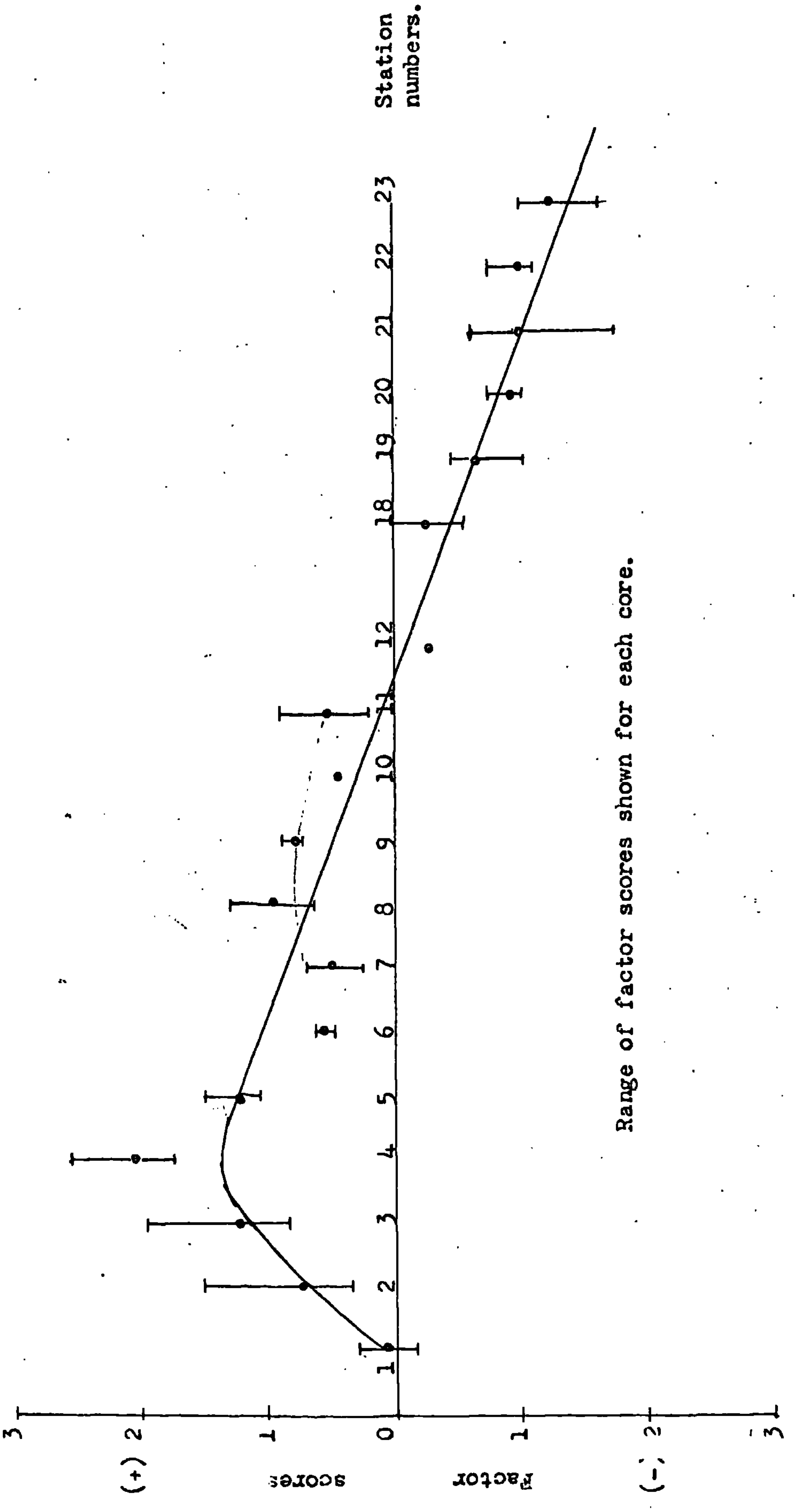
probability, in view of the Rb loading, and the coherence in nature of Rb and K, the hydrolysate fraction may represent illite: SiO_2 and TiO_2, as quartz and rutile respectively, would obviously occur as resistate minerals. In the discussion concerning the distribution of TiO_2, it was suggested that the bulk of TiO_2 would be present in the hydrolysate fraction, it is valid to suggest in the negative portion of the Factor 3, TiO_2 is present as a detrital since it does not score as high as in Factor 7, where it is undoubtedly scoring with the hydrolysate fraction. Figure 2.47 demonstrates a linear relationship between weight percent quartz, and the scores of factor 3, and a similar, though opposite relationship with weight percent total clay. The dominance of hydrolysates in stations 18 - 23 may be explained in terms of sedimentation rate with coarser material being deposited in the delta proper and the finely divided clay size fraction being carried out onto the delta front. This clay size fraction would be expected to contain predominantly hydrolysate minerals.

Factor 2

Factor 2 consists of TiO_2, S, CO_2, H_2O, Ni and Zr loaded against MgO, Ba, and Cu. This factor is not as clearly defined as those described above, but appears to represent another detrital to hydrolysate bipolar factor. TiO_2 and Zr would be possibly of detrital derivation from the minerals rutile and zircon respectively. However, the significance of Ni, H_2O and CO_2 is a little obscure, and may be due, as in the case of H_2O, to some analytical error. MgO, Ba and Cu could represent the montmorillonite fraction of the sediment as observed by Spencer et. al. (1968) p.994. Strong correlation between Factor 2, 3 and 7, shown in Table 2.4H, would support this suggestion. There is again a linear relationship between the scores of Factor 2 and weight percent quartz as shown in Figure 2.48. Figure 2.46 shows a change between the factor scores of stations 1 - 12 and 18 - 23, with MgO, Ba and Cu loadings

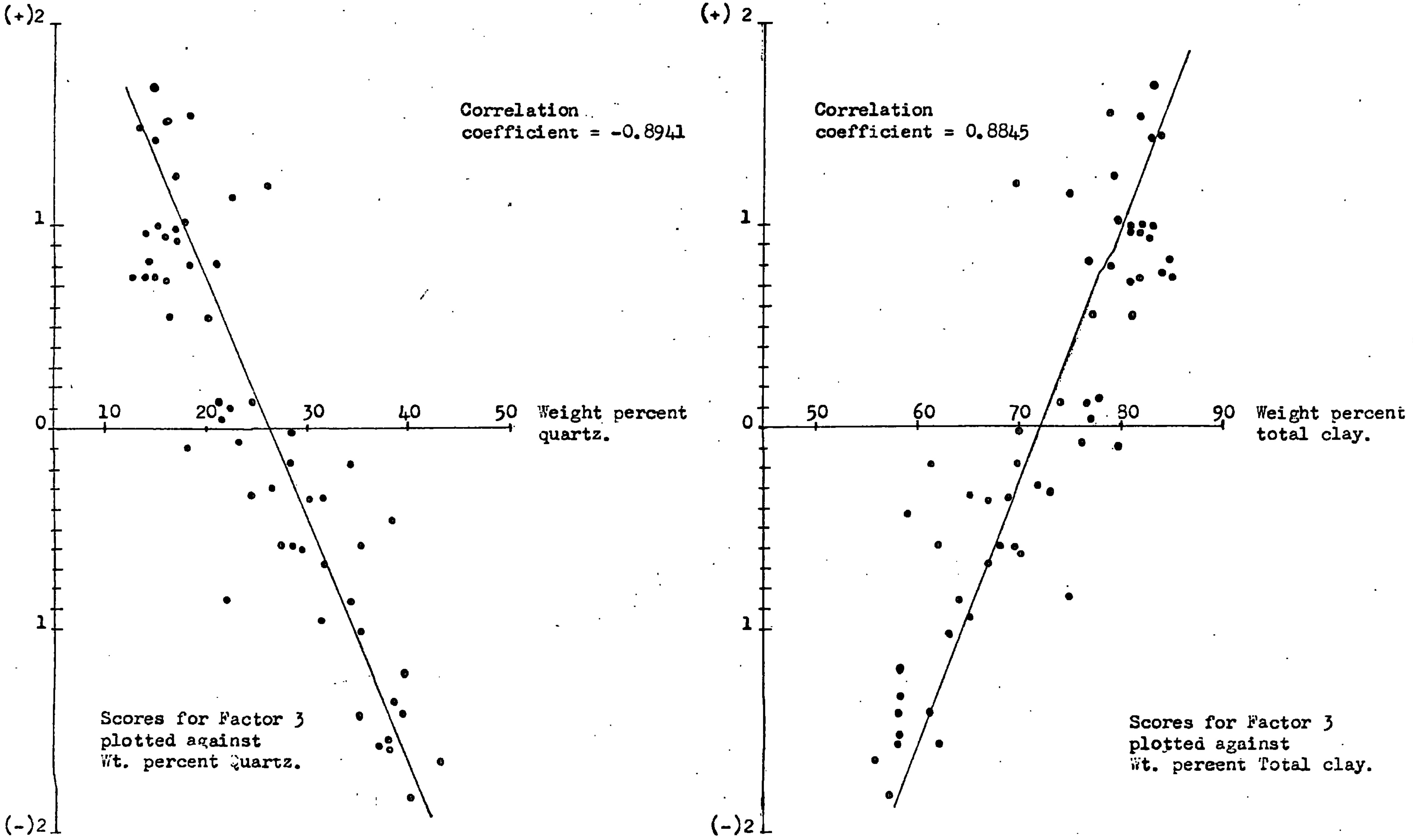
Figure 2.46

FACTOR 2.



Range of factor scores shown for each core.

Figure 2.47



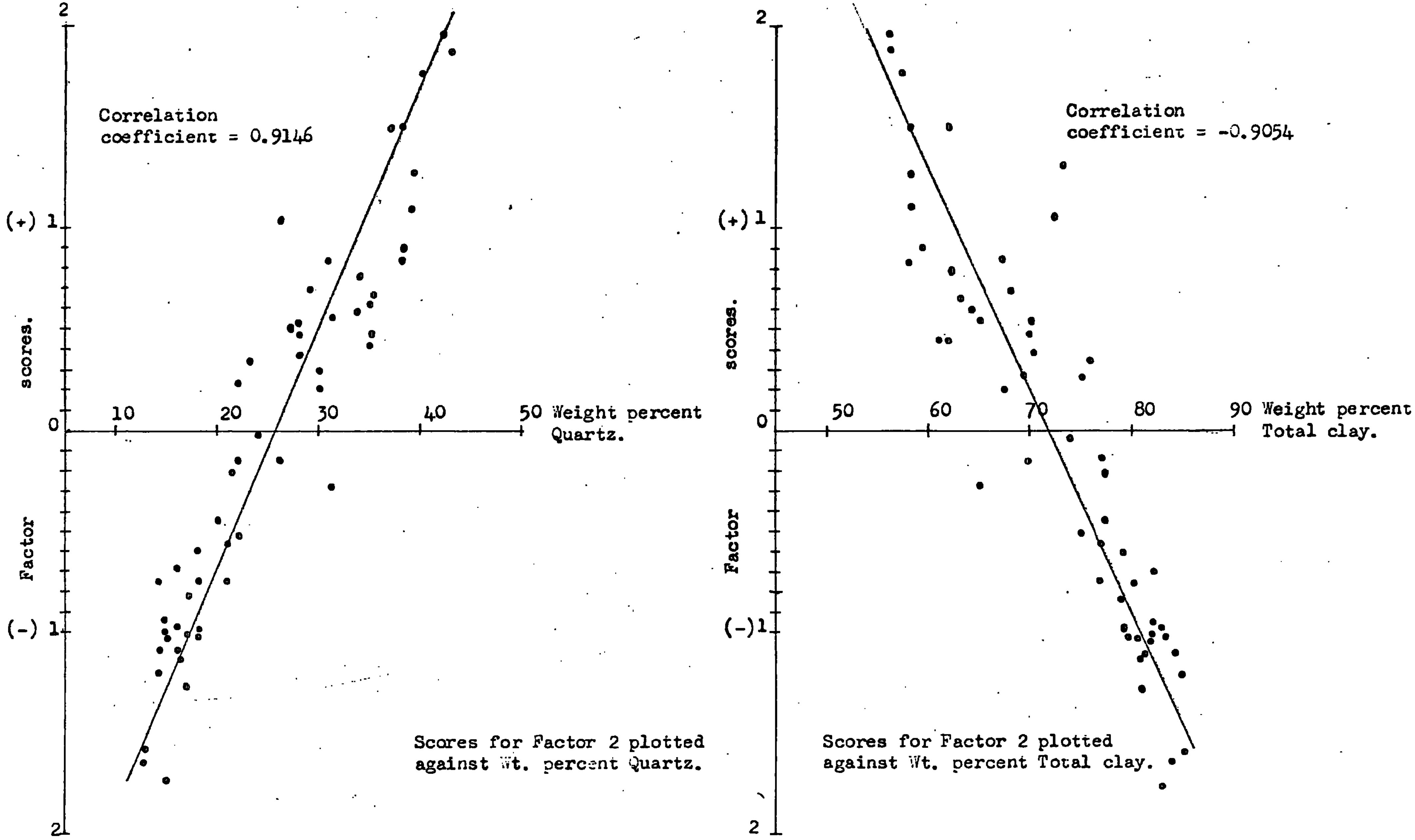
Correlation coefficient = -0.8941

Scores for Factor 3 plotted against Wt. percent Quartz.

Correlation coefficient = 0.8845

Scores for Factor 3 plotted against Wt. percent Total clay.

Figure 2.48



Scores for Factor 2 plotted against Wt. percent Quartz.

Scores for Factor 2 plotted against Wt. percent Total clay.

having the higher scores out into the Gulf. Van Andel and Postma (1954. p.78) suggest a change in the composition of the hydrolysate fraction about a boundary which would lie between stations 12 and 18, with a distinct increase in montmorillonite content north of this boundary. The linear relationship observed between Factor 2 and weight percent total clay, shown in Fig. 2.48, would suggest that the increase in montmorillonite indicated by van Andel and Postma (1954 p.78 Fig. 33) is due to an increase in the hydrolysate fraction as a whole, rather than in montmorillonite relative to illite.

Factor 1

Factor 1, has MgO loaded against S and is somewhat unclear. This may be the result of poor analytical precision for S resulting from low levels of concentration.

Factor 4.

Carbon scores alone on this factor. The low concentration of this element together with poor analytical precision will reduce the strength of associations to other constituents. This factor may thus represent analytical errors.

Factor 5

Phosphorus scores alone on this factor. Once again, low concentration and the resultant poor analytical precision may well have resulted in inaccuracy.

In summary, 4 dominant factors emerge from a study of the chemical date from the cores. Distinct trends are visible when the factor scores are considered on an areal basis, and good agreement is visible between the results of the present study and that of van Andel and Postma (1954), Hirst (1962 a,b) and Spencer et. al.(1968)

CONCLUSIONS

1. From a consideration of the grain size analyses, the cores studied consist of sediment deposited under relatively shallow sluggish water conditions. A restricted range of grain size is also noted.

2. There is a progressive decrease in the content of resistate minerals, and a concurrent increase in the content of the hydrolysate fraction towards the open Gulf. These changes are reflected in mineralogical analyses for quartz and total clay, as well as in chemical analyses for SiO_2 and Zr.

3. The change in rate of sedimentation, noted by van Andel and Postma (1954), can be recognised in the sediments, the break lying between stations 12 and 18. This change is marked by an increase in the proportion of the hydrolysate fraction and associated minor elements, notably Zn, Ba, Cu, Ni and Rb.

4. A small increase in the amount of biogenic debris in the sediment with distance from shorelines is coincident with an increase in pH of the surface sediment; some of this bioclastic debris may have been introduced by inflowing currents from the Serpents Mouth. The increase in bioclastic debris is reflected IN THE CONTENT of CaO, CO_2 and Sr in the cores.

5. Increases in the concentration of MgO, Ba, Ni and Al_2O_3 in stations 18 - 23 are suggested to indicate an increase in the total clay content, and hence both montmorillonite and illite in the sediment. The increase in montmorillonite noted by van Andel and Postma (1954 p.78 Fig.33) is due to an increase in the content of the hydrolysate fraction of the sediment relative to the detrital resistate material, and does not result from a change in the proportions of illite and montmorillonite.

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