ALI I. BELTAGY

Geochemistry of sediments from the Gulf of St. Lawrence

THE GEOCHEMISTRY OF SOME RECENT MARINE SEDIMENTS FROM THE GULF OF ST. LAWRENCE

A study of the less than 63 μ fraction

by

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A thesis submitted to the Faculty of Graduate Studies and Research,
McGill University, in partial fulfillment of the requirements for
the degree of Doctor of Philosophy in Marine Sciences.

Marine Sciences Centre,
McGill University,
Montreal, Quebec,

December, 1973.

Ph.D. Marine Sciences Centre

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ABSTRACT

The concentration and distribution of major, minor and trace elements in some Recent marine sediments from the Gulf of St. Lawrence have been studied. The geochemical characteristics of the sediments in the Gulf, as a mid-latitude sedimentary basin, are analyzed, and the factors that control the elements distribution are studied. The partition patterns of trace elements between the detrital and non detrital components of the sediments, are discussed, and their possible significance is indicated. Vector and factor analyses are applied to the data, and the results are interpreted in relation to various sources of material to the Gulf. In the lights of the information gained from the study of the Recent sediments, the geological history of five long cores from the area is discussed.

The present study shows the possibility of using some aspects of the chemistry of sediments as depth indicator. It also offers some base line information needed for further environmental work.

Ph.D Marine Sciences Centre

Ali I. Beltagy

GEOCHIMIE DE QUELQUES SEDIMENTS MARINS RECENTS RECUEILLIS DANS LE GOLFE DU ST. LAURENT

Etude sur les fractions inférieures à 63 µ.

Resumé

La concentration et la distribution des éléments dans les sédiments marins récents sont étudiées (éléments majeurs, mineurs et éléments trace). Les caractéristiques géochimiques des sédiments dans le Golfe, considéré comme un bassin sédimentaire de moyenne latitude, sont analysées, ainsi que les facteurs qui contrôlent la distribution des éléments. L'histoire géologique dans cinq carottes de sédiments prises dans cette region est discutée a la lumière des informations obtenues de l'analyse des sédiments récents.

La présente étude montre la possibilité d'utiliser certains aspects de la chimie de sédiments en tant qu'indice de la profondeur. Elle pourra également servir de base pour des travaux ulterieurs sur l'environnement.

ACKNOWLEDGEMENTS

I am indebted to my research director Dr. B.F. d'Anglejan for advice and critical reading of the manuscript. The thesis was also read by Drs. E. Mountjoy, of the Department of Geological Sciences, McGill University, and D.H. Loring, of the Bedford Institute of Oceanography, N.S., who also checked the analysis of four samples for purpose of standardization.

I have also benefited from discussions with Dr. G. Weber, of the Department of Geological Sciences, McGill University and with E. Smith and M. Brisebois, fellow graduate students at the Marine Sciences Centre.

I thank Mrs. S. Horska, of the Department of Geological Sciences, for her kind assistance in the laboratory work, and Professor D. Maclellan for her help in improving the manuscript.

Thanks are also due to the I.B.P., B.I.O. and GIROQ for ship time given on cruises to the Gulf. Some samples used in the present study were collected by Dr. B.F. d'Anglejan during 1967, 68 and 1969. Dr. D.H. Loring has kindly made available several core samples and information on the lithology and fauna of these samples.

This study was supported by the N.R.C. of Canada through grants to Dr. B.F. d'Anglejan.

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

1.1 Purpose of This Study

The importance of the Gulf as a sedimentary basin stems from the fact that it serves as a convergence basin for the whole of the St. Lawrence River System and several other smaller rivers.

The Gulf offers possibilities of well controlled studies, as sediments sources are only few and are well identified; also sites of deposition vary over small distances from shallow shelves and platforms to deeper troughs and basins. It is of particular interest for at least the ~~two~~ following reasons: (i) the Gulf provides a unique example of a shallow epicontinental sea in sub-arctic regions which has been influenced by glaciation and by ice as transporting mechanisms ; (ii) it has been suggested that the St. Lawrence System has greatly influenced the composition of the sediments of the North Atlantic Ocean between lat. 35 and 55 N° (Biscaye, 1964; Griffin et al., 1968; Beltagy et al., 1972).

Also, there is still a general lack of information on the sedimentary geochemistry of the Gulf, despite recent studies by Nota and Loring (1964) and Loring and Nota (1969). More particularly, the distributions and modes of occurrence of the trace elements are not known.

Hence, the present study was undertaken with the following objectives:

1. To study some geochemical characteristics of the sediments as indicated by the concentrations and distributions of various major and trace elements.

2. To analyse the factors which influence these distributions, and the various pathways by which the elements were incorporated into the sediments.

3. To attempt estimating the geological implications of the variations of these geochemical characteristics with time.

The results obtained will be of value in establishing new parameters for ice age studies and in supplying basic data for future detailed environmental investigations of the Gulf sediments.

It was decided in this work to use only the fine fraction i.e., the fraction of the sediments smaller than 63 μ (230 mesh) which [illegible] the lower limit of sands on the Wentworth scale. This decision was made for the following reasons: (i) One of the intentions was to study the geochemical characteristics of fine terrigenous detritus brought to the Gulf in suspension or as bed load and subject to large scale dispersal patterns. This perspective was thought particularly useful for the purpose of characterising the Gulf of St. Lawrence as a major source of sediments for the deep North Atlantic Ocean. (ii) It was felt that by removing the sands and coarser material, the influence on sediment composition of nearby sources was decreased; this also reduced the noise introduced by admixing to the sediments of ice rafted debris dispersed through the Gulf in a more or less random manner. (iii) Finally, in the course of sample preparation for chemical analysis the presence of coarse fragments may lead to results biased towards their particular chemical composition.

Furthermore, it could be claimed that the combined clay and silt fractions, as a complex mixture of material delivered to the Gulf in suspension, or as bed load, or by ice and wind, should provide a fairly good average of recent sediment composition in the Gulf. Particle size analysis of sediments from the Gulf indicates that about 80% by wt. of the sediments is in this range (Nota and Loring, 1964).

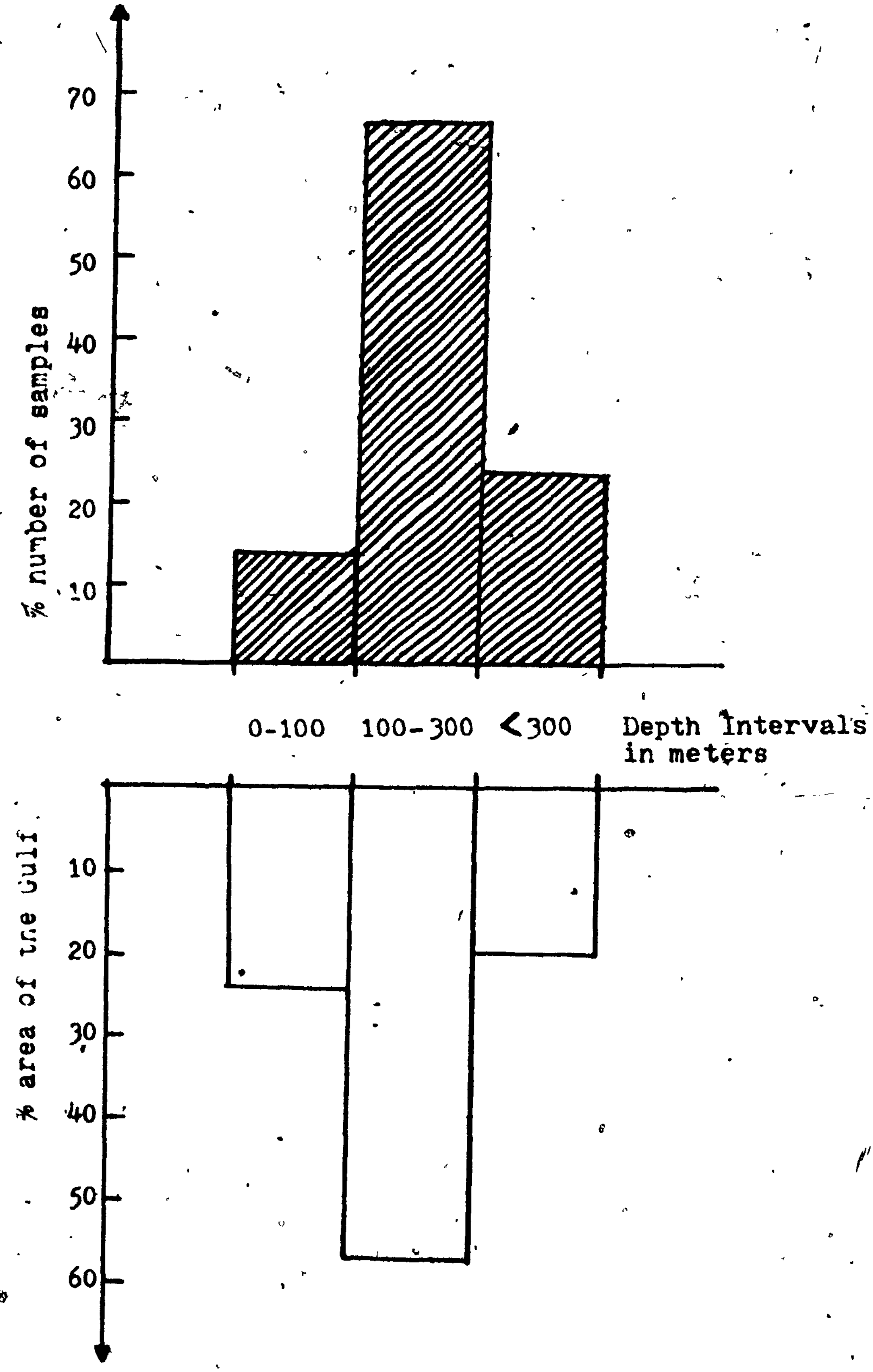
1.2 Limitations of the Present Study

Because of practical limitations, a total of only 55 surficial sediment samples and 5 suspended matter samples could be collected and analyzed. The geographic and depth distribution of the bottom samples are shown in Figure A.1, Appendix A, and Figure 1.1.

This is admittedly a very small number of samples in relation to the large area of the Gulf. The density of samples stands at one sample per four thousand square kilometers. However, a strict control over sampling patterns and the number of samples, as described by Griffiths (1967) for example, can not always be exercised in marine geochemical surveys. Many instances of studies based on a small number of samples can be found in the literature: Hirst (1962)

Figure 1.1

Percentage number of samples per depth interval compared to percentage area of the Gulf covered with this depth interval.


% number of samples
70
60
50
40
30
20
10
0-100
100-300
<300
Depth Intervals in meters
% area of the Gulf
10
20
30
40
50
60

studied the geochemistry of modern sediments from the Gulf of Paria using a total of 25 samples. Chester and Messiha-Hanna (1970) in investigating the distribution patterns of several trace elements in sediments from the North Atlantic Ocean, based their study on 38 samples. Wedepohl (1960) in studying the geochemistry of marine sediments from different oceans, used only 18 samples. The hydrogeochemistry of the whole Mackenzie River basin was investigated from the study of about 100 samples (Reeder et al., 1972).

The validity of any conclusions inferred from such studies, however, can be tested and reinforced by the application of necessary statistical tests. These are based on the premise that information about a phenomenon can be deduced from an examination of a small sample collected from an infinite set of potential observations.

The problem of low sampling density is even more pronounced in high Arctic areas because of operating conditions and prohibitive costs. Although it may be necessary there to proceed with a very open network of stations, great care must be applied to derive maximum information from the scattered data.

The present study should provide some test as to the value of low sample number reconnaissance surveys, at least for the major elements; our results may be compared with those of Loring (1973, in press) obtained from a much denser sampling programme carried out in recent years over the whole area of the Gulf of St. Lawrence.

1.3 Area Investigated

1.3.1 Geographical Setting

The Gulf of St. Lawrence is an inland sea occupying an area of about 226.7×10^3 sq. km. (Forrester et al., 1968), between Latitude 46° 36' and 50° 30' N and Longitude 56° 30' and 69° 00' W. It has a funnel-like configuration (Figure 1.2).

It is bounded by Quebec and Labrador to the north; Newfoundland and Cape Breton Island to the east; Prince Edward Island and New Brunswick coast to the south; and the Gaspe Peninsula to the southeast.

The Gulf communicates with the Atlantic Ocean through the Cabot Strait to the east and the shallow Strait of Belle Isle to the northeast.

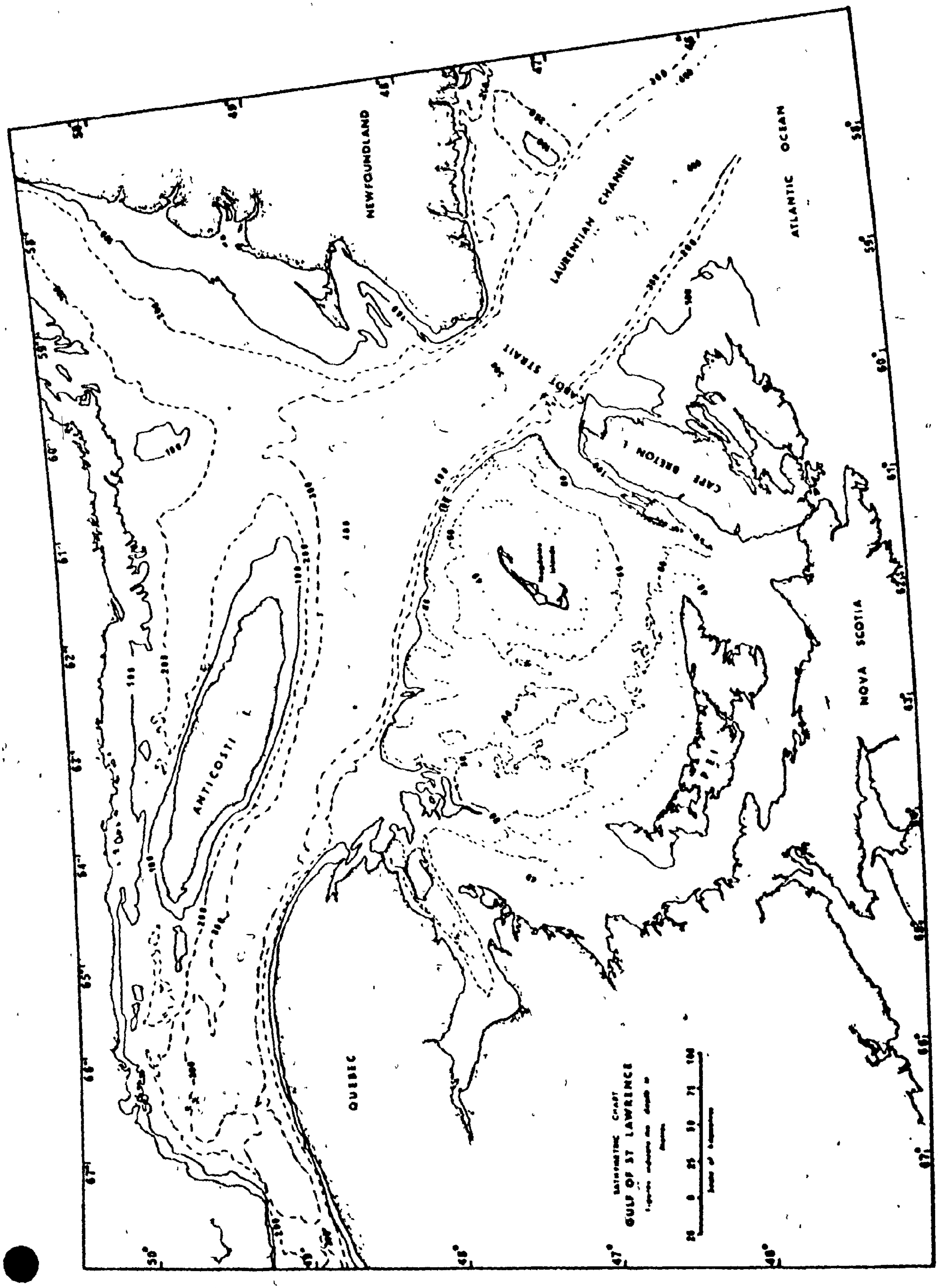
There are a few major islands: the Magdalen Islands, the Mingan Islands and Anticosti.

The entire Gulf acts as an estuary or mixing basin for the St. Lawrence River. However, strictly speaking, the St. Lawrence estuary is usually considered as the region extending between Quebec City and Pointe des Monts (Forrester, 1967).

The river is fed by the Great Lakes, has a total drainage area of 513×10^3 sq. km., and a mean yearly discharge at Quebec City of about 10.2×10^3 cu. m/sec (Parde, 1948). It has also a number of major streams as direct tributaries, the Ottawa, the Maurice and the Richelieu.

Figure 1.2

The Gulf of St. Lawrence, bathymetry and physiography.


BATHYMETRIC CHART
GULF OF ST LAWRENCE
25 0 25 50 75 100
NEWFOUNDLAND
LAURENTIAN CHANNEL
ATLANTIC OCEAN
CABOT STRAIT
CAPE BRETON I.
NOVA SCOTIA
P. E. I.
ANTICOSTI I.
QUEBEC
100
200
400
47°
48°
49°
50°
58°
59°
60°
61°
62°
63°
64°
65°
66°
67°

Other smaller rivers along the north shore and the south shore of Quebec, western Newfoundland and the northern part of New Brunswick also contribute waters to the Gulf. With these additional streams, the total drainage basin of the Gulf of St. Lawrence is about 13×10^5 sq.km. (El-Sabh et al., 1970), and the mean average fresh water discharge in the Gulf is 12.2×10^3 cu.m/sec (Forrester, 1964).

1.3.2 Bottom Physiography

The bottom topography of the Gulf of St. Lawrence has been the subject of several investigations (Hjort, 1919; Huntsman et al., 1954; Lauzier and Trites, 1958). A major feature is the Laurentian Channel, which extends from near the mouth of the Saguenay River to the edge of the Atlantic Continental Shelf, with depth ranging from 250 to 540 m. A north eastern branch forms the Esquiman Channel, which follows the western shore of Newfoundland towards the Strait of Belle Isle. The Esquiman Channel is more than 180 m deep, except as it approaches Belle Isle Strait.

South of the Laurentian Channel lies a platform known as the Magdalen Shallows, with the small Magdalen Islands almost in its central part. The area has an average depth of about 40 m. The Strait of Northumberland separates Prince Edward Island from the northern New Brunswick coast.

According to Lauzier et al. (1957), one quarter of the Gulf area is shallower than 50 m, while about 20% is deeper than 300 m.

On the basis of bathymetric and sedimentological data, Loring (1962) subdivided the Gulf into two regions (Figure 1.3). The first represents zones of recent deposition and soft sediments; the second is made up of acoustically hard bottom, which may range from exposed bed-rock to either gravel, sand or compact sediments.

1.4 Pleistocene Events in the Gulf of St. Lawrence

The following summary of the Pleistocene history of the Gulf is mainly condensed from detailed discussions by Loring (1973); Prest and Grant (1969); and Gadd (1971).

According to Loring (1973), since early Cenozoic times the valley system as it is known today, as well as the accompanying drainage system, developed along lines of structural and lithological weaknesses by a process of sequential fluvial erosion. This erosional evolvement has taken place with minor interruption with the latest period of valley entrenchment, probably occurring in Pliocene time or early Pleistocene time.

The glacial geology of surrounding areas and the submarine morphology and unconsolidated sediments provide evidence for the presence of central ice sheets in the Gulf during the Pleistocene, as well as for ice advance from local centers during the retreat stages of the continental ice mass. The evidence indicates that there were three ice lobes advancing in the area. The main ice flow appeared to have entered the Laurentian Trough from the north

Figure 1.3

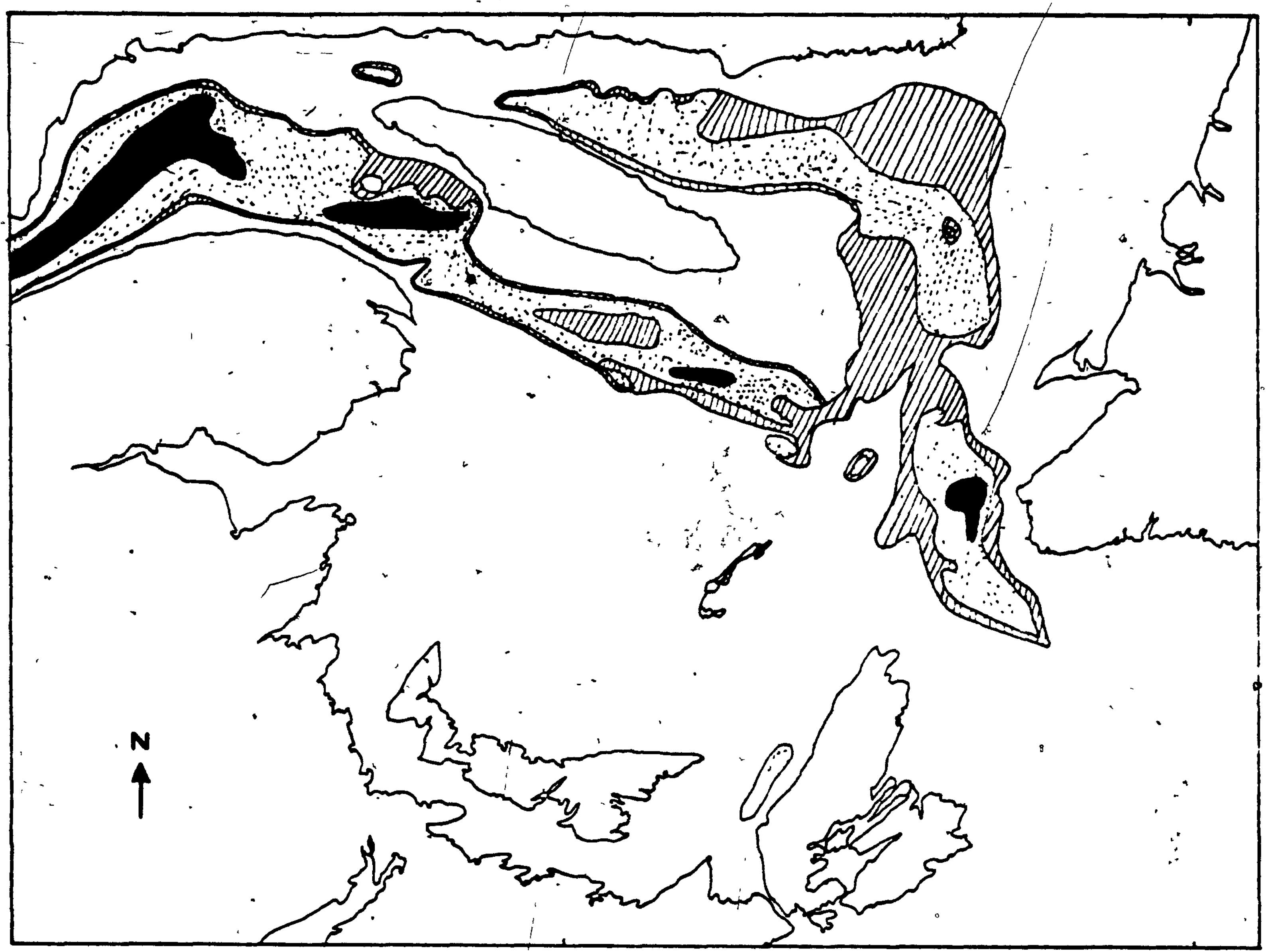
Different depositional environments in the Gulf of St. Lawrence (After Loring, 1962).

Shaded areas = Recent deposits

Unshaded areas = Non-recent depositional environment

Sediment thickness:

■	> 18 m
⬚	8 - 18 m
▨	< 8 m
□	uncovered bottom or sandy gravel bottom.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side. The second major ice flow may have come also from the north, and moved east in the Mingan Trough North of Anticosti. A third lobe from the highland of Labrador entered the Esquiman Trough and modified its topography. As this ice pushed south and west, it converged with the Mingan lobe and the Laurentian lobe at the south end of Newfoundland Shelf. The ice apparently began to wane between 14.5 and 15×10^3 years B.P., with ice withdrawing up the Laurentian Channel from Cabot Strait and into the tributary valleys permitting the invasion of deep water from the Atlantic Ocean into the Gulf.

By that time, parts of the coastal area adjacent to the St. Lawrence River and Gulf were submerged beneath the sea as the deglaciation progressed. The main cause of this submergence was the isostatic depression of the crust that resulted from the load of the ice, and the eustatic rise in sea level. As the ice withdrew and the rebound became greater than the eustatic rise in sea level, these coastal areas re-emerged.

Based on acoustical and sampling data, Loring (1973) indicated that the lowest sea level stand was about 110-120 m below the present sea level, with other higher standstills at about 58-68 m below the present sea level occurring between 5 and 13×10^3 years B.P.

1.5. Sediment Sources to the Gulf of St. Lawrence

Sediment sources to the Gulf include all rock formations in the areas marginal to the Gulf, and the suspended load carried by the St. Lawrence River System.

Areas marginal to the Gulf of St. Lawrence can be divided into two major subdivisions: (i) the region north of the St. Lawrence River, including the north shore of the Gulf to the Strait of Belle Isle; (ii) the region south of the St. Lawrence River extending over the Gaspe Peninsula, New Brunswick, Prince Edward Island and the Magdalen Islands. Formations there belong to the Appalachian Province which extends down to Georgia (U.S.A.). Formations occurring in Newfoundland are also part of it.

1.5.1 Region North of the St. Lawrence River:

This area belongs to the Grenville Province, which extends over the southern part of the Canadian Shield north of the St. Lawrence and Ottawa Rivers. Grout (1938); Dresser and Denis (1944) and Harrison (1963) have studied and described the different rocks found in this region. The rocks are essentially pre-Paleozoic granites, granodiorites, syenites, ultrabasics, gneisses and schists of the Canadian Shield. Paleozoic sediments are made up principally of limestones and shales (Figure 1.4).

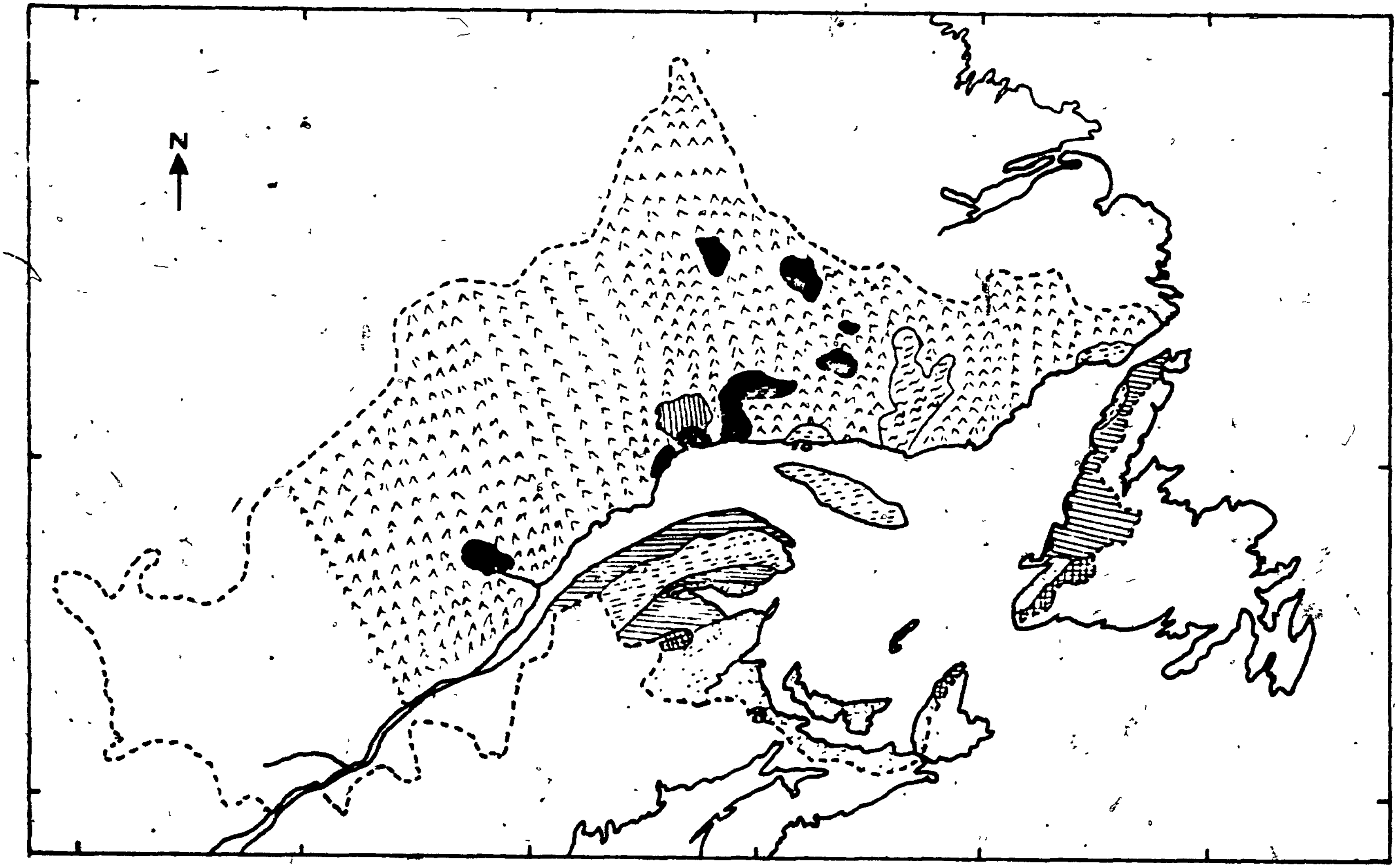
1.5.2 The Appalachian Region:

A great variety of rock types is represented in this area, namely granite, slate, argillites, quartzites, limestones and shales. Nearly all of these rocks were subject to deformation by the Acadian Orogeny at the end of the Devonian period.

Figure 1.4

Lithology and major rock types in the drainage basin of the Gulf of St. Lawrence.

■	Basic rocks (anorthosite and gabbro)
⌃	Acid rocks (granite and granodiorite)
▥	Metamorphic rocks (gneisse and schist)
░	Sandstone
▒	Limestone
▤	Highly deformed sedimentary rocks
▦	Granites and metamorphics
☰	Sediments and volcanic rocks
- - -	Boundaries of the drainage basin.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Marine limestone, dolomite, anhydrite, gypsum-rich evaporites, shales and siltstone are extensive in central New Brunswick and Nova Scotia.

Gaspe Peninsula and Chaleur Bay:

The most dominant rock types in the Gaspe Peninsula are the Gaspe sandstone and Gaspe limestone of Silurian-Devonian age.

The Chaleur Bay Group comprises a complex series of sedimentary and volcanic rocks of Upper Silurian age (Greiner, 1965). Among the sedimentary rocks are found conglomerates, coralline limestones, red feldspathic sandstone, brick-red sandstone, siltstone and shales.

The Group is also characterized by a number of magnetic deposits, sulfide veins and molybdenum occurrences.

Anticosti, Mingan and Magdalen Islands:

On the Mingan Islands, which lie close to the north shore, and on Anticosti Island, are exposed outcrops of Ordovician age. These outcrops are made up of limestones with minor amounts of shales, sandstone and conglomerates.

Rocks on the Magdalen Islands are made up of basalts intruding beds of limestone, gypsum and occasional sandstone.

Newfoundland:

Newfoundland forms the north eastern extremity of the Appalachian Tectonic Belt. Metamorphosed sediments and volcanic rocks of Ordovician and Sillurian ages outcrop north of the Strait of Belle Isle. The west coast of Newfoundland, near the Strait of Belle Isle, consists mainly of carbonate sediments. These thin-out further south along this coast to give place to clastic sediments of Cambrian age (Fleming, 1970).

North of Fortland Creek, older series of metamorphosed clastic sediments are exposed, extending as far as the Port au Basque Peninsula. They are interrupted here and there by ultramafic and mafic intrusions.

Clastic sediments of Silurian age, as well as volcanic rocks and some lime stones outcrop around St. Georges Bay (Figure 1.4).

1.5.3 Other Sources of Material to the Gulf

Tills in the St. Lawrence Valley, also marine re-working of glacial deposits of the St. Lawrence Valley during the Champlain Sea episode, followed by under cutting of Champlain Sea sediments during post glacial uplift have made available large quantities of easily eroded material as potential source of sediments (Karrow, 1961; Prest, 1961).

1.6 Previous Work on the Gulf as a Sedimentary Basin

The origin and physiography of the Laurentian Trough have been discussed by Johnson (1925), Shepard (1931, 1963) and by Mac Neil (1956). Structural aspects of the Trough in the region of Cabot Strait, leading outward from the Gulf of St. Lawrence to the Atlantic Ocean, have been investigated by Press and Beckmann (1954).

Studies relating to the conditions of sedimentation in the Gulf are rare. Nota and Loring (1964) have discussed the regional marine geology. According to them, the Pleistocene glaciation largely determined the present shape of the Laurentian Trough. The distribution pattern of the sediments is fairly regular and characterized by poorly sorted coarse grained, near-shore deposits and an extensive area of soft pelites in the deep parts of the Trough (Loring, 1962; Nota and Loring, 1964).

The above studies concluded that the sediments may be generally considered as mineralogically immature. The crystalline rocks of the Canadian Shield provide the dominant source of sands. Ice transport is the main agent of dispersal.

The Magdalen Shelf was the subject of more detailed studies by Loring and Nota (1966, 1969) and Loring et al. (1970). Their observations on the bottom morphology of the Magdalen Shelf suggest that it does not relate to the present environmental conditions (Loring and Nota, 1966). The surface sediments appear to be mainly the erosional products of the local bed rock.

The sediment dispersal pattern of the whole Gulf of St. Lawrence was inferred from a study of the sand size fraction of the sediments by Loring and Nota (1969). The authors concluded that detrital material from the Canadian Shield is dispersed south and east to the shore lines of New Brunswick, Prince Edward Island and Cape Breton Island.

Geochemical studies made by these authors (Nota and Loring, 1964; Loring and Nota, 1968) were confined to the major elements (Na, K, Al, Ca, Si, Fe, Ti and Mn), in the Gulf region extending between 64°W and 69°W. Their results will be discussed later.

As commonly found in marine sediments, in the Gulf of St. Lawrence one finds an inverse relationship between grain size and distance from shore; also, the greater the distance from shore the better sorted are the sediments. However, ice-rafted, medium to coarse sand is common in areas of fine sediments.

On the basis of sediment texture, Nota and Loring (1964) grouped sediments in the western and southern Gulf into three types: type I includes material from near shore areas, characterized by a low degree of sorting and a high content of coarse material; type II represents the deep water pelites, which have up to 60% clay size material and about 35% of silt size; type III is restricted to sediments similar to the Leda Clay deposits of the Champlain Sea and is found only in the estuary above the Saguenay River entrance (Nota and Loring, 1964).

Current rates of deposition may vary greatly from one place to another in the Gulf. Nota and Loring (1964) concluded that maximum deposition occurs in central, deeper parts of the Gulf, where they estimated a rate of deposition of 22 cm per 1000 years. However, this rate may only be valid for the gray olive-green mud deposits.

The pH of the Gulf waters ranges between 8.4 at the surface and 7.6 near the bottom (d'Anglejan and Dunbar, 1968; Loring and Nota, 1968). No systematic geographic variations were observed.

An oxygen minimum is present in the deeper waters of the Gulf. d'Anglejan and Dunbar (1968) measured the dissolved oxygen near the bottom in the deep waters of the Gulf; they found values of 4.5 ml/l in Cabot Strait, decreasing to concentrations below 3.0 ml/l in the western and northern parts of the Gulf. The water column is well oxygenated and anaerobic conditions do not exist anywhere in the Gulf. Loring and Nota (1968) showed that oxidizing conditions prevail at the surface of the deep water pelites, with Eh values +400 mv. However, the oxidizing layer is only 1 to 2 cm thick, and reducing conditions with negative Eh values develop below this depth in a reducing layer.

1.7 Definitions

Shallow water samples:	samples collected from water depths less than 200 m, unless otherwise stated.
Deep water samples:	samples collected from water depth greater than 200 m.
Detrital fraction (of the sediment, or an element):	The acid reducing mixture insoluble residue, mostly silicate minerals of terrestrial origin.
Non-detrital fraction:	The acid reducing mixture, soluble fraction, including carbonates derived from terrestrial sources.
Coarse clay fraction:	Particles with a diameter $< 4\ \mu$.
σ :	Standard deviation.
r:	Correlation coefficients

CHAPTER II

PARTICLE SIZE DISTRIBUTION AND MINERALOGY OF SEDIMENTS FROM THE GULF OF ST. LAWRENCE

2.1 Particle Size Distribution

2.1.1 Introduction

Marine sediments may be transported to the sites of deposition by one or more of several transport mechanisms (Sverdrup *et al*., 1942; Kuenen, 1965). In the Gulf of St. Lawrence sediments are mainly transported (i) by ice rafting; (ii) as suspended load by water movements; (iii) as bed load due to bottom processes. The fraction of the sediment which has been transported by the third mechanism is not easily identified. On the other hand, ice rafted material can be distinguished rather simply from sediments which have settled from suspension by the following general criteria; (i) sediments transported by ice rafting may contain the whole spectrum of particle sizes, from pebbles or boulders, down to clay size particles (Shepard, 1973); sediment particles carried in suspension have a narrow spectrum of fine sizes (Postma, 1969); (ii) the fraction of ice-rafted sediments is independent of the distance from the source; (iii) because coarse sediments may be carried by ice over long distances, their abundance will not show any prevailing tendency to correlate with water depth.

2.1.2 Methods of Analysis

Mechanical analysis was performed on 25 Gulf samples covering different water depths, Figure B.1, (Appendix B). Wet sieving was used to separate the coarse fraction ($>63\ \mu$). The pipette method was used for the particle size analysis of the fine fraction ($<63\ \mu$). A detailed description of these methods is given in Appendix A.

2.1.3 Results and Discussions

The results of the particle size analysis are given in Table 1 Appendix B. The coarse fraction makes up about 21% by weight of the sediment, ranging from 0% to 66%.

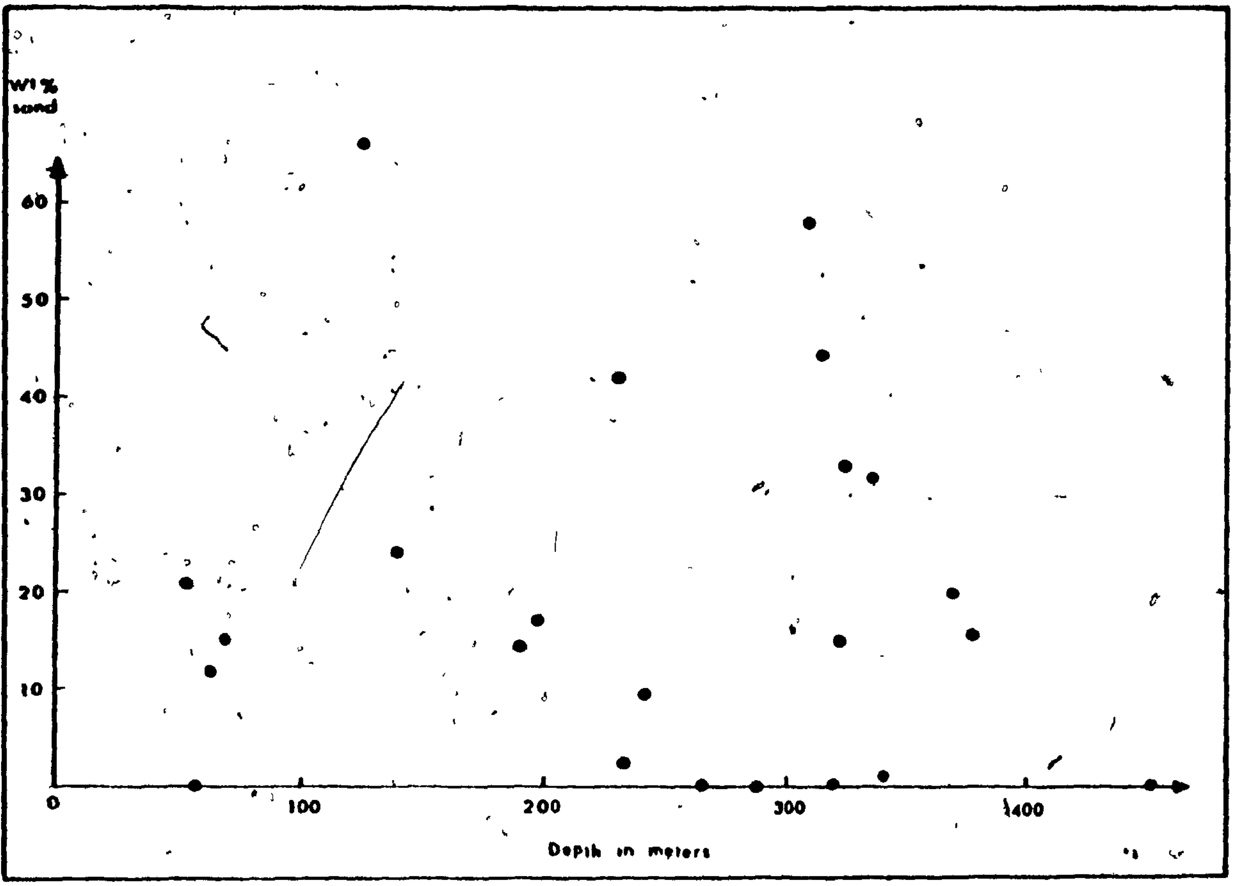
Figure II.1 shows the relationship between the weight percentage of the coarse fraction and the water depth. As shown in this Figure, there is no relationship between the amount of coarse material and the depth of water. Clearly, therefore, the sand and gravel (coarse fraction) could not have been transported by water movements, and ice rafting appears to be the main agent involved in transporting the coarse material. A supporting evidence comes from current measurements along the bottom in the Gulf which were made using seabed drifters (Lauzier, 1970). These measurements indicate that the bottom currents are in the range of 0.5 to 1.5 cm/sec. Such current velocities seem to be far below the current speed required to transport materials of sizes $>63\ \mu$.

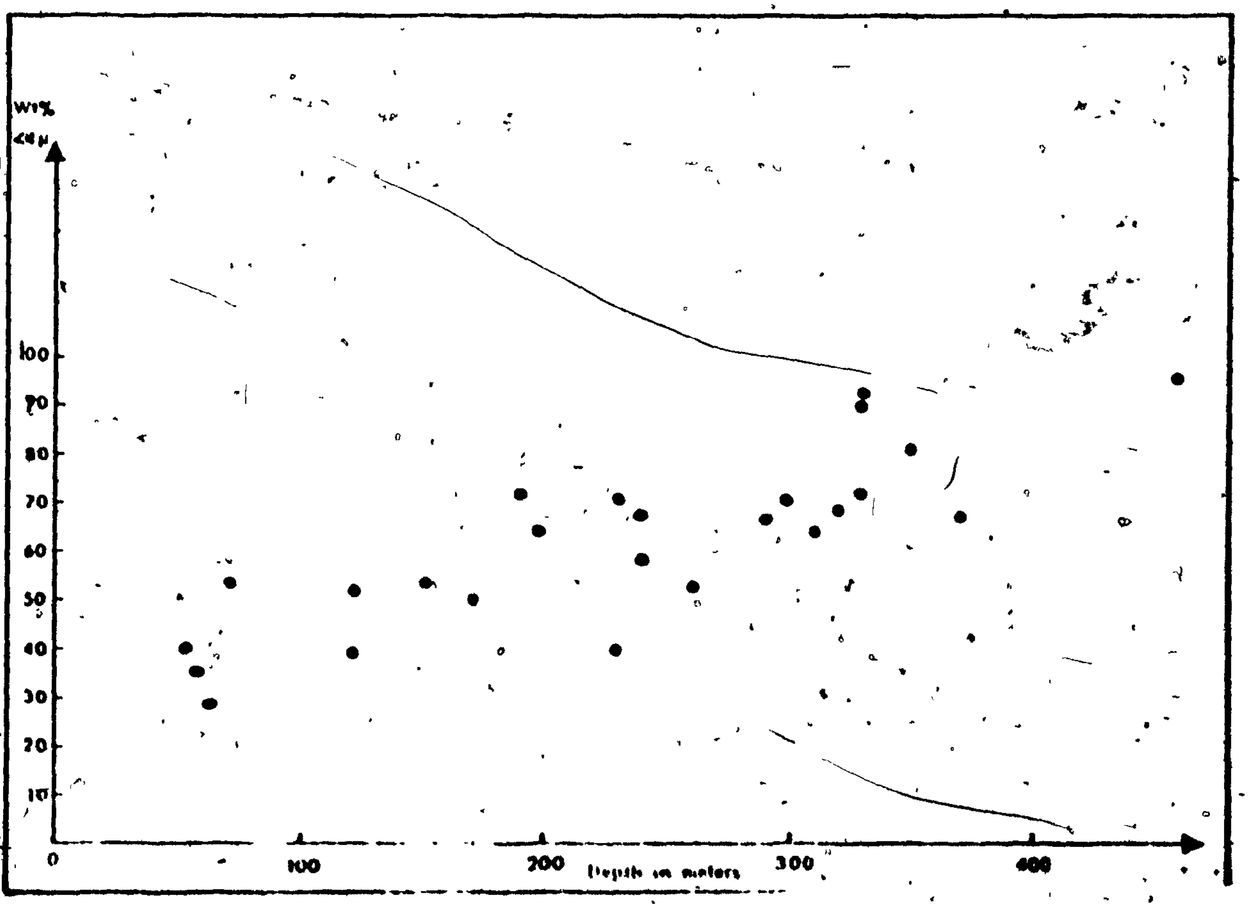
Figure II.1

Plot of the percentage coarse fraction (>63 μ) vs. water depth.

Figure II.2

The relationship between percentage clay size material of the fine fraction (>63 μ) and water depth.


Wt% sand
60
50
40
30
20
10
0
100
200
300
400
Depth in meters


Wt% <4 μ
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
Depth in meters

Nota and Loring (1964) found that the sand size fraction makes up to 25 % by weight of the total sediment and also concluded that ice transport is the main mechanism that brings this material to its depositional sites.

On the other hand, the material in the fine fraction (< 63 μ) may have been transported either by ice rafting or by currents. In either cases, water movements and bottom topography will affect its distribution.

Figure II.2 shows the relationship between the clay size content of the fine fraction (< 63 μ) and the water depth. It clearly indicates that the percentage of the clay size material increases with depth.

2.2 Mineralogy of the Coarse Fraction

The mineralogical composition of the coarse fraction (> 63 μ) has been discussed in detail by Loring and Nota (1969) in relation with probable source areas. Their study dealt with the 50 μ to 500 μ fraction. In the present study, 24 samples were examined for the mineral composition of their coarse fraction. No attempt was made to separate the heavy and light mineral fractions. Between 300 and 500 grains were identified and counted, each mineral component is expressed as a percentage of the total number of grains. The results are given in Table 2 Appendix B.

Sands from the northern Gulf contain, on the average, 35% quartz, 40% plagioclase feldspars, and 15% K-feldspars. Amphibole, pyroxene and garnet are abundant, making between 6 and 13% of the total number of grains counted. The ratio of the latter two components tends to decrease with distance from the north shore. Opaque minerals, including pyrite are frequent and represent between 1% and 3% of the counted grains.

In the sand-size fraction of samples coming from the southern part of the Gulf, quartz is the dominant mineral (up to 60%). Quartz grains are usually coated with iron oxide. As compared to other regions, the southern part of the Gulf contains considerably less plagioclase feldspars, generally less than 7%. K-feldspars are also somewhat less abundant and constitute less than 11% of the total number of grains. Amphiboles and pyroxenes are rare. Garnet is present in moderate quantities ($\leq$1%). Zircon is also present in some samples in amounts below 1%. Opaque minerals are abundant and make up between 3 and 6% of the counted grains.

Although based on a small number of samples, our conclusions concord with those of Loring and Nota (1969). They concluded that the Laurentian assemblage prevails over most of the Gulf and reflects southward and southeastward dispersal with little interference from other sources.

2.3 Clay Minerals in the $\leq 2\ \mu$ Fraction

The mineralogy of the clay size fraction in twenty-eight sediment samples and in five suspended matter samples, was examined using a Norelco high angle X-ray diffractometer. The samples were disaggregated, then treated to remove the carbonate and iron oxides using the procedures described by Biscaye (1964), which are modified after Jackson (1956). The peak area ratios of the first basal reflections were

Figure II.3

Distribution of clay minerals in sediments and suspended matter from the Gulf of St. Lawrence.

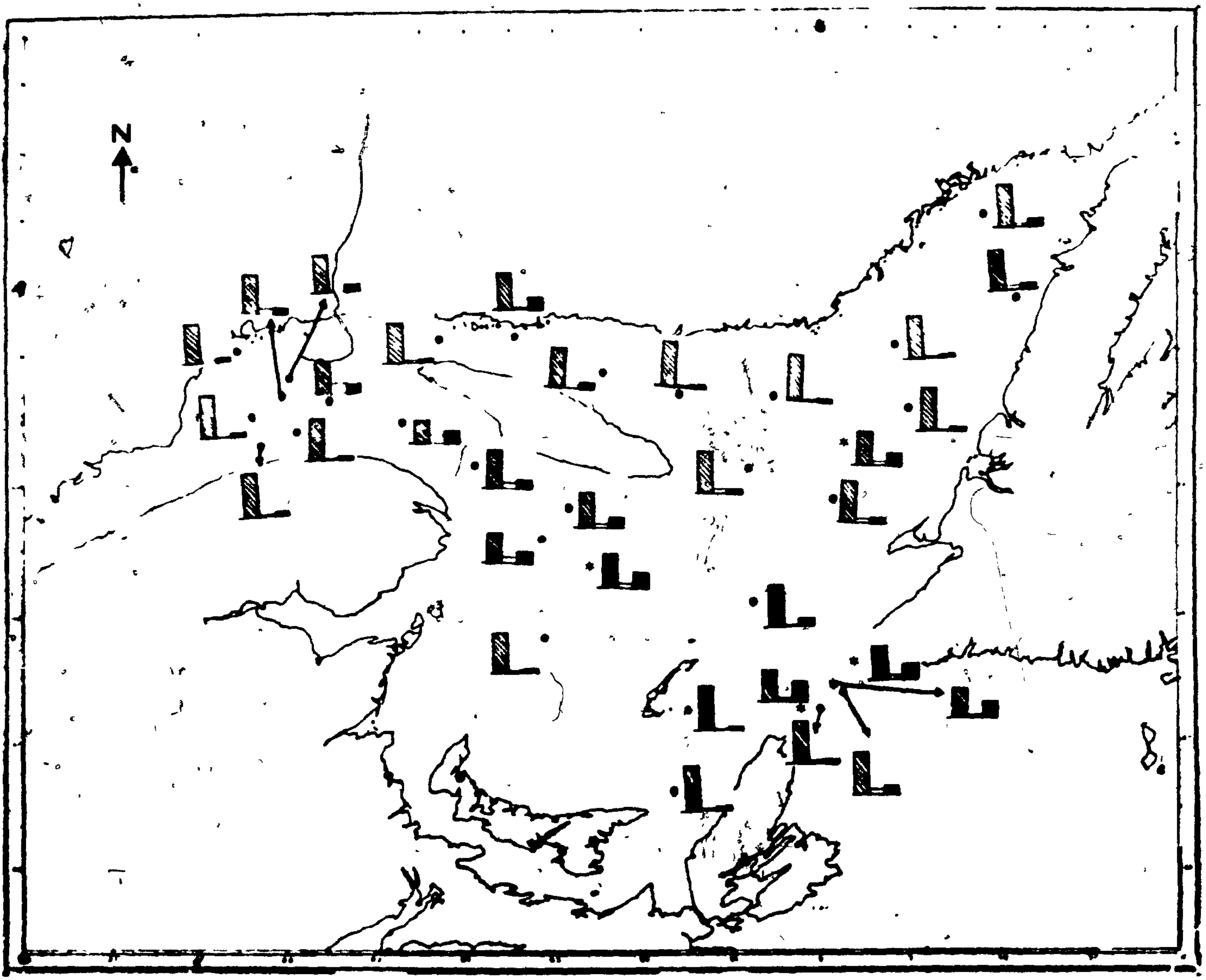
▨ Illite

■ Chlorite

□ Kaolinite

○ Sediment Sample

● Suspended matter sample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used to calculate, approximately, the relative clay mineral content, assuming that the three mineral groups identified account for 100% of the minerals in the clay size fraction (Weaver, 1964). Details of the method of analysis are given in Appendix A. The results are shown in Figure II.3 and are given in detail in Table 3 Appendix B.

In both the sediment and the suspended matter samples, illite and chlorite are the dominant clay minerals. Minor amounts of kaolinite were also detected. Quartz, feldspar and amphibole are present. Montmorillonite was not detected in any of the samples examined.

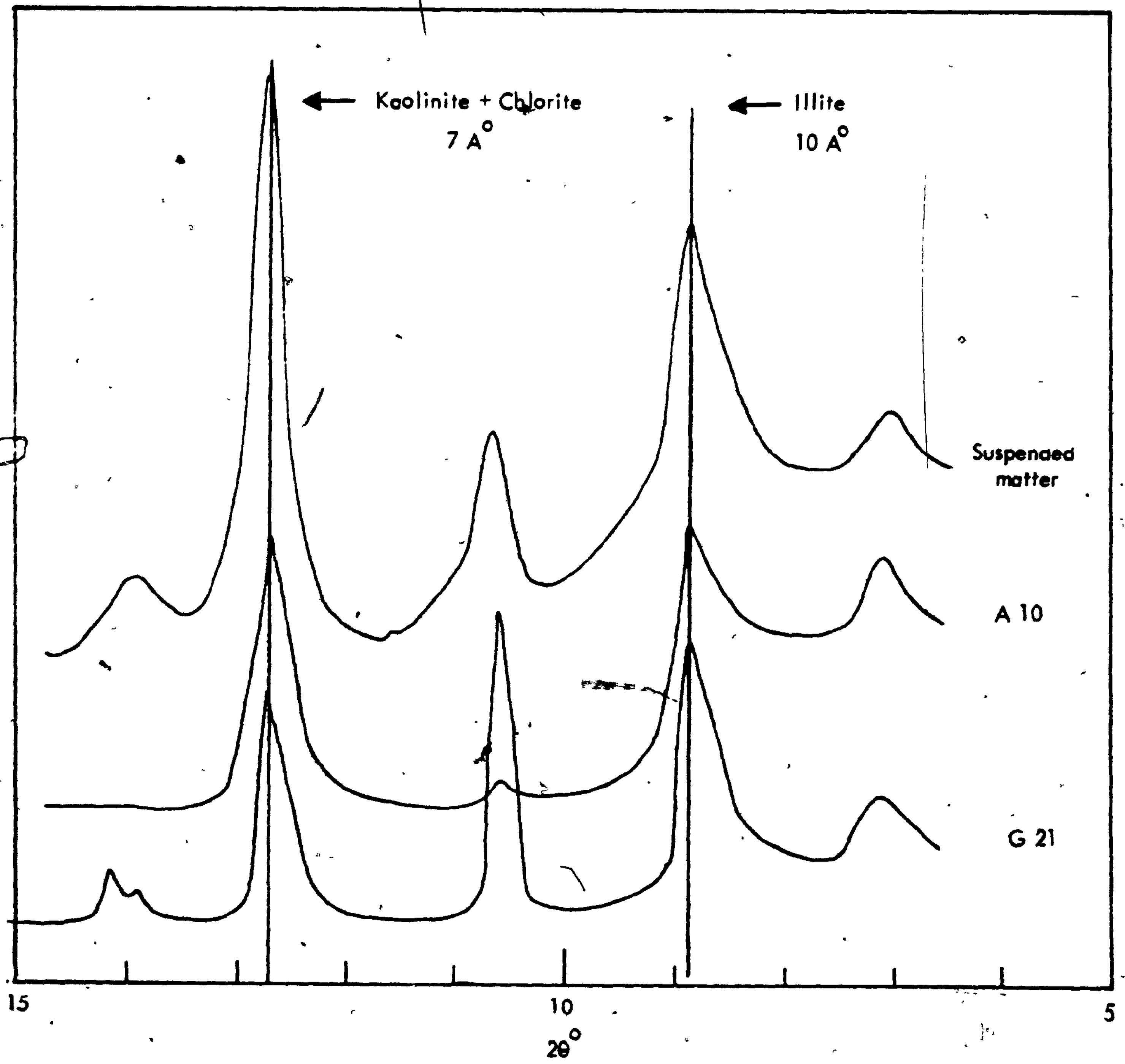
The illite first basal reflection (001) is asymmetrical and skewed toward the smaller angles (Figure II.4). This seems to be a regional characteristic which was described earlier by Allen and Jones (1960) and by d'Anglejan (1970). According to Gaudette et al. (1966), the asymmetry of the 10 A° peak may indicate the presence of a mixed-layer clay component; however, it should make up less than 10% of the total clay minerals, as no separate peak was detectable (Grim, 1968).

Chlorite was identified by its 14 A° (001) peak. The second and fourth-order reflections were always strong and sharp. According to Brindley and Robinson (1951) and Grim (1968) this may be indicative of substitution of Fe or Mn or other heavy atoms for Mg in the octahedral layer.

A second order basal reflection at 3.58 A°, was used to identify kaolinite and estimate its content (Biscaye, 1965).

Figure II.4

X-ray diffractograms showing the skewedness of the illite 10 A° peak.


Kaolinite + Chlorite
7 A°
Illite
10 A°
Suspended matter
A 10
G 21
15
10
5
2θ°

Samples from deep water stations contain, generally, more chlorite than shallow water samples (15% as compared to 7%).

Illite is the major clay constituent in all the sediment samples and in suspended matter samples. However, the suspended matter samples showed enrichment in chlorite, relative to the bottom sediments, they contain, on the average 30% chlorite.

The kaolinite/chlorite ratio is lower in the suspended matter samples, as compared to the sediment samples. This agrees with d'Anglejan (1970), who suggests that a break-down of chlorite material to ultra-fine sizes is achieved in the St. Lawrence basin, such that chlorite remains preferentially in suspension as compared to other clays.

2.4 Summary

The particle size analysis of the sediments shows that about 80% by weight of the sediments are of sizes below 63 μ.

In the less than 63 μ fraction of the sediments, the percent clay fraction ($< 4\ \mu$) increases with depth in a more or less linear manner. The deepest sample contains about 95% by weight of material below 4 μ.

The coarse fraction mineralogy reveals important differences in composition between samples coming from the northern and the southern Gulf. Quartz is a major component of that fraction, followed by plagioclase feldspars and to a lesser extent K-feldspars. The variations in mineralogy of the coarse fraction indicate that the Canadian Shield form the major source of sands and gravels supplied to the northern part of the Gulf. The southern part of the Gulf receives more contributions from the Appalachian region.

The major clay components are illite, chlorite and kaolinite, in order of abundance. No montmorillonite was detected. Strong peaks of quartz, feldspar, and amphibole were observed. It was found that the chlorite content in the less than 2 μ fraction of the sediments increases with depth. In comparison with the bottom sediments, the suspended matter is enriched in chlorite. This suggests that the transport in suspension is responsible for some fractionation among clay minerals.

CHAPTER III

DISTRIBUTION OF THE MAJOR AND MINOR ELEMENTS

3.1 Introduction

Analyses were performed on the fine fraction of the sediments using various analytical techniques. Details on the preparation of samples and the methods of analyses are given in Appendix A. The sediments were analyzed for the following components: carbonate, organic carbon, nitrogen, total phosphorus, Al, Ti, Fe, Mg, Ca, Na and K. Mn, although considered as a minor component by some investigators, was not dealt with in this chapter, as the range of its concentration lies within the range of the trace elements.

3.2 Results

Results of the analyses for the major and minor elements are given in Table 4, Appendix B. For purposes of discussion, they are arranged according to depth intervals. The results are presented as percentage of the total fine fraction of the sediment.

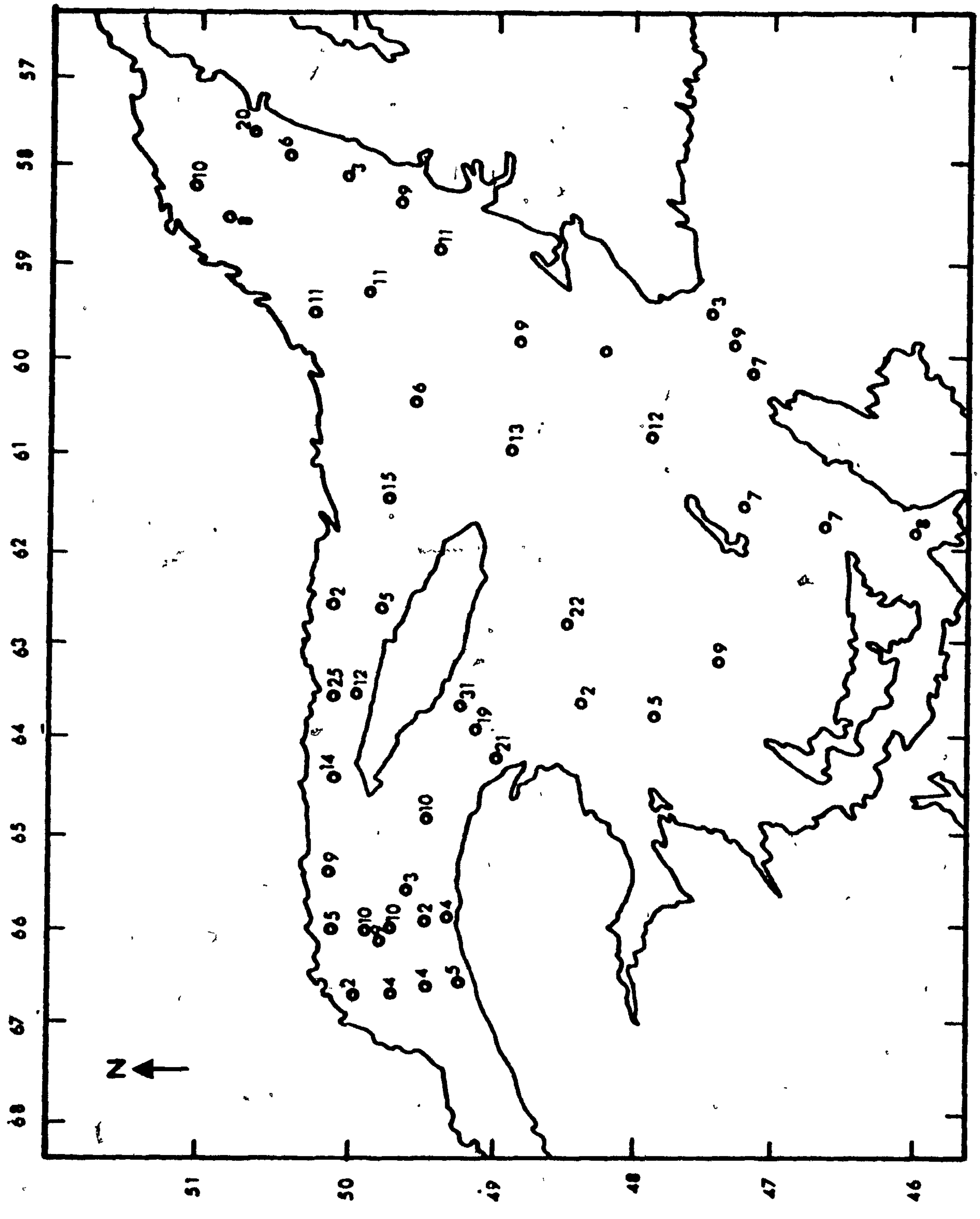
3.3 Discussions

3.3.1 Inorganic Carbon (Carbonate)

The carbonate content (expressed as $CaCO_3$) varies between 2% and 31%, with an average of 10.5%. The highest values occur near calcareous outcrops reflecting their direct contribution to the sediments.

Figure III.1

Distribution of calcium carbonate in the analyzed samples of the Gulf sediments (wt%).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Loring and Lahey (1962) have shown that the carbonate content in a section between Anticosti and Newfoundland, decreases away from Anticosti.

In the Gaspe Passage (Figure III.1), the carbonate content decreases away from both the shores of Anticosti and Gaspe toward the center of the Channel. At the same time, an increase in the fine fraction and the Al and Fe content is taking place.

Shell fragments also contribute to the total carbonate content, particularly in shallow water stations away from direct detrital carbonate sources. Patches of sediments with calcareous shells occur along the north shore and on the Magdalen Shelf (Sts. A-71, A-74 and R-4). Microscopic examination of these samples showed that molluscan shell fragments and foraminiferal tests are present in the coarse fraction of the sediments.

The Ca/Mg ratio in the carbonate fraction of the sediments was not studied. However, the acid soluble Mg represents less than 1% of the total Mg in the sediments, which suggests that carbonate in the Gulf consists of low Mg calcite or aragonite.

3.3.2 Organic Carbon and Nitrogen

The data shown in Table 4, Appendix B indicate that organic carbon in the sediments of the Gulf varies considerably with depth and geographic location. This was also observed by Loring (1970, 1972 p.c.). Areas indicated as recent depositional basins (p. 9), contain finer sediments and, on the average, higher organic carbon content than areas covered by reworked glacial till.

The organic carbon content in the analyzed samples is 1.69% on the average, and ranges between 0.2% and 3.39%. As expected, the Gulf sediments are higher in organic carbon than pelagic sediments, which normally have values less than 0.5% (Trask, 1955; El-Wakeel and Riley, 1961). On the other hand, when compared with shallow water sediments from the near-by Scotian Shelf, they appear somewhat deficient: Rashid and King (1969) have reported values between 2.29% and 4.97% for these sediments.

No statistically significant correlation occur between either the carbonate and organic carbon content, or the phosphorus and organic carbon.

The organic C/N ratio in the samples analyzed varies between 23 and 94 (average of 56). Bordovisky (1965) gives a range of 29 to 41 for the Caspian Sea, while a mean value of 21 is found for surface deep-sea sediments (El-Wakeel and Riley, 1961). McCorn (1967) found that the C/N ratio in the Hudson River estuary is on the average 12.9. The very high C/N ratio in the Gulf could be due to incorporation of organic matter deficient in nitrogen, presumably of terrestrial origin, such as wood fibers, since marine organisms have an average C/N ratio of 6.25 (Redfield et al., 1963).

In the sediments studied, wood fibers were frequent in the coarse fraction. Wood fibers were also found in the fine fraction of the near-shore samples.

Pocklington (1972,p.c.) has found that the C/N ratio in sediments of the upper Saguenay River reaches values above 30. He attributed this high ratio to the addition of legnin to the environment from the paper mills surrounding the area. Extensive peat deposits are present in areas marginal to the St. Lawrence estuary and the western Gulf.

3.3.3 Phosphorus

Total phosphorus (as P_2O_5) shows a nearly uniform distribution in the Gulf sediments. Its content varies between 0.1% and 0.26%, with an average of 0.19%.

The phosphorus in the Gulf sediments appears to correlate positively with Fe and Mn (correlation coeff. = + 0.72 and + 0.48 respectively).

Revelle (1944) has found a linear relationship between phosphorus and Mn content in pelagic sediments. Berner (1973) has shown that phosphorus is present in association with Fe oxides of volcanic origin in some samples from the Pacific Ocean. The degree of association of phosphorus with Mn was less than with Fe.

In the Gulf of St. Lawrence, it appears likely that phosphorus is present in the sediments in association with Fe and Mn, probably as the metal phosphates. This is suggested by the positive correlation of these two elements with phosphorus.

3.3.4 Aluminum

In samples collected from depths greater than 300 m, Al was found to vary between 4.45% and 9.8% of the total samples (average 7.35%).

Samples from depths less than 100 m have an Al content that varies between 7.37% and 10.31% (average 8.63%). Table III.1 shows the variation of Al content with water depth in the surficial sediments from the Gulf. Also shown, for comparison, are published Al values for different geological materials.

The Al content varies inversely with the depth of water. Thus the Al values appear to correlate with changes in texture: as the clay size fraction in the sediment increases with depth, the Al content decreases. This trend may be caused by a decrease in feldspar content and relative increase of the chlorite/illite ratio from shallow to deep water. Feldspars contain from 9.96% to 16.7% Al (Kerr, 1959), as against 10.3% to 13.4% for chlorite without any substitution.

Shallow water samples come mainly from nearby sources which may influence their composition considerably. Samples from along the north shore often contain a high content of unaltered feldspars derived from the Canadian Shield. Sediments on the Magdalen Shelf may similarly contain considerable amounts of feldspars, also derived from Shield rocks (Loring and Nota, 1969) and/or rocks from the Chaleur Bay Group. Chlorite content is higher in the deep water samples than in shallow water ones, while illite shows the opposite trend.

The relatively low Al figures of the deep water samples may also reflect the higher chlorite content in these sediments as compared to those from

TABLE III.1

Variation of Al with depth in surface sediments of the Gulf and Al values for different geological material reported in the literature.

Average		Al %	σ
7	samples from water depth < 100 m	8.63	0.83
20	samples from water depth between 100 and 200 m	8.08	1.51
12	samples from water depth between 200 and 300 m	7.16	1.54
14	samples from water depth > 300 m	7.23	1.30
55	samples from the Gulf	7.64	1.48
5	suspended matter samples from the Gulf	8.4	1.36
13	suspended matter samples from the St. Lawrence estuary,(Smith, 1973, P.C.)	7.1	
14	deep water pelites, Gulf of St. Lawrence (Nota and Loring, 1964)	7.75	
7	shallow water pelites, Gulf of St. Lawrence (Nota and Loring, 1964)	7.52	
3	up-river pelities, Gulf of St. Lawrence (Nota and Loring, 1964)	8.92	
39	granodiorites, Canadian Shield (modified from Maxwell *et al.*, 1965; Dresser and Denis, 1944)	9.05	
-	Igneous rocks (Clark and Washington, 1924)	8.13	
28	shales (Clark, 1924)	8.20	
52	terreginous shales (Clark, 1924)	9.10	
4	bluish clays, Gulf of Paria (Hirst, 1962)	7.77	
6	greenish mud, Gulf of Paria (Hirst, 1962)	8.79	
-	granodiorite (Barth, 1962)	8.29	

shallow water. The pelitic muds found in the deep water basins are believed by Nota and Loring (1964) to have settled from suspension after thorough mixing in the water column. The source of the suspended load to the Gulf is mainly the St. Lawrence River System. The similarity in Al content of deep water samples and suspended matter samples in the St. Lawrence estuary (Table III.1) supports the idea that these sediments have been mainly transported in suspension from this source.

3.3.5 Titanium

The Ti content of the analyzed sediments varies between 0.26% and 0.88% (average 0.48%). Table III.2 shows the Ti values obtained as compared to other values reported in the literature.

Data in Table III.2 indicates a slight increase of Ti in the sediments with water depth. In comparison, the suspended matter contributed by the estuary is significantly enriched in Ti as compared to the sediments. Loring and Nota (1968) also found that deep water pelites tend to contain slightly more Ti than near shore sediments. They have attributed that difference as being due to increasing amounts of material smaller than 16 μ in the pelites.

The same authors have also indicated that the concentration of Ti in sediments from the St. Lawrence estuary follows the concentration of Al fairly closely, despite marked changes in grain sizes. However, the data reported in

TABLE III.2

Ti content in sediments from the Gulf, together with Ti content in different geological materials, reported by other workers.

Average		Ti %	σ
7	shallow water samples < 100 m	0.39	0.06
20	samples from water depth of 100-200 m	0.51	0.08
12	samples from water depth of 200-300 m	0.47	0.10
14	samples from water depth of > 300 m	0.50	0.19
55	samples from the Gulf of St. Lawrence	0.48	0.10
5	suspended matter samples from the Gulf of St. Lawrence	1.0	0.16
13	suspended matter samples from the St. Lawrence estuary (Smith, 1973, P.C.)	0.84	
-	Igneous rocks (Clark, 1924)	0.64	
78	(composite) shales (Clark, 1924)	0.39	
212	terreginous mud and marine shales (Goldschmidt, 1937)	0.46	
-	Deep-sea sediments (Turekian and Wedepohl, 1961)	0.46	
-	Canadian Shield rocks (Grout, 1938)	0.48	

Table III.3 does not indicate any correlation between Al and Ti. The Al/Ti ratio tends to decrease in going from shallow to deep water, and is smaller in the suspended matter as compared to the sediments.

The Fe/Ti ratio, is on the other hand more constant. Landergran (1954) has drawn attention to the similarity between Fe/Ti ratios of igneous rocks and those of several deep sea cores, and has suggested that there is a close relationship between Fe and Ti in the sedimentary cycle. This also is supported by observations of Revelle et al. (1955) and El-Wakeel and Riley (1961).

The changes in the Al/Ti ratio as well as the Fe/Ti ratio suggest that Ti enters the Gulf sediments as Ti minerals, probably ilmenite and/or rutile. The decrease in the Al/Ti ratio from near-shore to deep water sediments and the comparatively high Ti content of the suspended matter, supports the view that the contribution of suspended matter increases with depth.

3.3.6 Iron

All analyses refer to total iron. Fe as Fe^{+2} was not determined.

Fe averages 3.97% and ranges from 2.26% to 5.46% in the fine fraction of the bottom samples. Table III.4 shows the variation of Fe content of the fine fraction with depth of water, as well as the Fe/Al ratios in the sediments and suspended matter.

On the average, the total Fe content of the fine fraction increases with depth. Suspended matter samples collected from various parts of the Gulf have values

TABLE III.3

Al/Ti and Fe/Ti ratios for the sediments of the Gulf and the suspended matter.

Average		Ti	Al	Fe	Al/Ti	σ	Fe/Ti	σ
7	shallow water samples<100 m	0.39	8.63	3.7	22.5	1.95	9.9	3.1
20	samples from water depth between 100 and 200 m	0.51	8.08	3.64	16.6	3.9	7.5	2.5
12	samples from water depth between 200 and 300 m	0.47	7.16	4.13	15.6	4.5	9.4	2.4
14	samples from water depth>300 m	0.50	7.23	4.25	14.6	5.6	9.2	2.8
5	suspended matter samples from all over the Gulf	1.0	8.4	10.0	8.44	0.01	10.0	0.4
13	suspended matter samples from St. Lawrence estuary, (Smith, 1973, P.C.)	0.84	7.1	4.80	8.4	-	5.7	-
-	Hydrolyzate sediments (Goldschmidt, 1954)	-	-	-	25.0	-	-	-

TABLE III.4

Variation of Fe content with depth, together with the Fe/Al ratios in the sediments of the Gulf, and other material.

Average		Fe %	σ	Fe/Al	σ
7	shallow water samples from water depth <100 m.	3.7	0.75	0.43	0.11
20	samples from water depth between 100 and 200 m.	3.64	0.85	0.46	0.14
12	samples from water depth between 200 and 300 m.	4.13	0.58	0.60	0.15
14	samples from water depth >300 m.	4.25	0.30	0.58	0.07
5	suspended matter samples from the Gulf.	10.00	1.74	1.20	0.05
13	suspended matter samples from the St. Lawrence estuary, (Smith, 1973, P.C.)	4.8	-	0.68	-
-	Canadian Shield rocks (Grout, 1938)	3.98	-	0.78	-

which are higher than the average for the Canadian Shield. Fe is covariant with Al, with a correlation coefficient $r = +0.76$. This high correlation coefficient between Fe and Al points out to their probable association in the same mineral phases (Chave and Mackenzie, 1961).

Carroll (1958) has shown that Fe may be associated with clay minerals in several ways: (i) as an essential constituent; (ii) as a minor constituent within the crystal lattice, when it is in isomorphous substitution; (iii) as Fe oxides precipitated or absorbed on the surface of the mineral platelets. Nontronite, some chlorites, vermiculite, glauconite and chamosite contain Fe as essential constituent. Kaolinite and halloysite can not accomodate Fe in their lattice. However, they may be surface-coated with either goethite or hermatite. Hirst (1962) has suggested that Fe may substitute for Al or Mg in the lattice of clay minerals (illite and montmorillonite).

Although Fe^{+3} could substitute for Al^{+3} within the octahedral layer of illite in the Gulf sediments, the bulk of Fe appears rather to be located in the chlorite phase for the two following reasons: (i) Fe is abundant in the suspended matter, which is enriched in chlorite as compared to the sediments; (ii) according to Loring and Nota (1968) Fe occurs in the sediments mainly as Fe^{+2}, which is the form present in chlorite (Griffin et al., 1968). Other sources of Fe are possible. Goldberg (1954) pointed out that Fe may be incorporated directly in the hydrogenous phase of marine sediments. The importance of biologically derived Fe has also been stressed by several workers, e.g. Clark and Wheeler (1922), Bradley and Bramlette (1942), and Revelle (1944).

In order to estimate the total contribution made by the hydrogenous and biogenous phases to the total Fe content of the sediments, samples were treated by an acetic acid-hydroxylamine hydrochloride mixture, described in Appendix A. The acid reducing mixture does not differentiate between the biogenous or the hydrogenous phases, but will separate detrital from the non-detrital components.

This chemical separation indicates that, less than 25% of the total Fe in the sediments from the Gulf is of non-detrital origin. Non-detrital Fe ranges between 0% and 61% of the total Fe. Using the dithionite extraction method, Loring and Nota (1968) found that between 3% and 16% of the total Fe is extractable. Even less was extractable by hydroxylamine hydrochloride alone. Both reagents are not as strong as the acid-reducing mixture used in the present investigation, and only partial removal of the non-detrital fraction is likely to occur when either of these reagents is used (Chester and Hughes, 1967).

As little organic matter accumulates in the bottom deposits of the Gulf, it is expected that non-detrital Fe is mainly incorporated into the sediments as ferro-manganese precipitates.

3.3.7 Magnesium

The Mg content in the fine fractions analyzed is 1.65%, on the average, with a range between 0.85% and 2.11%. It exhibits the same variation with depth as Ti and Fe, i.e., the lowest Mg content is found in shallow water samples and the highest in deep water samples (Table III.5).

Mg may be present in the amphibole, pyroxene or clay minerals (as indicated before, less than 1% of the Mg is associated with carbonates). As the first two components are present only in small quantities in the coarse fraction, the major host minerals for Mg are likely to be the clays. This is supported by the constancy of the Mg/Al ratio. The similarity of the Mg/Fe ratio of the sediments and the suspended matter suggests that the two elements are mostly concentrated in one mineral phase, possibly chlorite.

On the other hand, differences observed in the Mg/Al ratios of the fine sediments and the suspended matter could be explained as a result of a fractionation of the clay minerals between the water column and the bottom deposits. A high Mg values in the total fine fraction, coupled with a relatively low chlorite content in the clay size fraction, could occur if chlorite is increasingly abundant in the 2 μ to 63 μ fraction. Chlorite particles may vary considerably in size. Gibbs (1967) found that chlorite particles in a sample from the Amazon River vary in size from less than 1 μ to 32 μ. Also, Griffin et al., (1968), who examined some samples from the Gulf of St. Lawrence, found that chlorite exists in the whole particle size spectrum.

Chemical separation using acetic acid-hydroxylamine hydrochloride mixture (see Appendix A), shows that less than 1% of the total Mg content in the fine fraction is of non-detrital origin.

TABLE III.5

Variation of Mg content of the sediments with depth, together with the Mg/Al and Mg/Fe ratios. Some published values for different geological material are also given.

Average		Mg%	σ	Mg/Al	σ	Mg/Fe	σ
7	shallow water samples from water depth <100 m.	1.4	0.15	0.16	0.02	0.40	0.10
20	samples from water depth between 100 and 200 m.	1.69	0.24	0.22	0.07	0.46	0.15
12	samples from water depth between 200 and 300 m.	1.65	0.26	0.24	0.07	0.41	0.11
14	samples from water depth < 300 m.	1.69	0.16	0.24	0.06	0.41	0.06
5	suspended matter samples from different locations in the Gulf	4.1	0.85	0.48	0.04	0.40	0.02
-	Igneous rocks (Rankama and Sahama, 1950)	1.26					
-	Silts and shales and muds (Goldschmidt, 1954)	0.90-1.51					
-	Argillaceous sediments (Rankama and Sahama, 1950)	0.89					
12	Gulf of Paria clay (Hirst, 1962)	1.32					

3.3.8 Calcium

The average Ca content in the fine fraction of the sediments obtained from different depths in the Gulf is summarized in Table III.6, together with values reported for different geological materials by other workers.

The results indicate that Ca becomes more abundant with depth. On the other hand, it is clear that calcareous rocks exert a control on the distribution of Ca (Figure III.2). Samples from shallow waters are generally lower in Ca than deep water samples. This is true of samples coming from the Magdalen Shelf and the north shore of the Gulf where calcareous sources are lacking. In these, the calcium content of the non-carbonate fraction probably comes to a large extent from plagioclase feldspar, which is a dominant mineral in rocks along the north shore (see Chapter II above, and Loring and Nota, 1969). Only minor amounts of Ca could be present as apatite, since phosphorus is very low.

On the average, 63% of the total Ca is associated with acid soluble phase (mainly $CaCO_3$) of the fine fraction, while Loring (1972, p.c.) working on the whole sediment found 54% of the Ca in the non-detrital component. Thus, 40% or less of the Ca is bound with the detrital minerals. This would have to be mainly plagioclase, as Ca is not an essential component in clays or other minerals.

Ca does not show any strong correlation with Mg (correlation coefficient = +0.4). This and the fact that Mg and carbonate content are not

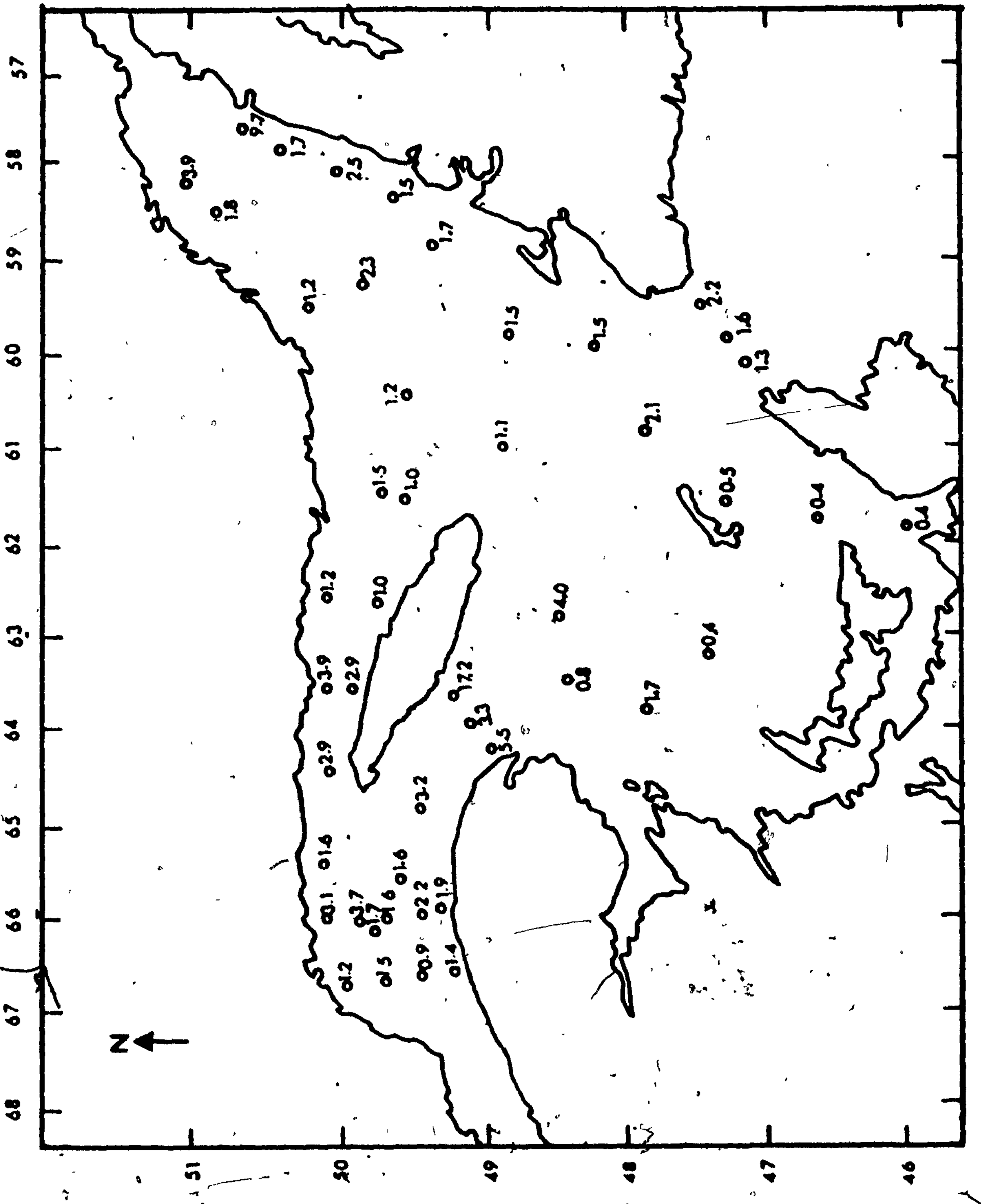
TABLE III.6

Average calcium content in the Gulf sediments and in different rock formations reported in the literature.

Average		Ca %	σ
7	shallow water samples from water depth < 100 m.	1.30	1.08
20	samples from water depth between 100 and 200 m.	1.84	0.78
12	samples from water depth between 200 and 300 m.	1.87	0.85
14	samples from water depth > 300 m.	3.68	4.20
12	samples from water depth > 300 m (excluding samples A-18 and 20)	1.94	0.70
55	samples from the Gulf of St. Lawrence.	2.34	
13	suspended matter samples from St. Lawrence estuary (Smith, 1973, P.C.)	2.45	
-	Igneous rocks (Rankama and Sahama, 1950)	3.63	
-	Argillaceous sediments (Rankama and Sahama, 1950)	2.23	
-	Rocks of the Canadian Shield (Grout, 1938)	3.39	

Figure III.2

Distribution of calcium in the analyzed samples of the Gulf sediments (wt%).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1.7
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correlated, indicate that carbonate minerals derived from calcareous outcrops in or around the Gulf are low Mg limestones.

3.3.9 Sodium and Potassium

In the geochemical cycle, Na and K become separated during weathering and deposition processed (Rankama and Sahama, 1950). Whereas, igneous rocks contain roughly comparable amounts of Na and K, marine sediments, particularly pelagic sediments, contain twice as much K_2O as Na_2O (Chester, 1965).

Table III.7 gives the average concentration of Na and K in sediments from different depths in the Gulf, together with some values from the literature. Excluding sediments from the Magdalen Shelf, there is a steady decrease in the absolute Na concentration, as well as the Na/K ratio with decreasing depth.

Na and K are mainly located in clays but may also be present in other mineral phases such as K-feldspar and alkali feldspar (Hirst, 1962a). In view of the relatively high abundance of feldspar minerals in the Gulf sediments, it is likely that they will affect the distribution of the two elements, particularly in areas where the coarse fraction is important. In this respect, Nota and Loring (1964) have indicated that the sodium content decreases with decreasing grain size.

The variations in the Na/K ratio in the fine sediments from several depths, and the value of this ratio in the suspended matter, suggest that finely

TABLE III.7

Variation of Na and K with depth in the Gulf sediments, together with the Na/K ratios and the same for other materials as reported elsewhere.

Average		Na %	σ	K %	σ	Na/K	σ
2	sediments from water depth < 100 m (North Shore)	1.52	0.07	1.94	0.05	0.78	0.02
5	sediment samples from water depth < 100 m (magdalen Shelf)	0.72	0.07	2.52	0.14	0.29	0.09
20	samples from water depth between 100 and 200 m.	0.51	0.2	2.42	0.14	0.60	0.10
12	samples from water depth between 200 and 300 m.	1.32	0.16	2.35	0.35	0.53	0.05
14	samples from water depth>300 m.	1.29	0.24	2.57	0.35	0.45	0.13
5	suspended matter samples from all over the Gulf.	3.84	0.85	2.6	0.45	1.47	0.09
13	suspended matter samples from the St. Lawrence estuary, (Smith, 1973, P.C.)	2.90		2.57		1.12	
-	Igneous rocks (Rankama and Sahama, 1950)	2.83		2.59		1.09	
-	Argillaceous sediments (Rankama and Sahama, 1950)	0.97		2.70		0.36	

divided feldspars are retained in suspension, while K-rich clays tend to settle out. This is to be expected as clay minerals in sea water tend to flocculate, while feldspars and quartz have less tendency to do so; hence, the deposition of the first leaves the latter in suspension.

It was pointed out earlier that in the Gulf a fractionation process leads to early deposition of illite, while chlorite remains in suspension to be finally sedimented in deep waters or outside the Gulf. A supporting evidence is provided by the change in Na/K ratio of the suspended matter between the estuary and the Gulf: it increases from 1.1 in the estuary to 1.5 in the Gulf.

3.4 Summary

As the particle size distribution of the fine fraction, as well as the clay mineral assemblage are found to be dependent on depth, the bathymetry of ~~the~~ Gulf plays a major role in determining the major element composition of the fine sediments.

This is reflected in the trends observed in the major element composition of the sediment fine fraction: the amount of Ti, Fe, Mg, Ca and K increases with depth, approaching slowly the even higher values which occur for these elements in the suspended matter. The element ratios Ti/Al, Fe/Al, Mg/Al obey the same rule: in deep water they get progressively closer to their values in the suspended matter.

These results underline the importance of settling from suspension as a mode of deposition for fine material in the deep areas of the Gulf. They confirm therefore, the conclusion reached in Chapter II which was based on the respective increase of the clay size fraction and the chlorite content with depth.

Some information is also provided as to the main mode of occurrence of the major elements. Because of the high Fe/Al ratio in the sediments and the dominance of illite among the clays, it has been suggested that Fe^{+3} may be substituting for Al^{+3} in illite. However, the Fe/Mg ratio does not vary in the fine fraction of sediment samples collected at various depths. Its value is also the same in suspended matter, although in the suspended matter both elements occur in higher concentrations. This strongly suggests that Fe and Mg should be associated in the same mineral phase. As the high values of Fe and Mg in the suspensoids go with a marked increase in chlorite as compared to the sediments, chlorite appears to be the major host for these two elements.

There is very little Mg (less than 1%) in the non-detrital phase of the sediments, which indicate that no Mg-rich calcite is supplied by either local biogenous or lithogenous sources. On the other hand, Ca is largely provided by the carbonate fraction. Most of the calcium carbonate is derived from calcareous rocks rather than shell debris. The detrital Ca, which is probably bound in plagioclase feldspar, accounts for less than 40% of the total Ca.

The abundance of Na and K in the Gulf sediments is controlled by both the clay minerals and the feldspars. However, the evidence suggests that K is mainly present in the illite phase, while Na is associated with the sodic feldspars.

Ti appears to be present in Ti rich minerals, ilmenite and rutile, and is not associated with the clays. As it correlates with Fe, it occurs more likely as ilmenite rather than rutile.

The C/N ratio in the Gulf sediments is very high, possibly because of abundant land-derived organic matter deficient in nitrogen being supplied to the sediments.

CHAPTER IV

GEOCHEMISTRY OF THE TRACE ELEMENTS

4.1 Introduction

The distribution and mechanisms by which various elements are incorporated in marine sediments have been studied extensively for the last 20 years or more (see for ex. Wedepohl, 1960; Turekian and Imbrie, 1966; Chester and Messiha-Hanna, 1970; and Jones, 1973). However, the ecological importance of determining the concentration levels of trace elements in marine environments, and particularly in estuaries, has been more emphasized in recent years (Goldberg et al., 1971; Brown Jr., 1971; Turekian, 1971). For the region of the Gulf of St. Lawrence, published information is lacking, except for Mn (Loring and Nota, 1968).

The following discussions on trace elements in the fine fraction of the Gulf sediments, makes use of the distinction between the detrital and non-detrital fractions as defined in Chapter I. This distinction helps to establish the relative importance of the various contributing sources. If a proper chemical separation technique is used, the composition of the detrital fraction is essentially the composition of the source material. On the other hand, the contribution made by the non-detrital fraction, is essentially related to the intensity of chemical weathering on land. It is also a measure of the inputs due to human activities in the surroundings: either directly as by injection of trace elements in river waters or the atmosphere, or indirectly by re-enforcing chemical weathering through mining activities or the introduction of highly corrosive materials into the environment.

4.2 Geochemical Criteria of Association

In order to fully understand the distribution of trace elements in sediments, one must first determine the component mineral or minerals with which it is associated. As an effective separation of each mineral followed by its analysis is cumbersome or impossible, such an association must be inferred from indirect evidence.

The following parameters have been selected as relative measures of the detrital contribution to a particular element: i) the ratio of that element to Al will be considered to indicate the variation of that element with respect to total clay minerals; ii) its ratio to Mg and K will be assumed to indicate its variation relative to chlorite and illite respectively.

Admittedly, these assumptions are not strictly correct: there are other sources of Al, Mg, and K beside the clay minerals, particularly feldspars and ferro-magnesium minerals. Also degraded chlorite may contain K in its structure (Holland, 1965). As a rule, however, the ratios of trace elements to Al, Mg, and K may be used as a fair indication of their association with different clay species (Hirst, 1962b). High rates of sedimentation presumably do not allow for trace elements to enter the mineral structures in the surface sediments. Thus, the detrital fraction of the trace elements essentially reflects the chemical composition of various source materials which contribute to the sediments.

In dealing with the non-detrital fraction, four criteria are used: I) the variation of an element as a function of the particle size, hence total available surface area, is taken as an indication of the degree of physical adsorption; ii) since it is not possible to remove separately carbonates of detrital and biogenous origin (Wangersky, 1970,p .c.), the variation of an element with respect to carbonate is considered to reflect its association with biologically derived skeletal material. This is somewhat arbitrary as carbonates (mainly derived from Paleozoic carbonate rocks) may have different and modified chemical composition. However, such assumption may be justified for the following reasons: I) Paleozoic carbonate rocks have been reported elsewhere to contain very small concentrations of various trace elements; 2) if the samples collected from nearby carbonate sources are excluded, the average $CaCO_3$ content of the sediments is reduced to about 8.5% i.e. about 85% of the carbonate content of the Gulf sediments may be accounted for by sources other than detrital carbonates, presumably of biogenic origin. iii) the variation of an element with respect to non-detrital Mn is assumed to give a measure of its association with ferro-manganese hydrogenous phases; iv) the variation of an element with respect to organic carbon is interpreted as an indication of its association with organic detritus, probably as sorbed ions (Nicholls and Loring, 1962).

4.3 Methods of Analysis

The following trace elements were determined: Co, Cr, Cu, Mn, Ni, Pb, Se, Sr, and Zn. The analyses were performed on a Perkin-Elmer M 403 atomic absorption spectrophotometer. Standard solutions for calibration were prepared from A.R. grade reagent or Fisher certified chemicals. Standard rock solutions were analyzed with each new batch of samples. Analyses were made on both the samples before the acid reducing mixture treatment, and the reducing mixture extracts. The chemical composition of the detrital fraction was calculated by difference. The sediment residues of some samples were also analyzed directly. Details of the methods of analysis are given in Appendix A.

4.4 Results

Analytical results for both the non-detrital fraction and the total trace element content of the fine fraction, are given in Tables 5 and 6 Appendix B. In the following discussions the elements are dealt with in alphabetical order, except for some pairs of elements usually treated together in the geochemical literature.

4.4.1 Chromium

Detrital Cr: the average detrital Cr content of sediments from various depth intervals are given in Table IV.1. On the average, the Cr content in the detrital fraction increases with water depth.

The fine fraction of the Gulf sediments appears to contain Cr levels consistent with values reported in the literature for other sediments (Table IV.1). The Cr content of the detrital fraction of the deep water samples (>200 m) is very close to the average Cr content in the detrital fraction of the deep-sea North Atlantic sediments as reported by Chester and Messiha-Hanna (1970).

Analysis of variance of the Cr- major element ratios, indicates that Cr/Al, Cr/Fe, Cr/K ratios exhibit wider variations than the Cr/Mg ratio, particularly in samples from deep water. This may reflect the high and variable quartz and non-chlorite mineral content of the shallow water samples relative to the deep ones.

For depths above 100 m, both the Cr/Al and the Cr/K ratios remain nearly invariant, suggesting that Cr is associated with the clay minerals. The Cr/Mg ratio shows the least variation in all samples. This would suggest that although Cr is generally present in all clay minerals, it is mainly associated with chlorite. Thus, though Frohlich (1960) has shown that most of the Cr present in marine sediments from different oceans is associated with illite, in the Gulf sediments, Cr appears to be mainly present in chlorite.

Figure IV.1 depicts the relationship between Cr and Mg in the detrital fraction of the sediments. A regression analysis shows that about 77% of the Cr is in association with Mg, probably substituting for that element in chlorite.

TABLE IV.1

Detrital and total Cr content, Cr/Al, Cr/Fe, Cr/Mg and Cr/K ratios for the fine fraction at various depths in the Gulf of St. Lawrence and comparison with published results.

		Detrital Cr ppm	σ	Cr/Al*	σ	Cr/Fe*	σ	Cr/Mg*	σ	Cr/K*	σ	Total Cr ppm	σ
7	shallow water samples (depth < 100 m)	47.5	7.3	6.32	1.87	20.76	3.47	36.21	13.1	24.00	4.95		
20	samples from water depth between 100 and 200 m.	52.0	13.3	6.7	2.20	16.66	2.08	29.78	4.24	21.78	5.84		
12	samples from water depth between 200 and 300 m.	88.0	26.0	12.7	3.9	29.1	8.71	38.82	8.46	44.31	18.55		
12	samples from water depth > 300 m.	74.0	14.0	10.1	1.48	23.54	4.50	30.70	6.79	35.75	4.49		
55	Gulf Sediments.											59	± 22
-	Argillaceous pelagic sediments (El-Wakeel and Riley, 1961)											55.0	
12	near shore muds from the Gulf of Paria (Hirst, 1962)											31.0	
38	North Atlantic Sediment (Chester and Messiha-Hanna, 1972)	72											

* Ratios x 10^4

Non-Detrital Cr: non-detrital sources contribute from 1% to 40% of the total Cr content (average 17%).

The relationship between non-detrital Cr and the four non-detrital control parameters listed above, is analyzed statistically. The results are shown in Table IV.2. The analysis show that there is a negative correlation between the element and the carbonate content, a positive correlation between Cr and both organic carbon and non-detrital Mn. The relative importance for each parameter can be assessed from the partial correlation coefficients given in Table IV.2.

The negative correlation between Cr and the carbonate content in the Gulf, confirms observations made elsewhere (Nicholls et al., 1959; Hogdahl, 1963). It indicates that with respect to Cr, carbonates act as diluent for contributions made by other sources. On the other hand, sorption reactions on both organic matter and ferro-manganese hydroxides appear to be important mechanisms by which Cr is incorporated into the Gulf sediments.

4.4.2 Cobalt and Nickel

Detrital Co and Ni: the average Co and Ni content in the fine fraction of the Gulf sediments do not show any steady increase or decrease with depth. However, sediments from water depths >300 m contain more Co than samples from other depths (Table IV.3).

TABLE IV.2

Correlation and regression analysis of the non-detrital Cr contribution.

Parameter	Corr. coeff.	Significant at 95% level	Regression equation	Number of Samples
Carbonate	- 0.32	Yes	$Y = -0.29X + 10.5$	51
*N.D. Manganese	+ 0.41	"	$Y = 0.02X + 0.21$	51
Organic carbon	+ 0.40	"	$Y = 0.41X + 3.90$	25
Particle size	- 0.27	No	$Y = -0.08X + 6.2$	25

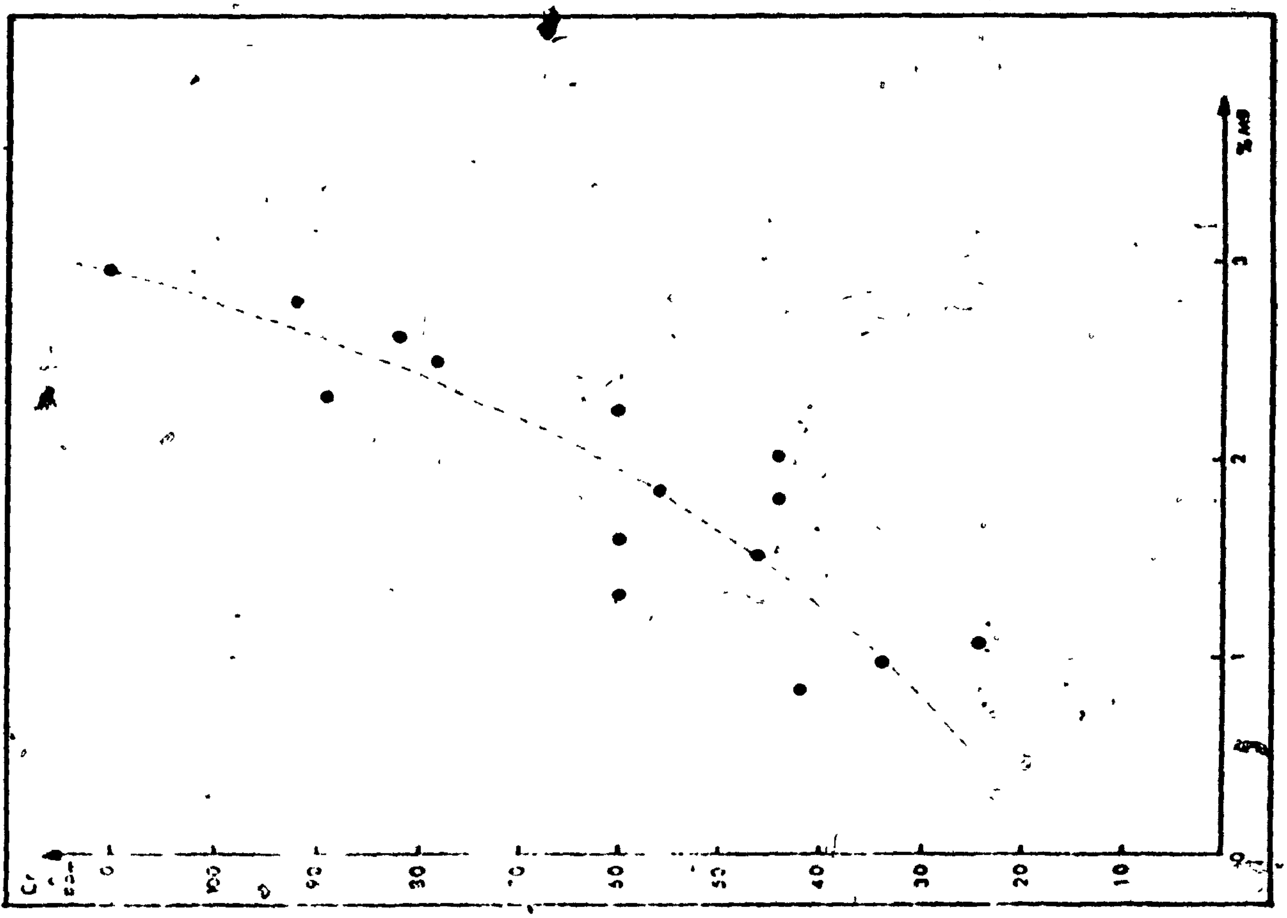
* N.D. = Non-detrital manganese.

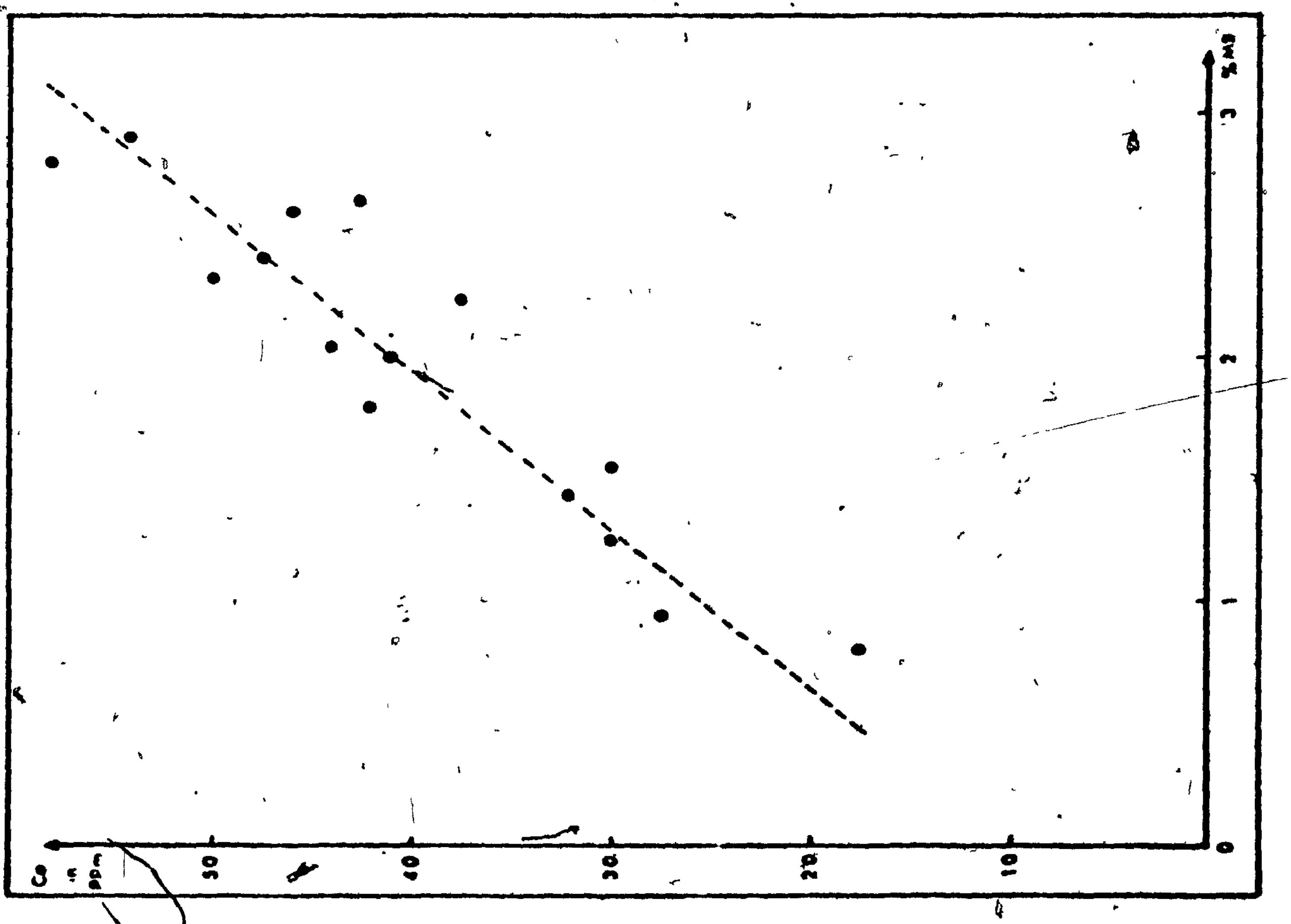
Figure IV.1

Relationship between detrital Cr and detrital Mg.

Figure IV.2

Relationship between Co and Mg contents in the detrital fraction.


Cr ppm
110
100
90
80
70
60
50
40
30
20
10
0
1
2
3
% MgO


Co in ppm
50
40
30
20
10
0
1
2
3
% MgO

Compared with other geological materials, the fine fraction of the sediments from the Gulf, is enriched in Co relative to Ni. The Co/Al, Ni/Al; Co/Fe, Ni/Fe, and Co/Mg, Ni/Mg ratios indicate that Co and Ni have more constant ratios to Fe and Mg than they have to Al. Therefore, both elements should be preferentially associated with ferro-magnesium minerals, mainly chlorite. On the other hand, the average Co/Ni ratio differs for samples from different depths. This may reflect the fact that Co and Ni do not occur in the same mineral (Chave and Mackenzie, 1961). As discussed above, variations in mineral assemblages exist: shallow water samples contain other ferro-magnesium minerals beside chlorite, which becomes more abundant with depth.

A strong correlation exists between detrital Co and Mg (Figure IV.2). Also, the Co/Mg ratio is almost constant for samples from different water depths. On the other hand, there is no correlation between Ni and Mg, and the Ni/Mg ratio is quite variable.

On the basis of the criteria defined above, a nearly constant Co/Mg ratio would mean that Co is enriched in chlorite.. In this mineral, it is known to be associated with Fe^{+2} and Mn^{+2} which tend to replace Mg (Grim, 1968). There is no evidence that Ni is associated with any specific clay mineral.

TABLE IV 3c

Average Co and Ni, Co/Ni, Co/Al, Co/Fe, Co/Mg and Co/K ratios for the sediments from the Gulf of St. Lawrence, compared to other values reported in the literature.

Average		[illegible]													
		Co	σ	Ni	σ	Co/Ni	σ	Co/Al*	σ	Co/Fe*	σ	Co/Mg*	σ	Co/Mn	σ
7	shallow water samples (water depth <100 m)	33.5	12.4	26.0	5.3	1.35	0.45	4.47	1.57	14.00	4.26	24.0	8.07	0.097	0.007
20	samples from water depth between 100 and 200 m	30.8	14.1	34.0	6.0	0.905	0.16	5.16	1.02	11.47	1.07	10.10	2.4	0.28	0.008
12	samples from water depth between 200 and 300 m	30.5	3.8	37.5	3.27	0.81	0.06	4.65	1.26	11.33	3.86	19.24	5.7	0.096	0.016
12	samples from water depth > 300 m	45.0	19.6	31.7	9.30	1.54	0.58	6.07	0.85	14.02	2.1	19.57	1.4	0.110	0.016
6	greenish mud from the Gulf of Paria (Hirst, 1962)	11.0		28.0		0.42									
–	Shales (Rankama and Sahama, 1950)					0.33									
–	Pacific pelagic clays (Carr and Turekian, 1961)					0.48									
–	Granite Standard G1	2.2		1.2		1.80									
–	Diabase standard W1	3.8		8.2		0.46									
–	Schists and gneisses (Nockolds and Mitchell 1948)	12.0		27.0		0.43									

* ratios x 10^4

TABLE IV.3b

Average Ni/Al, Ni/Fe, Ni/Mg, Ni/K and Ni/Mn ratios in the detrital fraction of the sediments of the Gulf of St. Lawrence.

Average		Ni/Al*	σ	Ni/Fe*	σ	Ni/Mg*	σ	Ni/K*	σ	Ni/Mn	σ
7	shallow water samples water depth<100 m.	3.29	0.41	11.13	1.34	18.71	5.56	13.14	3.36	0.086	0.04
20	samples from water depth between 100 and 200 m.	4.77	1.33	13.8	8.1	20.70	10.20	16.69	1.4	0.069	0.015
12	samples from water depth between 200 and 300 m.	5.78	1.11	14.20	5.83	20.71	11.20	19.05	1.76	0.119	0.029
12	samples from water depth > 300 m.	4.35	1.17	10.35	3.96	12.90	5.2	15.68	4.23	0.085	0.032

* ratio x 10^4

Non-Detrital Co and Ni : the examination of non-detrital Co and Ni is interesting as it reveals a different behaviour for each element during the geochemical cycle in the Gulf. The average non-detrital Co makes up 28% of the total Co (range between 0% and 60%). Non-detrital Ni varies between 1.5% and 70% (average 48%). In comparison, Hirst (1962) found that 32% of Co and 16% of Ni are of non-detrital origin in sediments from the Gulf of Paria.

The high percentage of non-detrital Ni as compared to Co in the fine fraction, may reflect the influence of river waters composition on sediments. Livingstone (1963) has reported higher values for dissolved Ni as compared to Co in major North American rivers. In these, dissolved Ni is 12 times as abundant as Co.

The correlation coefficients between non-detrital Co and Ni and the reference parameters are given in Table IV.4. Co and Ni do not correlate with non-detrital Mn, and show a very low correlation with Fe. This is unexpected as both Mn and Fe oxides are well known scavengers of trace metals (Chester, 1965). A possible explanation may be that Mn is present as sorbed ions on Fe hydroxide precipitates, rather than as an independent mineral phase, and that in this form it is not subject to isomorphous substitution. It has been established by Barnes (1967), that the type of Mn mineralization controls the relative abundance of trace elements in ferro-manganese precipitates.

TABLE IV.4

Correlation and regression analysis of the non-detrital Co and Ni contributions.

Parameter	Corr. Coeff.	Significant at 95% level	Regression equation	Number of samples
Carbonate a	+ 0.30	Yes	$Y = 0.36X + 10.1$	51
*N.D. Manganese a	- 0.09	No	$Y = 0.02X^2 + 0.0003X + 11$	51
Organic carbon a	- 0.51	Yes	$Y = -4.59X + 20.2$	25
Particle size a	- 0.15	No	$Y = -0.06X + 17.4$	25
Carbonate b	- 0.36	Yes	$Y = -2.1X^2 + 0.07X + 35.2$	51
*N.D. Manganese b	- 0.13	No	--	51
Organic carbon b	+ 0.38	Yes	$Y = 6.81X + 18.9$	25
Particle size b	- 0.42	No	$Y = -1.88X^2 + 0.02X + 38.5$	25

* N.D. = Non-detrital

a = Co

b = Ni

-- = Not calculated

Co shows a postitive correlation with carbonate and a negative correlation with organic carbon, which suggest that it is contributed by the carbonate fraction, while sorption reactions on organic detritus are not important for its deposition. On the other hand, Ni exhibits the opposite trend; it correlates negatively with carbonate and positively with organic carbon. Here, sorption on organic matter appears to be important.

4.4.3 Lead and Copper

Detrital Pb and Cu: the average Pb and Cu content of the fine fraction in samples from various depths is given in Table IV.5 together with the Pb/Al, Cu/Al; Pb/Fe, Cu/Fe; Pb/Mg, Cu/Mg and Pb/K, Cu/K ratios.

Statistical tests indicate that detrital Pb does not vary with depth. The average Pb content in the fine fraction is significantly higher than that given for continental shales.

Cu shows a steady increase toward deeper water, while in shallow water samples it has concentrations similar to near shore muds, as reported by Hirst (1962 b); Cu values increase with depth, approaching those reported for the North Atlantic deep-sea sediments by Van der Weijden et al. (1970).

The variable ratios of Pb and Cu with respect to the major elements indicate that neither is preferentially concentrated in one of the major mineral components. However, the high detrital Pb concentrations as compared to continental shales may reflect its association with K and Ca in feldspars.

69

TABLE IV.5

Cu and Pb content and their ratios* with Al, Fe, Mg and K in the sediments from the Gulf of St. Lawrence, compared with other data from the literature.

N	sample	Cu	σ	Pb	σ	Cu/Al	σ	Pb/Al	σ	Cu/Mg	σ	Pb/Mg	σ	Cu/Fe	σ	Pb/Fe	σ	Cu/K	σ	Pb/K	σ
	shallow water samples water depth < 100 m	17.0	6.0	33.0	14.0	2.52	1.68	5.1	3.85	14.56	9.7	28.66	21.26	7.84	3.96	15.43	9.1	8.34	2.57	16.41	7.33
20	samples from water depth between 100 and 200 m	16.0	7.3	28.0	8.5	2.28	1.10	3.88	1.35	7.45	3.17	14.9	2.25	4.92	2.29	9.91	2.23	7.22	3.30	12.64	3.93
12	samples from water depth between 200 and 300 m	23.5	7.9	33.5	22.2	3.54	1.04	4.64	2.62	12.7	6.82	14.31	7.96	8.60	3.70	10.21	5.26	11.76	3.35	17.18	9.7
12	samples from water depth > 300 m	38.3	15.1	54.0	31.1	5.28	2.33	7.66	5.45	14.13	3.9	19.26	6.97	11.87	4.41	17.04	11.00	19.10	8.18	27.6	18.87
–	Igneous rocks (Sandell and Goldich, 1943)	70.0		19.0																	
–	Schists and gneisses (Nockolds and Mitchell, 1948)	43.0																			
6	near shore muds from the Gulf of Paria (Hirst, 1962)	17.0																			
7	cores from the North Atlantic Ocean (Van der Weijden, et al., 1970)	50.0																			
–	Shales (Wampler, 1972)	20.0		20.0																	

† total sample

* Ratios x 10^4

Non-Detrital Pb and Cu: non-detrial Pb varies between 3% and 70%, with an average of 53%. Non-detrital Cu ranges from 27% to 85% (average 61%). These values are considerably higher than those reported for fine sediments in higher latitude environments (Table IV.II).

Non-detrital Pb strongly correlate with non-detrital Mn, while there is no correlation between Pb and organic carbon. On the other hand, Cu correlates positively with organic carbon, and shows a relatively weaker correlation with non-detrital Mn (Table IV.6).

In a study of organic rich sediments from the West African Shelf, Calvert and Price (1970) also found a high correlation of organic carbon with Cu, and a weak correlation for Pb. They concluded that Cu is associated with organic detritus, either as sorbed ions or as metallo-organic complexes.

4.4.4. Molybdenum

Detrital Mo: the distribution of detrital Mo in the fine fraction appears to be independent of depth. Although its average value is close to those reported by Sandell and Goldich (1943) for igneous rocks (Table IV.7), there is no preferential relationship between Mo and any of the major elements.

An explanation might be that Mo occurs in the sediments of the Gulf as the mineral molybdenite. Several areas of Mo mineralization are reported for regions contigious to the Gulf. Contributions from other detrital phases are unlikely, as Mo is not a trace element of clays or other major minerals (Vlasov, 1966).

Table IV.6a

Correlation and regression analysis for non-detrital Cu.

Parameter	Corr. Coeff	Significant at 95% level	Regression Equation	Number of Samples
Carbonate	+ 0.20	No	$Y = 3.6X^2 - 0.1X + 23$	51
*N.D. Manganese	+ 0.35	Yes	$Y = 0.06X + 22.0$	51
Organic carbon	+ 0.64	Yes	$Y = 7.2X + 6.8$	25
Particle size	- 0.23	No	$Y = 2.56X + 67.8$	25

* Non-detrital manganese.

Table IV.6b

Correlation and regression analysis for non-detrital Pb.

Parameter	Corr. Coeff.	Significant at 95% level	Regression Equation	Number of Samples
Carbonate	+ 0.42	Yes	$Y = 4.67 X^2 - 0.15X + 15.0$	51
*N.D. Manganese	+ 0.42	Yes	$Y = 0.07X + 16.0$	51
Organic carbon	- 0.30	No	$Y = 30.0X^2 - 7.2X - 11.5$	25
Particle size	- 0.22	No	$Y = 2.37X^2 - 0.04X - 38.3$	25

* Non-detrital manganese.

Non-Detrital Mo: non-detrital Mo averages 46% of the total Mo content. The degrees of correlation between non-detrital Mo and the reference parameters are given in Table IV.8.

At least two factors contribute positively to the non-detrital Mo content of the sediments of the Gulf: i) association with carbonates; ii) adsorption onto the clay particles. As Paleozoic detrital carbonates have been shown elsewhere (Krejci-Graf, 1972) to have Mo content below detection limits, its positive correlation with carbonates is due rather to the presence of Mo in fine skeletal calcareous debris present in the sediments. Mo is an important element in living organisms. It is particularly known to be a growth factor for many species of marine plankton (Provasoli et al., 1953). However, its biogeochemistry remains poorly known.

Statistical tests suggest that Mo may be present as sorbed ion on clay particles, but not on organic matter, as Mo and organic matter correlate negatively.

Mo may be associated with pyrite, which occurs as a minor component of the fine fraction. The element is known to be associated with sulfides (Bertine, 1972; Cronan and Thomas, 1972) and to accumulate during the formation of sulfide minerals (Berner, 1971; Stumm and Morgan, 1970; Rankama and Sahama, 1950). If the pyrite in the Gulf sediments is authigenic, as proposed by Conolly et al., (1967), it may have acquired Mo in situ, as a result of bacterial oxidation of organic matter.

TABLE IV.7

Average Mo and Se content in different sediments from the Gulf of St. Lawrence, compared with other values from the literature (ppm).

Average		Molybdenum				Selenium	
		Detrital	σ	Total sediment	σ	Total sediment	σ
7	shallow water samples (water depth < 100 m)	15.5	7.1	35.0	21.0	98.0	48.5
20	samples from water depth between 100 and 200 m.	20.0	8.0	28.6	18.1	54.6	27.6
12	samples from water depth between 200 and 300 m.	14.0	8.4	23.0	14.7	41.7	15.9
14	samples from water depth > 300 m. (12 samples for the detrital fraction)	14.3	10.5	19.6	14.5	44.7	24.8
-	Shale from Utah (Barth *et al.*, 1939)					0.6-96.3	
-	Iron sulfide from sedimentary rocks (Minami, 1935b)					up to 32	
-	Igneous rocks (Sandell and Goldich, 1943)	15.0					
-	Sediments from streams and rivers of Bathurst area, New Brunswick (Boyle *et al.*, 1966)	2-98.0					
-	Soils from Alabama (Clark 1973)					up to 170	

TABLE IV.8

Correlation and regression analysis for non-detrital Mo.

Parameter	Corr. coeff.	Significant at 95% level	Regression equation	Number of samples
Carbonate	+ 0.33	Yes	$Y = 1.49X^2 - 0.04X + 1.1$	51
*N.D. Manganese	+ 0.20	No	--	51
Organic carbon	- 0.47	Yes	$Y = - 58.9X^2 + 12.3X + 76.7$	25
Particle size	-0.38	Yes	$Y = - 0.11X + 10.0$	25

* Non-detrital manganese.

-- Not calculated.

4.4.5 Selenium

Se in the fine fraction of the Gulf sediments was analyzed using A.A.S. (Robinson, 1966), after being concentrated and separated as described by Chau and Riley (1965).

Se in the Gulf sediments shows a definite enrichment as compared to other geological material, particularly deep-sea sediments (Table IV.7). Generally Se is enriched in the shallow water samples relative to deep water ones.

According to Rankama and Sahama (1950), Se closely follows sulfur in the geochemical cycle, being concentrated in the sulfide minerals. As Se concentrations are relatively high in the sediments, which at the same time contain only minor amounts of sulfides, this element may be contributed by other minerals or may occur in sorbed state. The associations could be with: i) sulfate minerals such as barite; ii) sulfate ions acquired or trapped in the sediments due to flocculation of suspended clay particles; iii) ferro-manganese oxide, particularly in association with iron oxides.

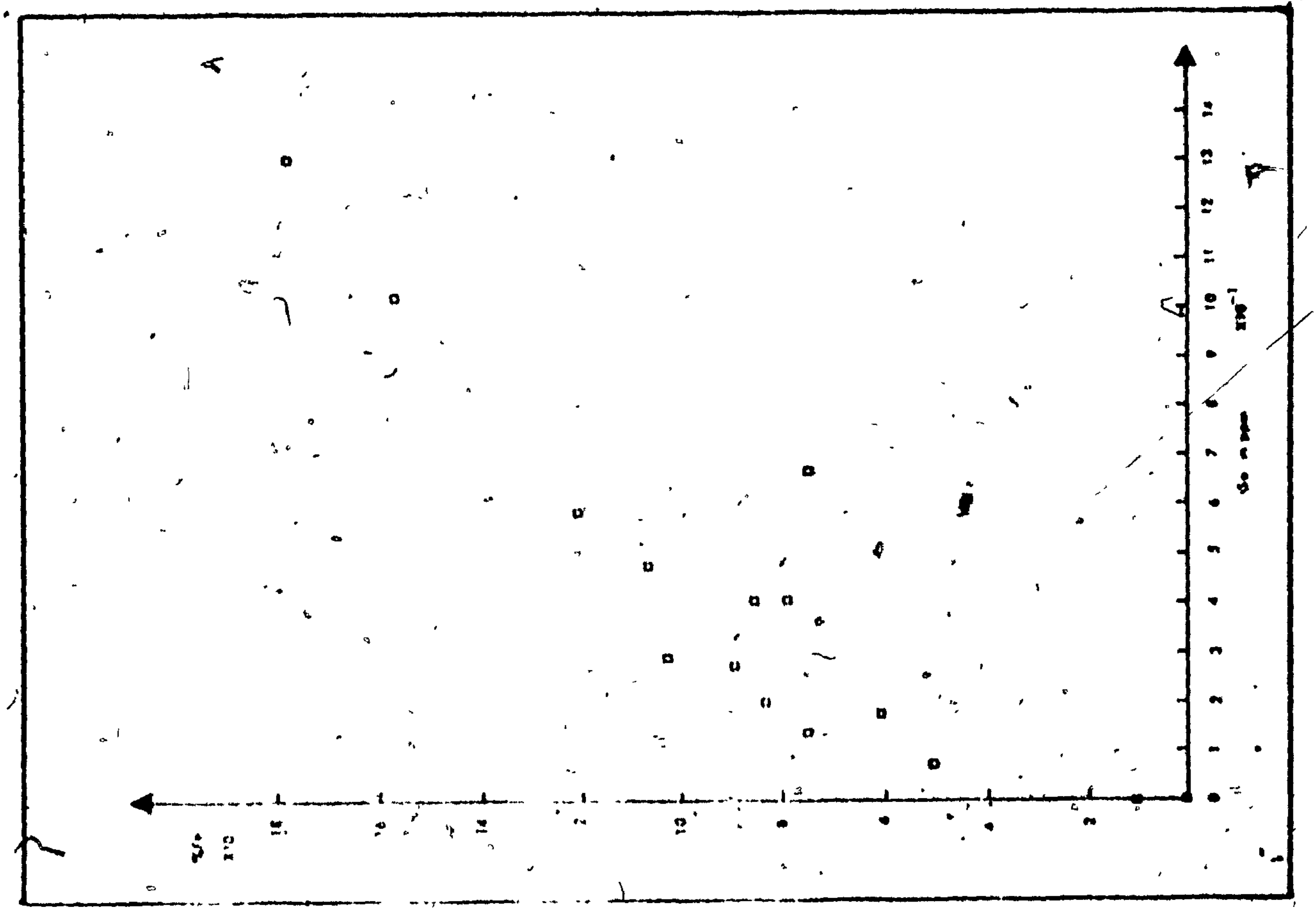
Barite has been reported in the heavy mineral fraction of the sediments from the Gulf (Loring and Nota, 1969). High Se content in samples from shallow stations as compared to deep water stations may be attributed to the presence of pyrites and barites, in relatively higher content than in the sediments from deep water

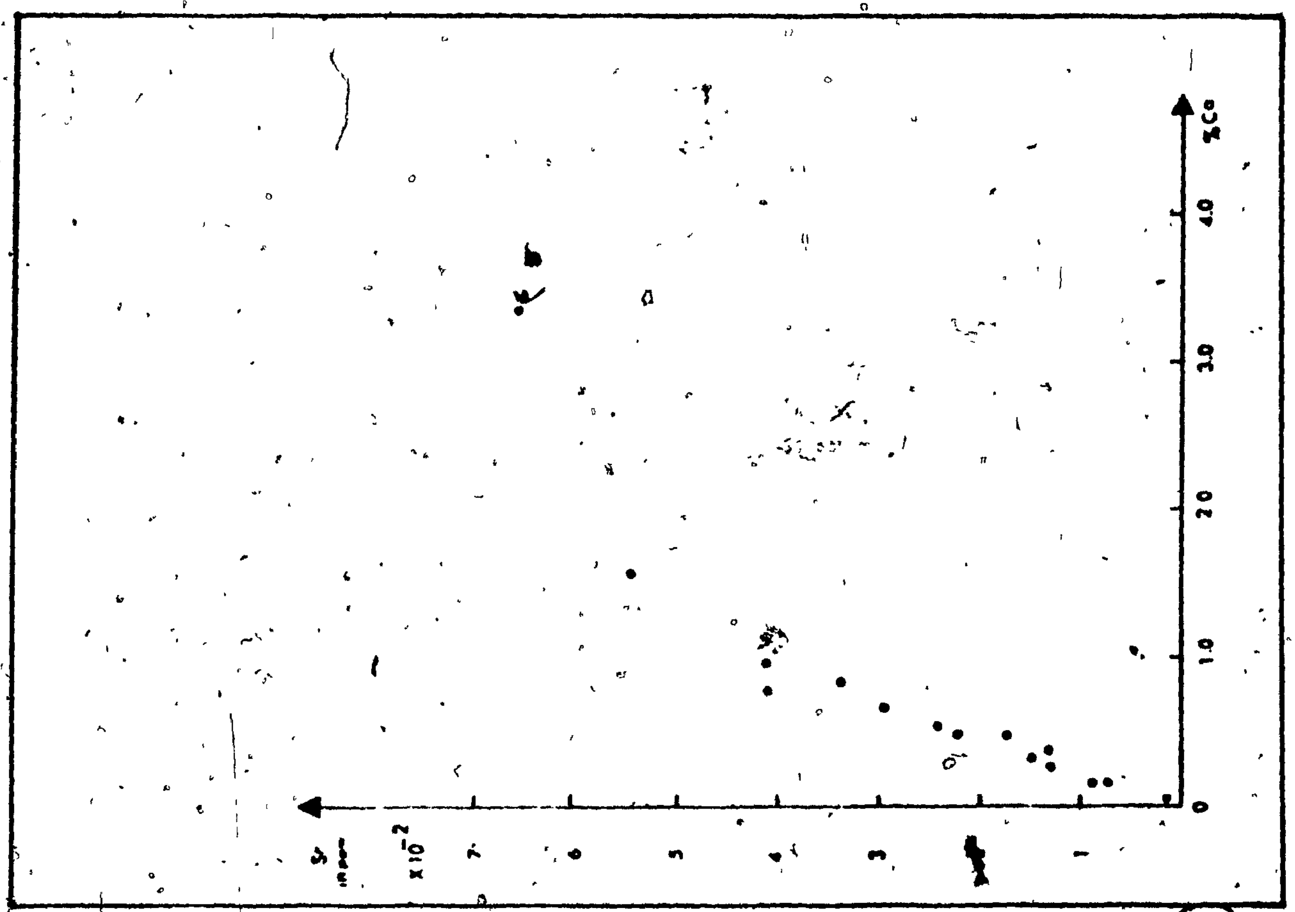
Figure IV.3

Relationship between total Se and non-detrital Fe in the Gulf sediments.

Figure IV.4

Relationship between Sr and Ca contents in the detrital fraction of the Gulf sediments.


Ga in ppm
x10^{-1}
1
2
3
4
5
6
7
8
9
10
11
12
13
14
2
4
6
8
10
12
14
16
18
x10


%Ca
1.0
2.0
3.0
4.0
1
2
3
4
5
6
7
Sr in ppm
x10^{-2}

stations. According to Turner (1957), the highest concentrations of Se are confined to beach and lagoon deposits.

Rankama and Sahama (1950) state that Fe and Mn hydroxides are able to adsorb Se complexes from aqueous solutions. The element is more efficiently removed from solutions by Fe $(OH)_3$ (Chau and Riley, 1965). As ferro-manganese oxides occur in the Gulf sediments (mostly as coating of the sediment particles) they may well be the main host for Se. The relationship between total Se and non-detrital Fe is shown in Figure IV.3. Some degree of association between the two elements may be inferred from that figure.

4.4.6 Strontium

Detrital Sr: detrital Sr of the fine fraction of the Gulf sediments, makes up 32% of the total Sr. The latter varies between 80 and 1997 ppm with an average of 398 ppm (σ = 338 ppm). No statistical correlation was found between detrital Sr and either Al, Fe, Mg, or K: a high correlation does exist with Ca. The variation of Sr with Ca is shown in Figure IV.4.

According to Vlasov (1966), Sr does not enter the clay minerals as an isomorphous inclusion, contrary to its behaviour in igneous alumino-silicates, where it frequently replaces Ca and K. The relationship between Sr and Ca in the detrital fraction of the Gulf sediments, thus, may indicate its association with feldspars. The lack of correlation between K and the high positive correlation with Ca indicate that Sr is replacing Ca in plagioclase feldspar, most of which has presumably been derived from granitic rocks from the north shore. A high correlation between Ca and Sr, differentiates grantitic rocks from basaltic ones (Wehmiller, 1972).

Non-Detrital Sr: non-detrital Sr (Table IV.9) accounts on the average, for 68% of the total Sr, with a range between 40% and 90%.

This fraction may have been introduced in the sediments by either one or both of the following pathways: i) co-precipitation with $CaCO_3$ in skeletal material, or in association with detrital carbonates; ii) sorption on clay particles and organic matter. The positive correlation with particle size (inversely proportional to surface area), and the negative correlation with organic carbon, both indicate that sorption reactions are not important mechanisms by which the element was incorporated in the Gulf sediments. In Pacific pelagic clays, Goldberg and Arrhenius (1958) found that about 13% of the total Sr occurs in the sorbed state.

The positive correlation with carbonate content suggests that Sr may be associated with it in the fine fraction of the sediments. The relatively low correlation coefficient, however, is expected if only part of the carbonate is aragonite shell material able to accomodate Sr. The remaining may be detrital calcite from local limestones.

4.4.7 Zinc

Detrital Zn: the average detrital Zn makes up 64% of the total Zn, and ranges from 34% to 88%. Total Zn content in the analyzed samples averages 121 ppm (σ = 37 ppm).

TABLE IV.9

Correlation and regression analysis for non-detrital Sr.

Paramter	Corr. coeff.	Significant at 95% level	Regression equation	Number of samples
Carbonate	+ 0.57	Yes	Y = 30.1X - 16.5	51
Organic carbon	- 0.47	Yes	Y = - 428.8X + 1337.0	25
Particle size	+ 0.90	Yes	Y = 62.4X - 204.8	25

Figure IV.5 a,b illustrates the variations of detrital Zn with Fe and Mg. The correlation is good, and suggests that Zn tends to follow these two elements. It appears likely that detrital Zn in the Gulf sediments is linked with the chlorite phase, rich in Fe and Mg. The similarity between the atomic radius of Zn and the atomic radii of Fe and Mg supports this possibility. Rankama and Sahama (1950) state that the abundance of Zn in nature depends on its property of replacing Fe^{+2} diadochically in mineral structures.

Non-Detrital Zn: on the average, 36% of total Zn is non-detrital. statistical analysis yields a positive correlation between non-detrital Zn and i) organic carbon (r = +0.66), ii) non-detrital Mn (r = +0.56); iii) particle size (r = + 0.37). There is no correlation between non-detrital Zn and carbonate content. Thus, sorption by organic matter would appear to be the major pathway by which Zn was incorporated into the sediments. A secondary process might be precipitation with some ferro-manganese oxide phase. These two processes are known to be involved in the deposition of Zn in sediments elsewhere (Rankama and Sahama, 1959; Calvert and Price, 1970).

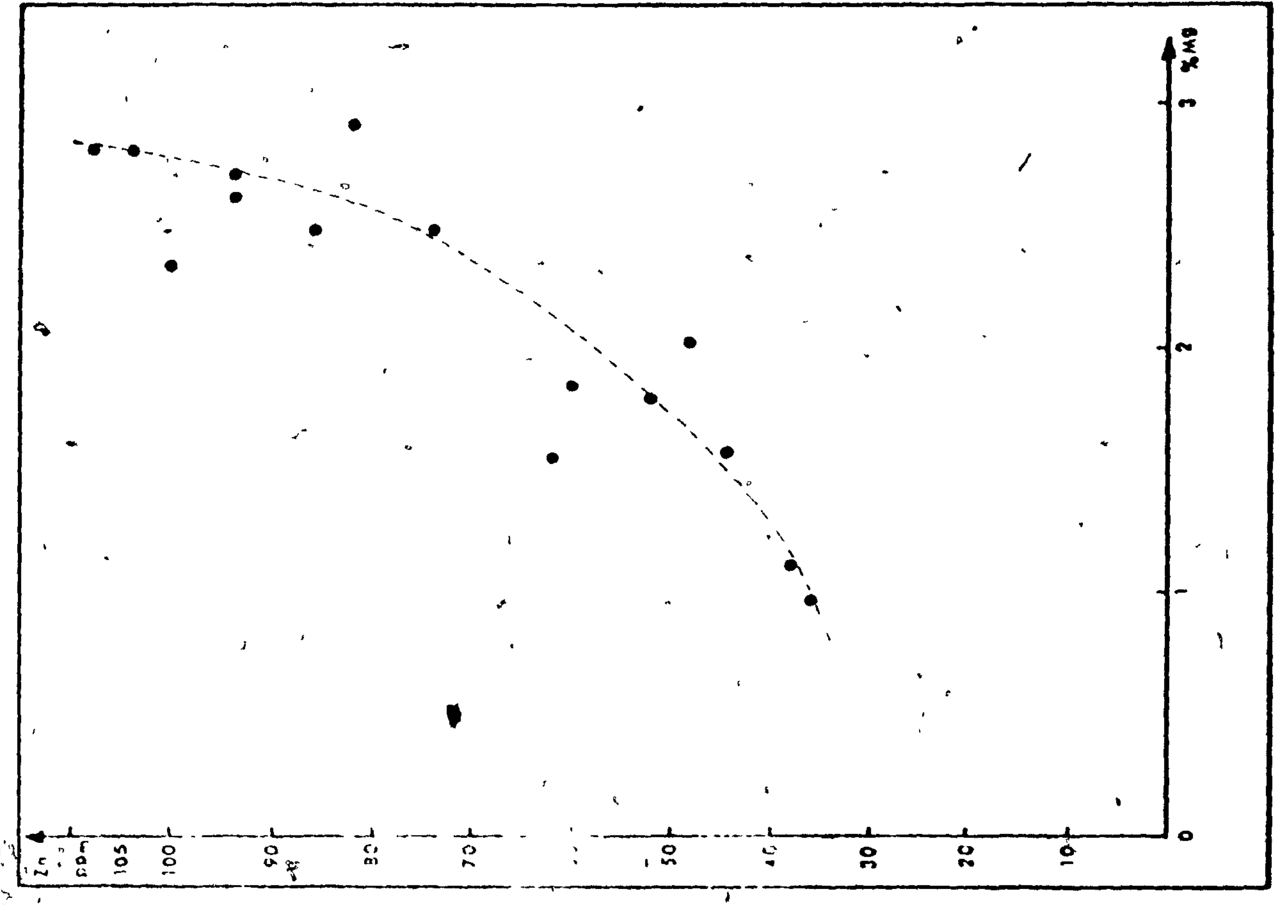
The positive correlation between non-detrital Zn and particle size suggests that adsorption on clay particles is not an efficient mechanism in the removal of the element.

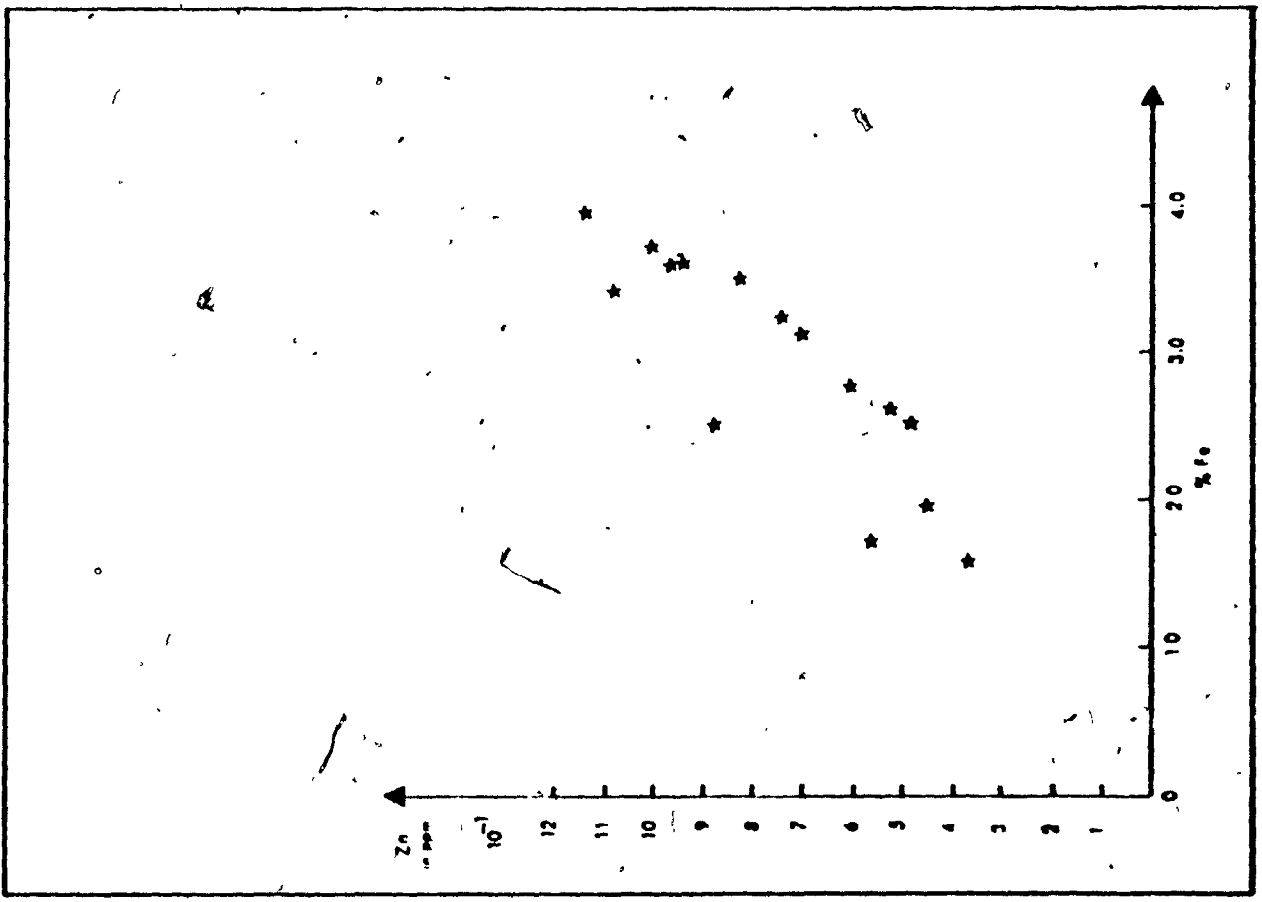
Figure IV.5a

Relationship between detrital Zn and detrital Mg

Figure IV.5b

Relationship between detrital Zn and detrital Fe


Zn ppm
105
100
90
80
70
50
40
30
20
10
0
1
2
3
% Mg


Zn ppm
10^1
12
11
10
9
8
7
6
5
4
3
2
1
0
10
20
3.0
4.0
% Fe

4.4.8 Manganese

Detrital Mn: the average values for the detrital Mn content in the fine fraction of the Gulf sediments, as well as the total Mn values, are given in Table IV.10 . The Fe content and Mn/Fe ratios are also indicated. Figure IV.6 shows the relationship between detrital Mn and Mg in the sediments.

Detrital Mn has an almost constant ratio with detrital Fe (0.013). The ratio for the total elements is 0.018. This may indicate that Mn is supplied in relatively larger amounts than Fe by the non-detrital fraction.

Figure IV.6 illustrates that Mn varies with Mg. Hence, if as discussed earlier, Fe and Mg occur mainly in chlorite in the Gulf sediments, Mn may be associated with this clay mineral.

Non-Detrital Mn: the non-detrital Mn contribution to the fine fraction varies between 8% and 74%, with an average of 45%. The non-detrital Fe averages 24%. The non-detrital Mn is negatively correlated with both organic carbon and carbonate content. No correlation was found between non-detrital Mn and particle size; a strong correlation between non-detrital Mn and non-detrital Fe exists (Figure IV.7).

The Mn/Fe ratio in the non-detrital fraction is almost constant. This may indicate that both elements are present in the same minerals (Chave and Mackenzie, 1961). In the non-detrital fraction this would be the ferro-manganese oxides. However, compared with ferro-manganese oxides from other environments

TABLE IV.10

Mn content in the detrital fraction and the total sediment samples, together with Fe values in the same samples and the Mn/Fe* ratios compared to other geological material from elsewhere.

Average		Detrital fraction				Total sample		
		Fe	Mn	Mn/Fe*	σ	Fe	Mn	Mn/Fe*
7	shallow water samples (water depth < 100 m)	2.43	346	149.3	41.8	3.70	667	181
20	samples from water depth between 100 and 200 m.	2.92	448	161.2	37.2	3.65	694	190
12	samples from water depth between 200 and 300 m.	3.41	398	115.0	15.9	4.13	644	160
14	samples from water depth > 300 m (12 samples for the detrital fraction)	3.92	467	121.8	11.6	4.25	813	190
5	suspended matter samples from all over the Gulf	10.0	3000	300.0				
50	St. Lawrence Gulf sediments (Loring and Nota, 1968)					4.24	720	170
-	Canadian Shield (Grout, 1938)	3.98	560	140				
-	Delta clays from the Gulf of Paria (Hirst, 1962)	4.21	500	120				
-	Igneous rocks (Goldschmidt, 1937)	5.0		200				
-	Igneous rocks (Clark and Washington, 1924)		1000					

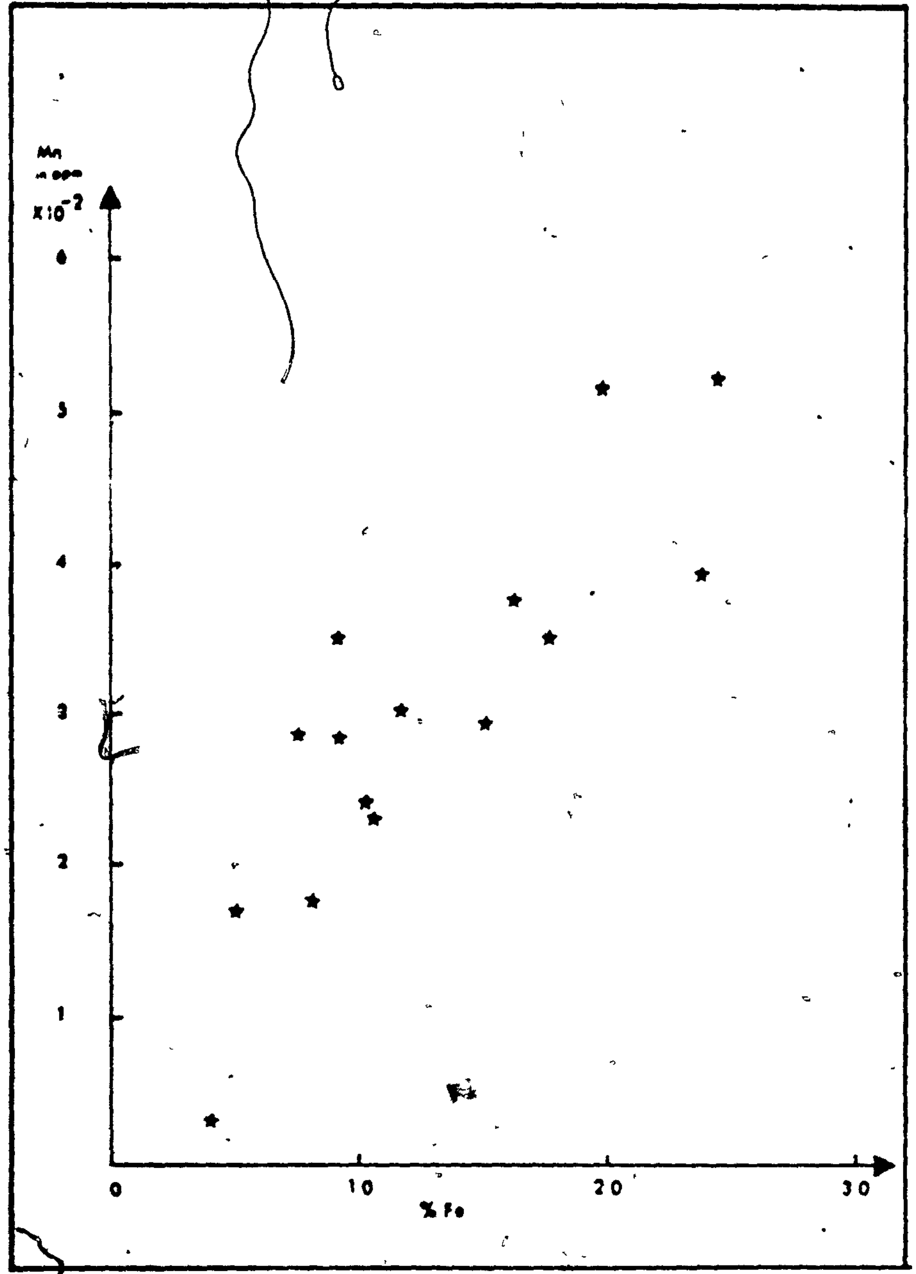
Mn is given in ppm Fe is given in % * Ratios x 10^4

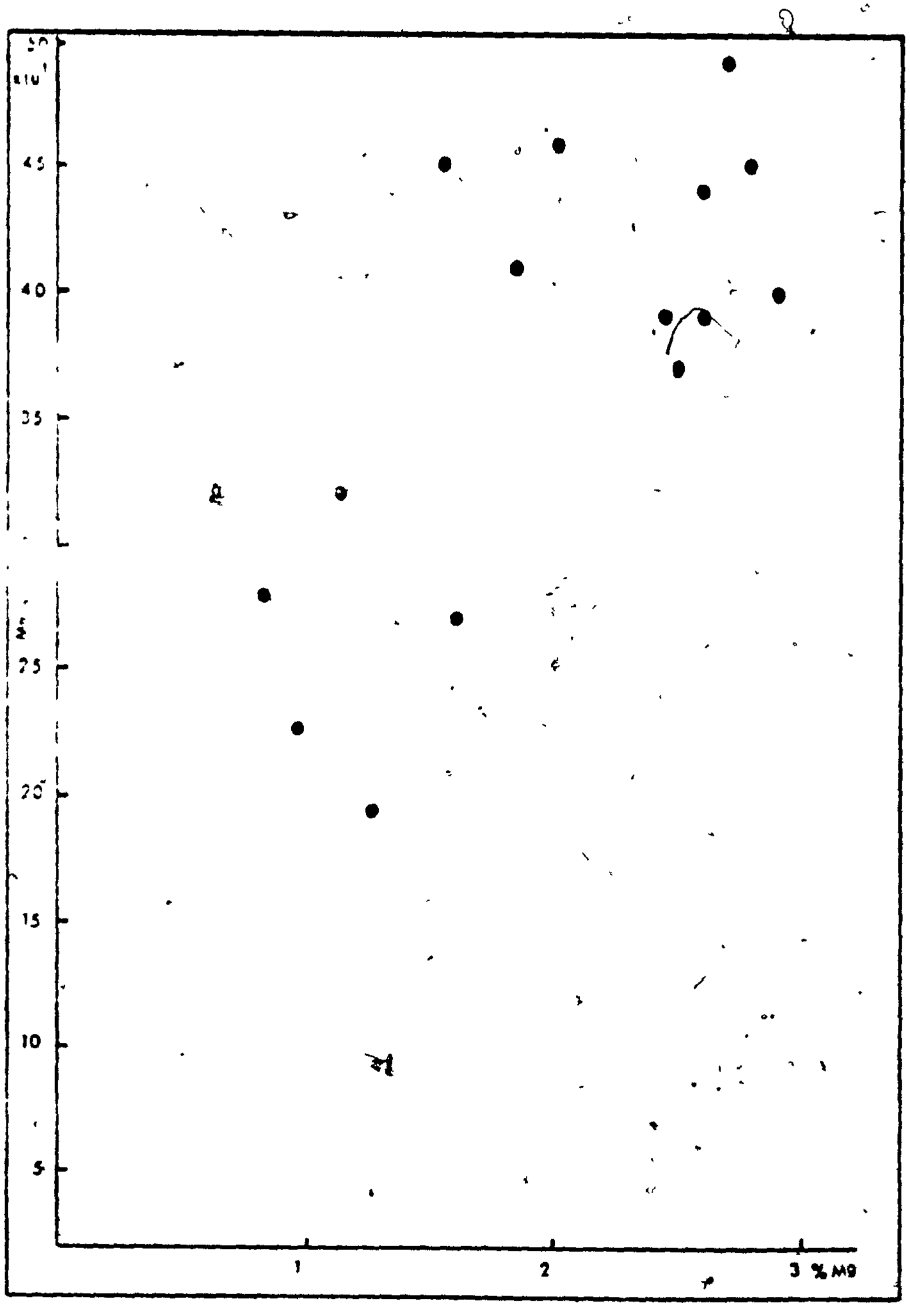
Figure IV.6

Relationship between Mn and Mg contents in the detrital fraction of the Gulf sediments.

Figure IV.7

Relationship between non-detrital Mn and non-detrital Fe in the Gulf sediments.


Mn
in ppm
x 10^-2
6
5
4
3
2
1
0
10
20
30
% Fe


50
45
40
35
25
20
15
10
5
1
2
3 % Mg

(see for ex. Price, 1967) the Mn/Fe is very small.

Both non-detrital Fe and Mn enter the sea i) in true solution, ii) as sorbed ions on particulate matter; iii) as precipitates or co-precipitates on detrital grains (Gibbs, 1973). The differences in the average content of both elements reflect the relative availability of their ions in solution.

Like Fe, Mn is soluble to low Eh and pH values (Garrels and Christ, 1965). The fractionation of the two elements may take place at or near the source, or later in the sedimentary cycle (Ljungren, 1953). Ferrous iron in solution is more easily oxidized than Mn^{+2} (Krauskoph, 1957). It is stabilized as Fe_2O_3 or Fe $(OH)_3$ and taken out of solution. On the other hand, Mn^{+2} oxidizes to Mn $(OH)_3$ or MnO_2 (Manheim, 1965). Low Eh values reported by Loring and Nota (1968) as well as the presence of a reducing layer 1 to 2 cm below the sediment surface, indicate that much of the Gulf sediments may have redox potentials below the stability level of Mn^{+4} and possibly in some areas below that of Fe^{+3}. This may explain the low concentration of Mn as Mn hydroxides.

The negative correlation between non-detrital Mn and organic carbon is to be expected, as local concentrations of organic matter within the sediment will decrease the Eh and pH. The negative correlation with carbonate is also not surprising: carbonates are known to contain very little Mn (Turekian, 1965).

4.5 Discussion

The total abundance of the trace elements in sediments is a measure partly of their availability in the source material, and partly of their reactivity. By using proper fractionation methods, as done in this work and in previous studies (Hirst, 1962 b), it is also possible to interpret physical and chemical pathways which lead to their concentration in bottom sediments.

The analytical results presented in this chapter indicate that, unlike the major elements which are mainly introduced into the sediments via the detrital (lithogenous) fraction, a significant part of the trace elements is associated with the non-detrital fraction, which accumulates through reactions taking place in the water column or at the water-sediment interface. This point is illustrated by the variations in element concentrations as a function of water depth: while the abundance of major and minor elements, Ca, Fe, Ti, Mg, and K increases with depth in the fine fraction, mainly as a result of the higher percentage of clay minerals present, no particular trend appears for trace elements studied with the exception of Cr which occurs mainly in the detrital fraction.

When compared to values for sediments of other latitudes, after normalization to a constant $CaCO_3$ value of 10.5%, the average non-detrital contribution of Cu, Pb, Mn, Ni, and Sr in the Gulf sediments, appears quite high (Table IV.11). This may be explained in part as a result of trace element enrichment in the source rocks: mineralization zones for Mo, Cu, Ni and some associated elements occur around the Gulf; some of them are or have been mined. On the other hand, Pb, Cu, Zn, and Ni are used in various industrial and domestic products and the St. Lawrence River waters, fed by the great lakes, receive considerable inputs of trace elements as byproducts and wastes from industrial cities in the U.S.A. and Canada. Injections via the atmosphere are also likely. The estuary of the St. Lawrence River and the Gulf together act as a major sink for these various substances.

It is difficult to estimate quantitively how much man's influence may raise the natural levels of trace elements in sediments. Simple calculations based on published analysis indicate that the Mackenzie River, which may be considered still unpolluted (Reeder et al., 1972), transports proportionally four times less Cu and twice less Zn yearly as the St. Lawrence River. It thus may be already too late to refer to a natural back-ground baseline for further changes in trace elements concentrations in the Gulf sediments.

When compared to those for fine sediments in the Gulf the non-detrital fractions of the trace elements are significantly higher in the estuary of the St. Lawrence River (Smith, 1973, p.c.). This holds true for all of the elements except Cu (Table Iv.12): after normalization to 10.5% $CaCO_3$, non-detrital Cu in the estuary is only on the average 36% of the total element, as against 61% in the Gulf. Thus trace elements removal is important in the estuary, possibly as a result of surface sorption, precipitation or flocculated particles (Gibbs, 1973). These reactions may not be reversible for all trace elements in the particular conditions of the St. Lawrence estuary, which may explain the particular behaviour of Cu (Turekian, 1971).

TABLE IV.11

Contribution made by the non-detrital fraction of the sediments in the Gulf as compared to other sediments, recalculated to 10.5% carbonate content

% contribution made by the non-detrital fraction	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sr	Zn
* Gulf of St. Lawrence	28	17	61	45	46	48	53	68	36
** Low latitude sediments	58	8	67	--	--	43	4	--	--
*** High latitude sediments	11	19	17	13	--	10	--	24	--
+* Deep-sea sediments	12	6	11	14	--	9	--	17	--
-* St. Lawrence estuary	26	19	36	100	--	78	--	--	73

TABLE IV.12

Average percentage contribution made to the total element content by the detrital fraction.

Element	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sr	Zn
average % detrital contribution	72	83	39	55	54	52	47	32	64

* present work
** Hirst (1962b)
*** Beltagy (1969)
+* Chester and Messiha-Hanna (1970)
-* Smith (1973, P.C.)

Statistical analysis applied to values of the non-detrital fraction has suggested that the mechanisms by which elements are incorporated into the Gulf sediments vary from one element to another. Sorption by organic matter is important for Cr, Cu, Ni, Pb and Zn. On the other hand precipitation in association with ferro-manganese hydroxides provides a major depositional pathway for Cr, Cu, Pb, Zn and Se. Carbonates may contribute to concentrations of Co, Pb, Mo and Sr. Adsorption on the clay particles (surface reactions) appears to be particularly efficient for the removal of Mo from sea water.

The mineralogical association of the trace elements studied, was inferred from the study of the detrital fraction of the sediments. Based on the average contribution of that fraction to the total trace element content (Table IV.12), the results indicate that the detrital character of the elements decreases in the order Cr > Co > Zn > Mn > Mo > Ni > Pb > Cu > Sr.

According to their mineral association in the detrital fraction the elements can be divided into three groups:

Group I: consists of trace elements mainly associated with clay minerals, particularly chlorite, as indicated by their respective relations to Mg. This group includes Cr, Co, Mn and Zn. Regression analysis shows that 77% Cr, 73% Co, 75% Mn and 67% Zn are contributed by chlorite.

Group II: is made up of elements associated with non-clay minerals. To this group belongs only Sr, which substitutes for Ca and K in feldspars. Plagioclase feldspar appears to contribute over 90% of the element in that fraction.

Group III: members of this group do not associate themselves with any major mineral component of the sediments but either occur as separate minerals or are distributed randomly among all the mineral constituents of the sediment. Ni, Mo, Pb and possibly Se fall in this category.

Se which was studied in the total fine fraction of the sediments, shows very high values. Although Se is being mined in Quebec and Ontario on the edges of the Canadian Shield, there is no Se mineral deposits in the St. Lawrence drainage basin. The high values found may point out to occurrence of concentration zones there. The relationship between Se and non-detrital Fe suggests that Se in the sediments was precipitated from solution with Fe hydroxides. This may have taken place at the source or during transportation.

The correlation found in the detrital fraction between Cr, Co, Mn and Zn on one hand and Mg on the other may be characteristic of the lithology of the source areas.

CHAPTER V

SEDIMENTATION IN FIVE LONG CORES FROM THE GULF OF ST. LAWRENCE

5.1 Introduction

The stratigraphic interpretation of geochemical data obtained from cores, is a very difficult task, particularly in the absence of any information on rates of sedimentation (Wangersky, 1962). The partition of the elements among the various inorganic and organic phases is in itself a major problem. Also, following incorporation in sediments, some elements may be re-mobilized and may migrate from their original sites to be re-precipitated elsewhere (Lynn and Bonatti, 1965). For purposes of correlation and stratigraphic studies, the selection of elements to be analyzed is therefore critical. Finally, in order to come to any valid conclusion the data must be subjected to sensitive statistical techniques.

In spite of the difficulties involved, the geochemical analysis of core samples may be the only tool available for stratigraphy in areas such as the Gulf where radiometric, paleontological or other type of information are lacking. In addition, having considered regional trends in the chemical composition of the surface sediments, it is worthwhile to investigate vertical changes in element distributions as these might reflect some modifications of the environment.

In the current investigation, sub-samples were taken along five piston cores collected in the Gulf of St. Lawrence at locations given in Table V.1.

TABLE V.1

Core location and water depths.

Core No.	Location		Water depth	Length of core
	Long.	Lat.		
BIO 115	60° 11' 8	48° 10' 0	485 m	1060 cm
BIO 36	60° 14' 9	48° 59' 0	302 m	350 cm
Sack 3	63° 08' 0	48° 34' 0	372 m	225 cm
Sack 17	65° 33' 0	49° 36' 0	410 m	225 cm
Sack 21	60° 11' 0	48° 17' 0	345 m	125 cm

These were analyzed for the following elements: Na, K, Ca, Al, Fe, Mg, Ti, Mn, Cr, Co, Cu, Mo, Ni, Zn, and Sr.

The results for the major elements and Mn are the only ones presented here. Results of other elements are given in Appendix C. The elements discussed in this chapter were chosen for the following reasons: (i) as the distribution of the major elements in the Gulf is largely controlled now by depth, their variations along core length may reflect changes in regional water depth with time; (ii) except for Ca, the major elements appear to be supplied to the sediments mainly via suspended matter input from the St. Lawrence River. Accordingly, their variations in the cores may also result from fluctuations in this source with time, including changes of the mineral assemblage supplied in suspension; (iii) post depositional alterations affecting the distribution of major elements are belived to be long term diagenetic effects (Weaver, 1967). They may be considered negligible over the time period, of about 60,000 years, represented by the longest core; (iv) although Mn may migrate vertically (Lynn and Bonatti, 1965), an attempt is made to interpret the variations in non-detrital Mn in terms of physico-chemical processes; (v) it may be risky to attempt core correlation on the basis of vertical changes in trace elements; their distribution is influenced by depth, but also by several additional factors, particularly, the presence of sulfide minerals in some samples, their absence in others constitute a major problem, as some trace elements Mo, Cu, Ni and Zn tend to occur in association with sulfide minerals.

Two different statistical approaches are used simultaneously to treat the data. First a simple correlation analysis between the elements taken two at a time is applied. This is a standard technique used in dealing with geological problems (Eisma et. al., 1966; Jones, 1972). The other method involves Q-mode factor analysis, as described and applied by Imbrie (1963); Imbrie and Van Andel (1964); and Imbrie and Kipp (1971).

Factor analysis yields a theoretical solution of the problem at hand by indicating the minimum number of factors responsible for the observed variance in the samples. A remaining task for the analyst is to establish if these theoretical factors may correspond to physical, and measurable ones. For this purpose, he may make use of the so called "oblique solution" (Imbrie, 1963). The results may be very informative. They may be used as a guide for further experimentation and allow to construct a model for prediction and quantification of natural processes (Spencer et al., 1968; Imbrie and Kipp, 1971).

5.2 . Core Lithology

Information on texture and on the mineralogical composition of the coarse fraction is summed up in Figures V.1 and V.2 respectively. The lithology of the cores is illustrated in Figure V.3.

Three different stratigraphic units, numbers 1 to 3, can be identified in the cores on the basis of sediment colour (Figure V.3).

Figure V.1

Ternary diagram showing the difference in texture between the gray olive-green sediments and the reddish-brown sediments

● Gray olive-green sediments

★ Reddish brown sediments

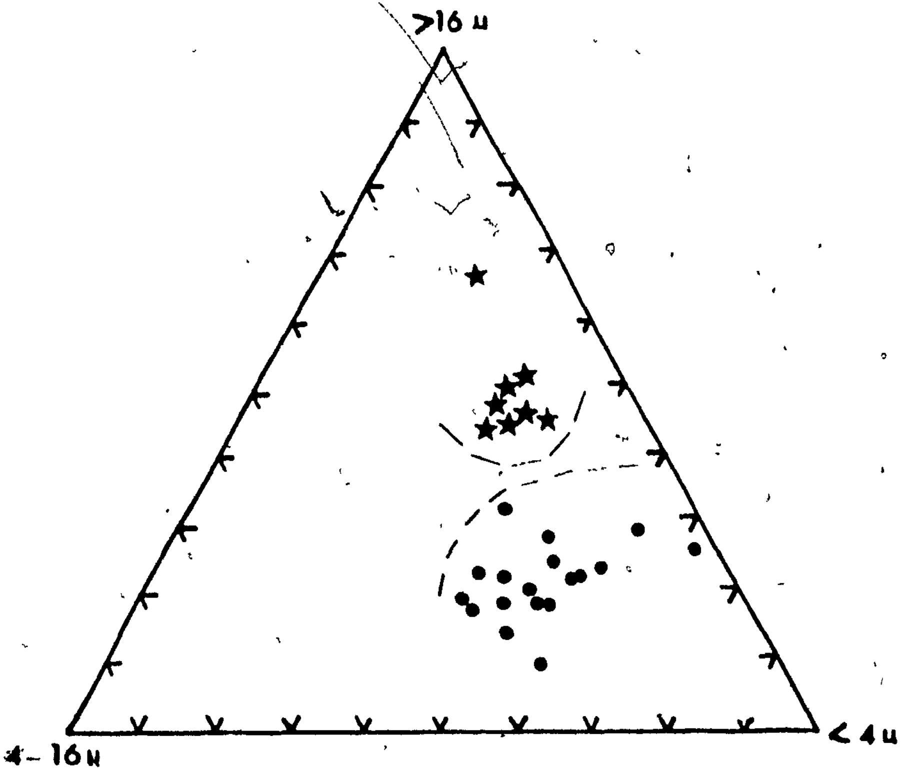

>16 μ
4-16 μ
< 4 μ

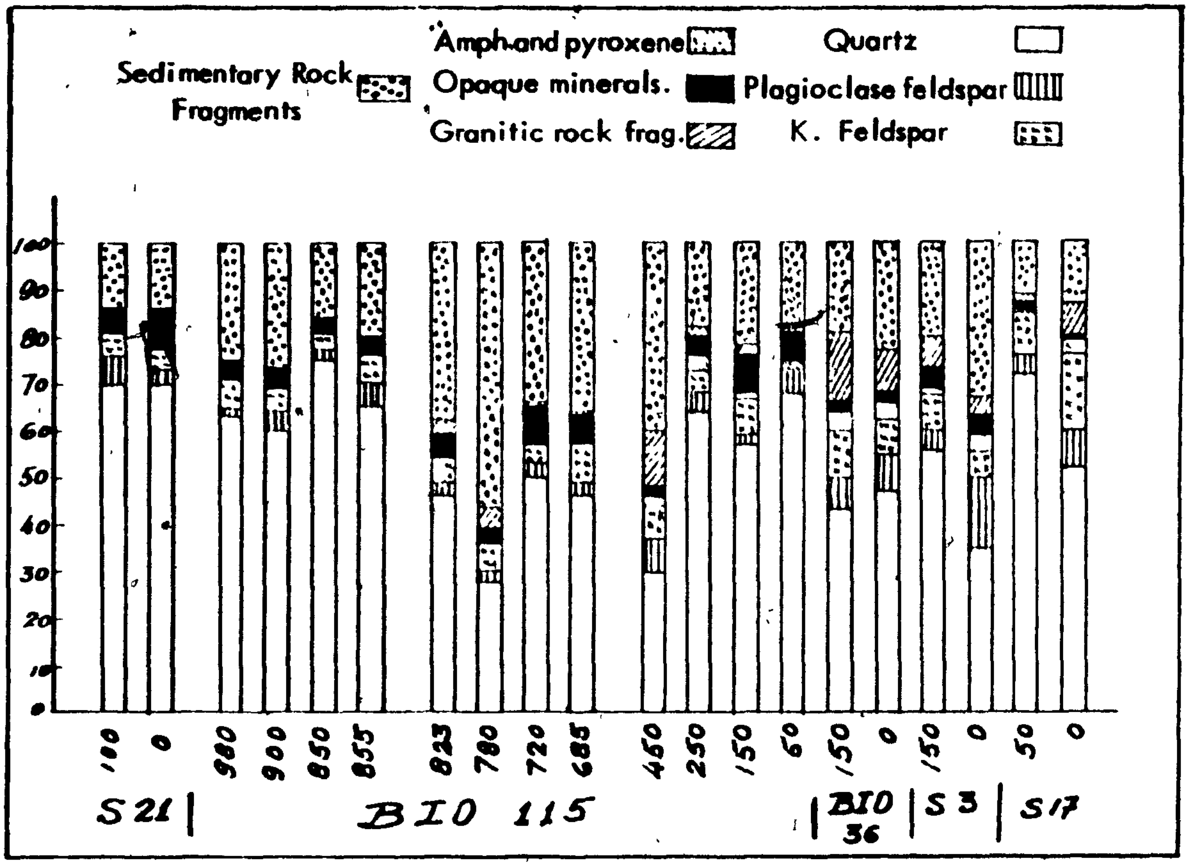
Figure V.2

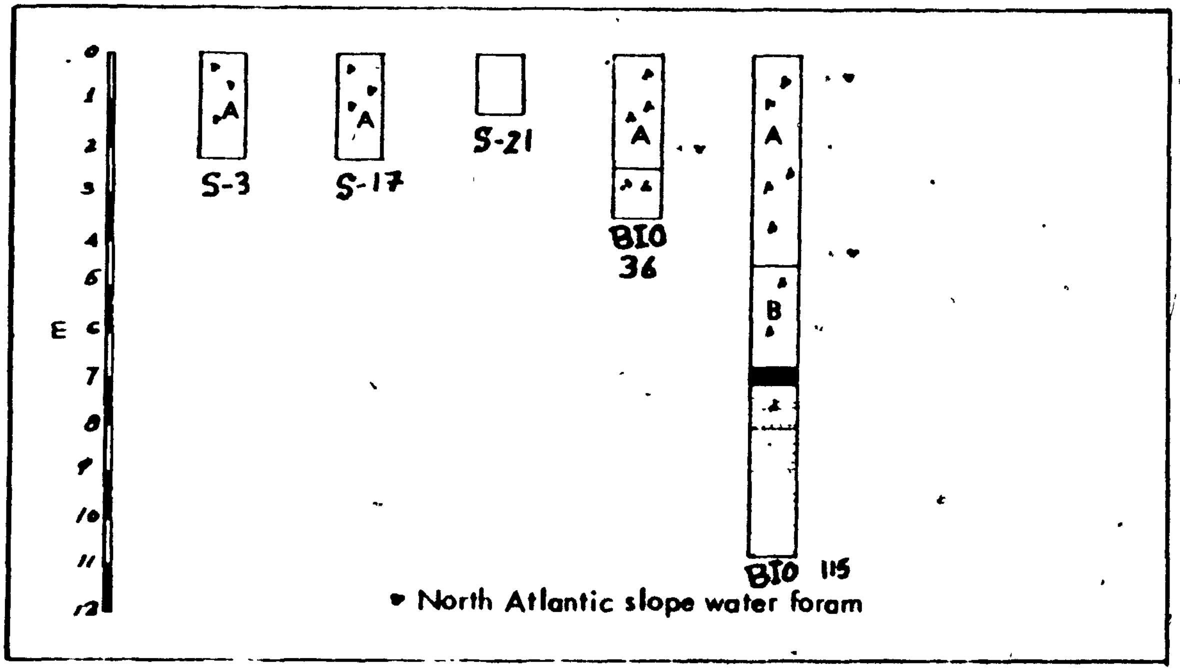
Mineralogy of the coarse fraction in selected core samples

Figure V.3

Lithology of the cores analyzed

A	Gray olive-green sediments
B	Brown sediments
■	Reddish sediments
⁚	Reddish-brown sediments with sandy layers
● ●	Foraminifera


Sedimentary Rock Fragments
Amph. and pyroxene
Opaque minerals.
Granitic rock frag.
Quartz
Plagioclase feldspar
K. Feldspar
100
90
80
70
60
50
40
30
20
10
0
100
0
980
900
850
855
823
780
720
685
450
250
150
60
150
0
150
0
50
0
S21
BIO 115
BIO 36
S3
S17


0
1
2
3
4
5
6
7
8
9
10
11
12
E
S-3
S-17
S-21
BIO 36
BIO 115
A
B
North Atlantic slope water foram

Unit 1, at the surface, is made up of gray olive-green sediments. Nota and Loring (1964); Conolly et al., (1967) and Stanley et al., (1971) all agree that this surface material which occurs in the Laurentian Channel and on the Scotian Shelf, is post-Pleistocene in age. Unit 1 corresponds to horizons III a and b in Conolly's subdivisions (Conolly et al., 1967). It is underlain by older reddish-brown glacial marine sediments, making up unit 2 (Conolly's horizon II). Unit 3 below consists of red sediments marked by sandly layers and an increased frequency of pebbles. It corresponds to horizon I of Conolly et al., (1967), according to whom it represents a glacial till.

Textural analysis (Figure V.1, also Table I, Appendix C) clearly indicates that the coarse fraction (>63 μ) is more abundant in the reddish-brown sediments (units 2 and 3) than in the gray olive-green deposits (unit 1). The latter do not contain any significant amount of sand. Texturally, they range from silty clays to clayey silts. Conolly et al. (1967) also found that the upper gray to brown sediments (horizon III a and b) in their cores from the Laurentian Channel, belongs to this class. In contrast, the reddish-brown sediments are characterized by a high percentage of coarse sand and pebbles.

In core BIO 115 the three different stratigraphic units are present (Figure V.3). Cores BIO 36, S 17 and S 3 are all in unit 1. In contrast, core S 21 consists entirely of unit 2 on the basis of colour, although its texture makes it more akin to unit 3.

5.3 Mineralogy of the Sand Size Fraction

To confirm the three stratigraphic units suggested by visual and textural examination of the cores, the coarse fraction of selected sub-samples were examined under the stereomicroscope. Between 300 and 500 grains were identified and counted in each sample. The results are expressed as percentage number of grains, and are given in Table 2, Appendix C; and illustrated in Figure V.2 .

Minerals identified were: quartz, K-feldspar, plagioclase feldspar, amphibole, pryoxene, garnet and opaque minerals. Igneous rock fragments (mostly granite) were frequent in all the samples studied, as were fragments of slate and quartzite and to a lesser extent, foram tests.

Quartz:

In unit 1, quartz grains make up between 30% and 70% of the total counted grains. The grains are angular and have a fresh appearance.

In unit 2, quartz makes up between 28% and 50% of the grain counts. The grains are always well rounded and coated with iron oxide. Similar quartz grains appear in unit 3 at a much higher frequency, between 60% and 75%.

Samples from core S21 (unit 3) contain 70% quartz. Quartz overgrowths were noticeable on some grains.

Feldspars:

Angular and subangular feldspar grains were frequent in all the samples studied, but the relative proportion of plagioclase and K-feldspars differs between units.

In unit 1, K-feldspar and plagioclase feldspars are both present in relatively large quantities. Each type makes up about the same proportion of the total coarse fraction; K-felspar between 5% and 16%, and plagioclase feldspar between 4% and 15%. Grain surfaces bear no traces of alterations.

Unit 2 has less feldspar than unit 1, with possibly a higher proportion of K-feldspar. K-feldspar makes up 4% to 8%; plagioclase feldspar 2% to 7% of the grains.

In unit 3, the feldspar content decreases even further with the plagioclase feldspar abundance below 5%.

With tespect to their feldspar content, samples from core S 21 have composition approaching unit 3 rather than unit 2.

Hornblende, Augite and Garnet:

These three heavy minerals were found only in unit 1, where they make up from 1% to 4% of the sand fraction.

Opaque Minerals:

Opaque minerals are common to all three units, but were found to be more abundant in units 1 and 2 (up to 8% of the grain count), than in unit 3 (3% to 4%).

Pyrite occurs as discrete grains; it was also found as filling in foraminiferal tests present in units 2 and 3.

Granitic Rock Fragments:

Granitic rock fragments are very abundant in unit 1, in which they make between 2% and 16% of the sand fraction. They occur also in unit 2, but they do not exceed 5% of the sand fraction. They were not identified in unit 3 (BIO 115); and were not observed in core S 21, another point identifying it as a sample of unit 3.

Sedimentary Rock Fragments and Foram Tests:

The sedimentary rock fragments consist of red siltstone and quartzite fragments. Their maximum abundance is in unit 2 (Figure V.3). Foraminifera are not abundant, but are always present in all units.

In conclusion, on the basis of this rapid coarse fraction analysis, the mineral compositions of the three units seem significantly different. The following generalizations can be made: (i) the source material of the sands in unit 1 probably to be found mainly in crystalline rocks of the Canadian Shield. The presence, in unit 1, of blue-green hornblende, which is characteristic of the Shield rocks of Eastern Quebec (Stockwell, 1957; Loring and Nota, 1969) supports this opinion; (ii) sediments of unit 2 seem to be derived from older sedimentary outcrops. A likely source is the complex of Carboniferous and Permian formations outcropping in the Appalachian region, with some contribution from the Canadian Shield; (iii) unit 3 must be strictly derived from Appalachian sources, since it contains no granitic fragments.

5.4 Chemistry of the Core Samples

5.4.1 Methods of Analysis

The samples analyzed were taken along the cores near levels where marked changes occurred in either colour or texture; where no such changes appeared, samples were taken every 50 cm.

As in previous analyses, only the $< 63\ \mu$ fraction was used. The preparation and methods of analysis are the same as those used for surficial sediments (Appendix A).

5.4.2 Results

Results of the chemical analysis of the core samples, are given in Tables 3, 4 and 5 (Appendix C).

5.4.3 Discussion

By inspection of Table V.2, it is evident that cores BIO 115, BIO 36, S3 and S 17 are very similar in their chemical composition, but are markedly different from core S 21. However, the composition does not vary appreciably along the length of the five cores, suggesting that their respective sources did not change over the greater part of the time involved in their deposition.

Core S 21 comes from the slope of the Laurentian Channel before it branches into the Esquiman Channel. No sediments representing unit 1 occur at the top, which consists mainly of reddish-brown sediment (unit 3). The sediments are very similar in texture and composition to sediments exposed on the Magdalen Shelf, which, according to Loring and Nota (1969), are reworked from pre-Pleistocene material. Discussing the composition of these sediments, they pointed out that they are deficient in Al, Fe, Mn and Na. Table V.2 indicates that material in core S 21 has similar characteristics and contrasts markedly with units 2 and 3 in core BIO 115.

Chemical similarities with sediments of the Magdalen Shelf suggest that sediments in core S 21 are also residual from pre-Pleistocene sediments. In addition, as discussed above, the mineralogy of the sand size fraction, is not the same as in younger deposits. It can then be safely inferred that other sources were available to this region of the Gulf in preglacial times.

TABLE V.2

*Average content and standard deviation of the elements in the core samples.

Element % Core No.	Na	σ	K	σ	Mg	σ	Ca	σ	Fe	σ	Al	σ	Ti	σ	Mn ppm	σ
BIO 115	1.534	0.41	2.66	0.32	1.66	0.188	1.44	1.07	4.65	0.27	6.89	0.42	0.75	0.098	668	73
BIO 36	1.81	0.32	2.62	0.15	2.01	0.11	1.91	0.86	4.64	0.24	5.72	0.63	0.62	0.056	561	47
Sack 3	1.75	0.07	2.35	0.14	1.83	0.03	0.80	0.06	4.57	0.19	6.90	0.44	0.89	0.037	417	39
Sack 17	1.89	0.13	2.54	0.18	2.03	0.24	1.66	0.40	4.50	0.42	7.02	0.54	0.82	0.074	353	49
Sack 21	0.93	0.11	2.08	0.38	1.70	0.21	1.79	0.40	3.33	0.22	5.31	0.75	0.79	0.051	267	10

* wt.%

The variation with depth of some of the major elements in the four short cores (BIO 36, S 3, S 17 and S 21) is shown in Figures V.4 to V.8. No specific trend appears to exist, except possibly for core S 21 where K, Al and Mg tend to increase with depth in the core. This is to be expected since the three other cores sample only the post-glacial sediments (unit 1). The sources of material to the Gulf during post-glacial times presumably remained the same through this period, which explains the more or less constant composition across unit 1.

Figures V.9 to V. 16 illustrate the variation with depth in the core for the 8 elements studied in core BIO 115. There is no evident trend in the vertical distribution of some elements along the core. Na and Mg are exceptions, as they appear to decrease in concentration with depth in the core. A degree of covariance is suggested for Na and Mg and K, as they have maxima and minima at corresponding depths. Variations in Fe and Al could also be related. On the other hand, Ti, Ca and Mn do not show any definite trend, nor can they be correlated with each other, or with any of the other elements.

The three units identified on the basis of both lithology and mineralogy have, however, a distinct, different chemical composition as shown in Table V.3. Unit 2 has a relatively low concentration of Na, K, Ca, Mg and Mn when compared to units 1 and 3, with the highest concentrations of the elements being in unit 1.

TABLE V.3

Average chemical composition* of the three stratigraphic units in Core BIO 115 .

Element Stratigraphic unit	Na	K	Ca	Mg	Al	Fe	Ti	Mn●
1 0-680 cm	1.79	2.62	1.03	1.76	7.47	4.85	0.758	707
2 680-820 cm	1.24	2.20	0.74	1.47	7.00	4.67	0.754	569
3 820-1040 cm	1.37	2.34	2.26	1.63	6.50	4.41	0.649	632

* concentrations are given in wt. %.

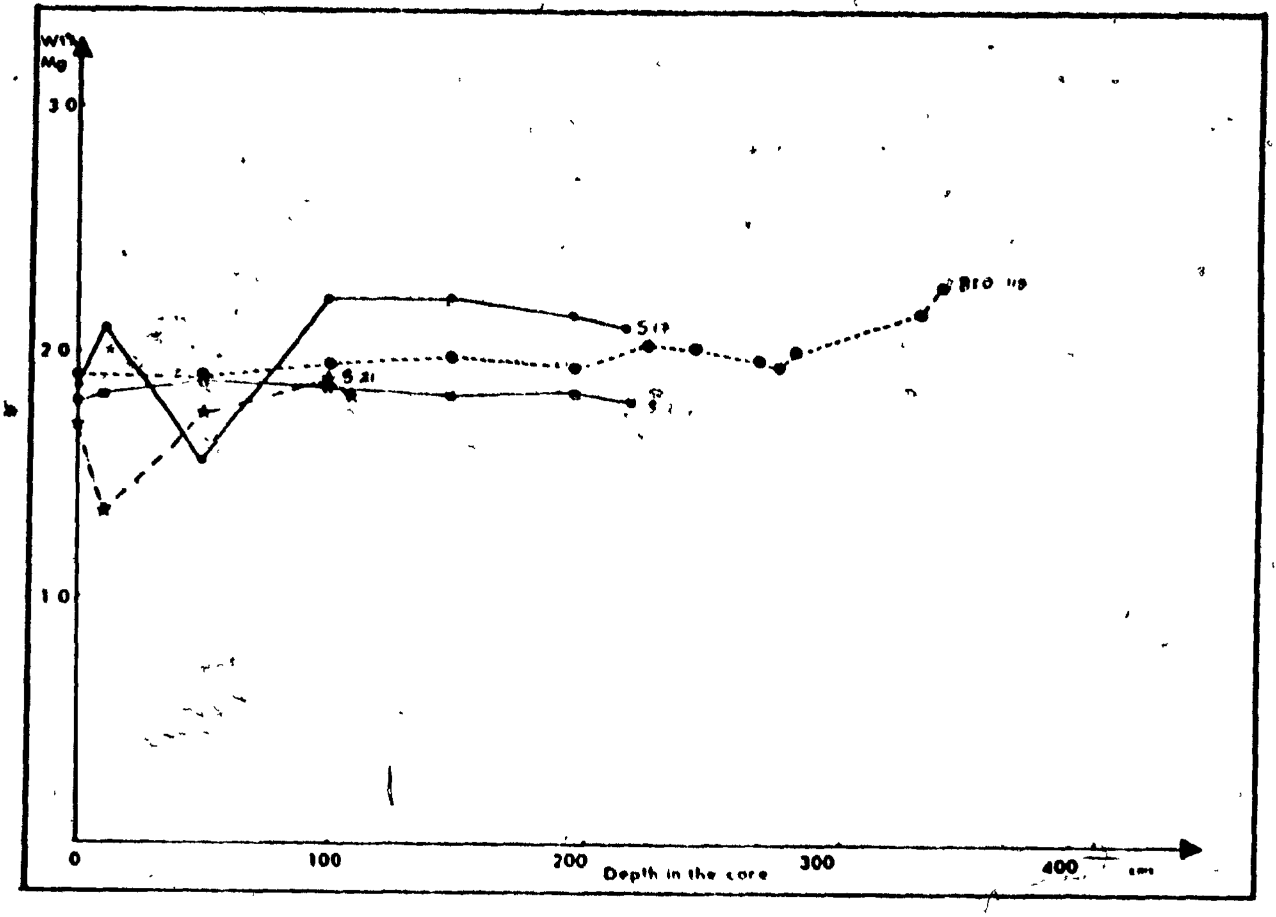
● concentrations are given in ppm.

Figure V.4

Variation of Mg content with depth in the core, for the four short cores analyzed.

Figure V.5

Variation of K content with depth in the core, for the four short cores analyzed.


Wt% Mg
3.0
2.0
1.0
0
100
200
300
400
Depth in the core
cms
S17
S21
S3
B10 119

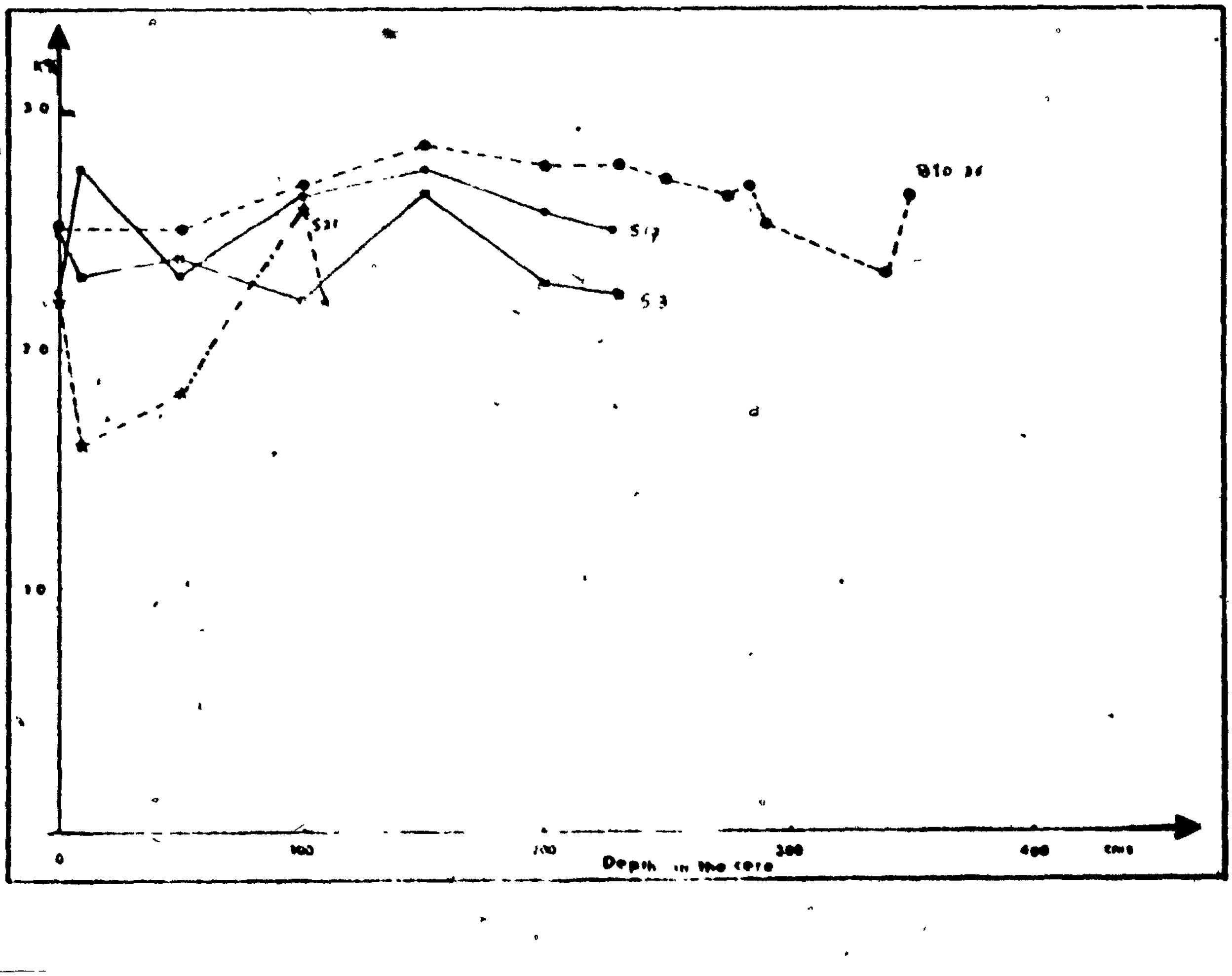
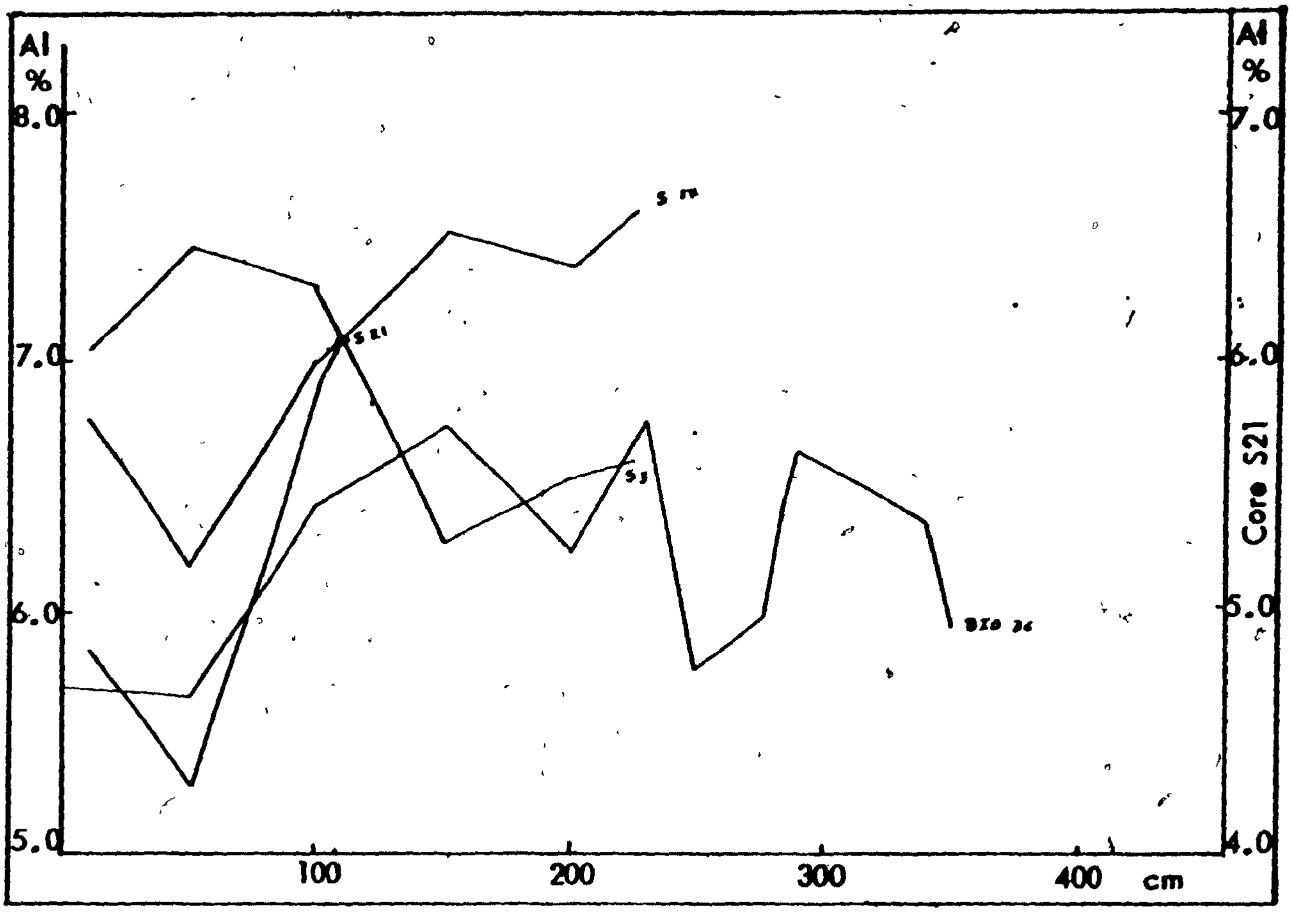

Wt%
3.0
2.0
1.0
0
100
200
300
400
Depth in the core
cms
B10 34
S17
S21
S3

Figure V.6

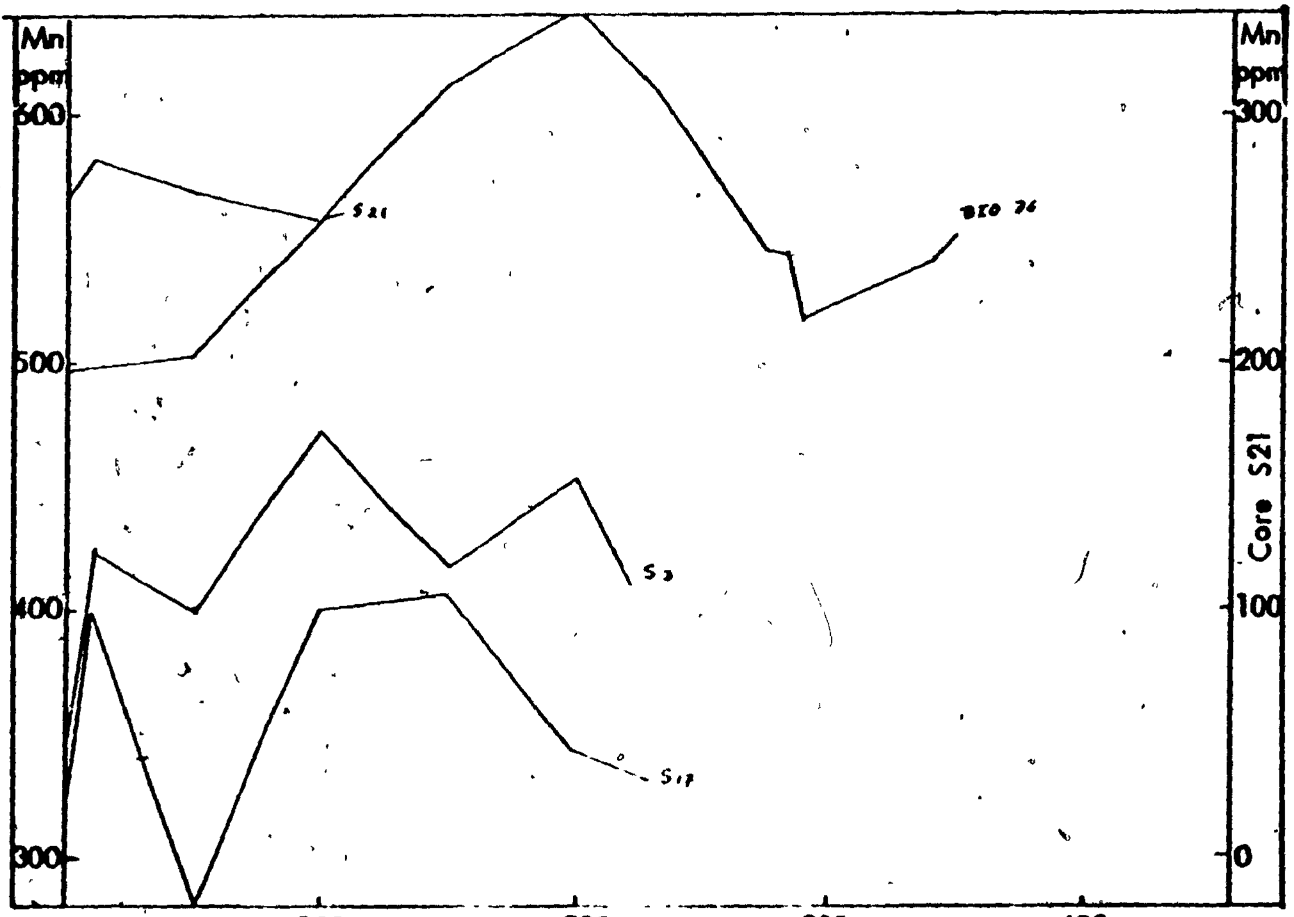
Variation of Al content with depth in the core, for the four short cores analyzed.

Figure V.7

Variation of Mn content with depth in the core, for the four short cores analyzed.



Depth in the core



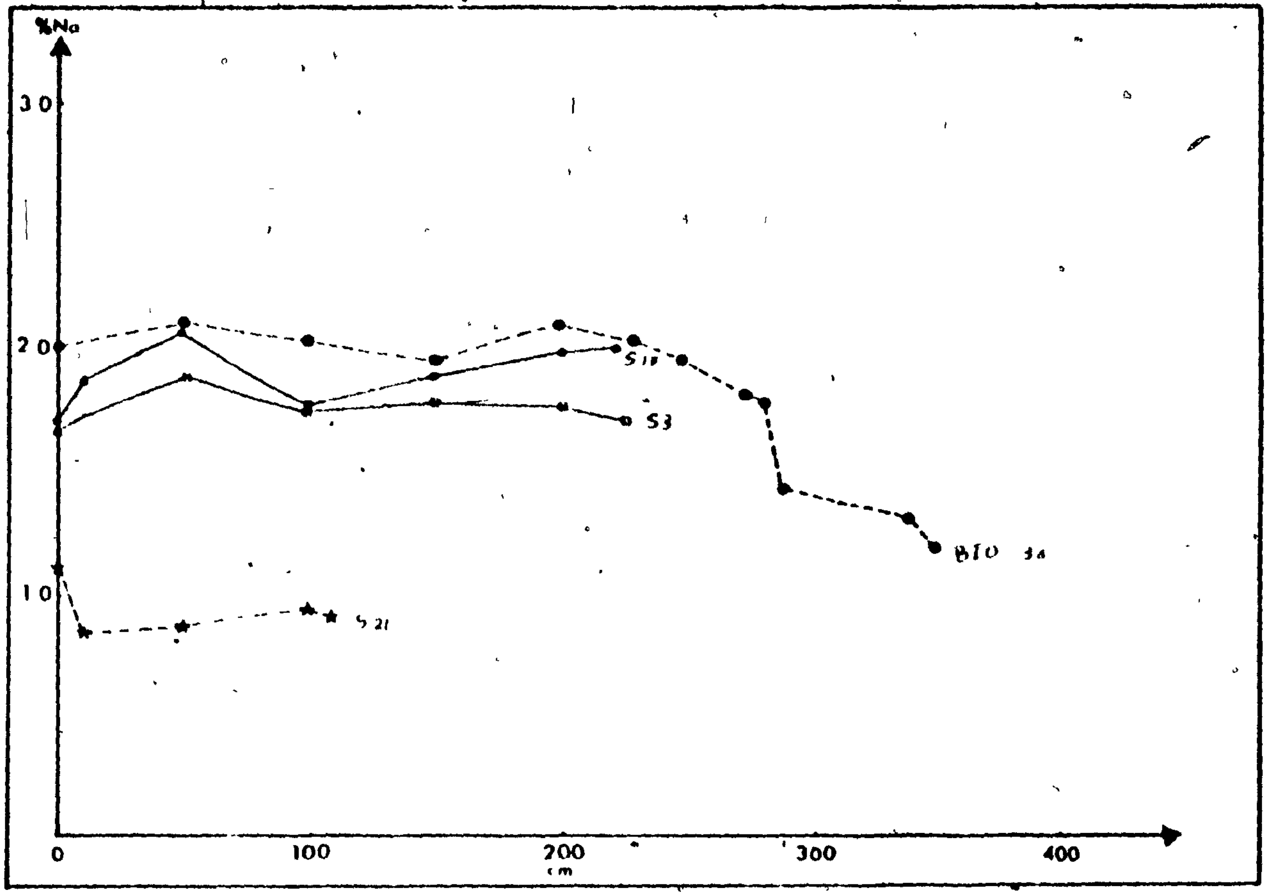
Depth in the core.

Figure V.8

Variation of Na content with depth in the core, for the four short cores analyzed.

Figure V.9

Variation of K content with depth in the core; core BIO 115.


%Na
3 0
2 0
1 0
0
100
200
300
400
cm
S 11
S3
BIO 34
S 21

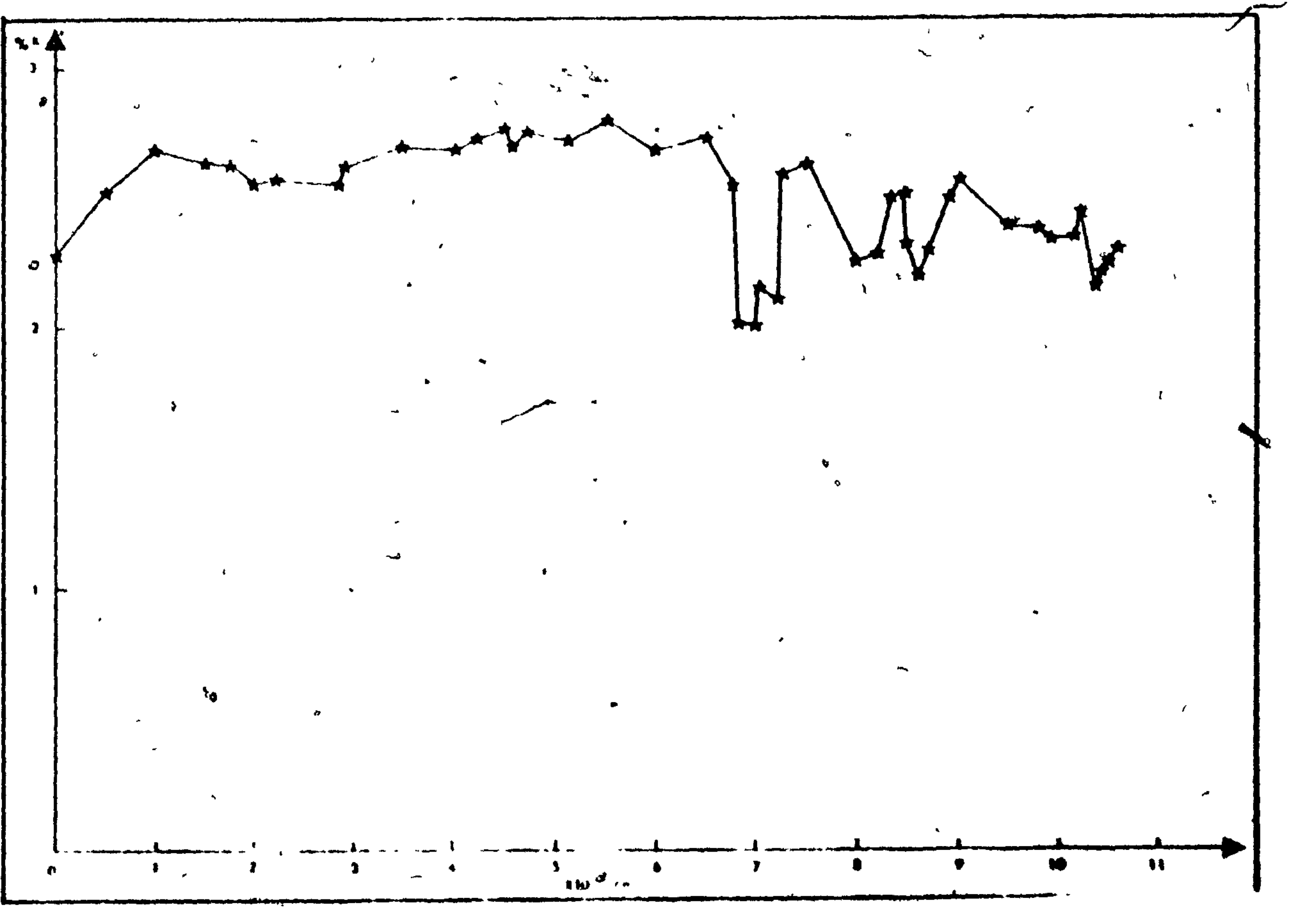
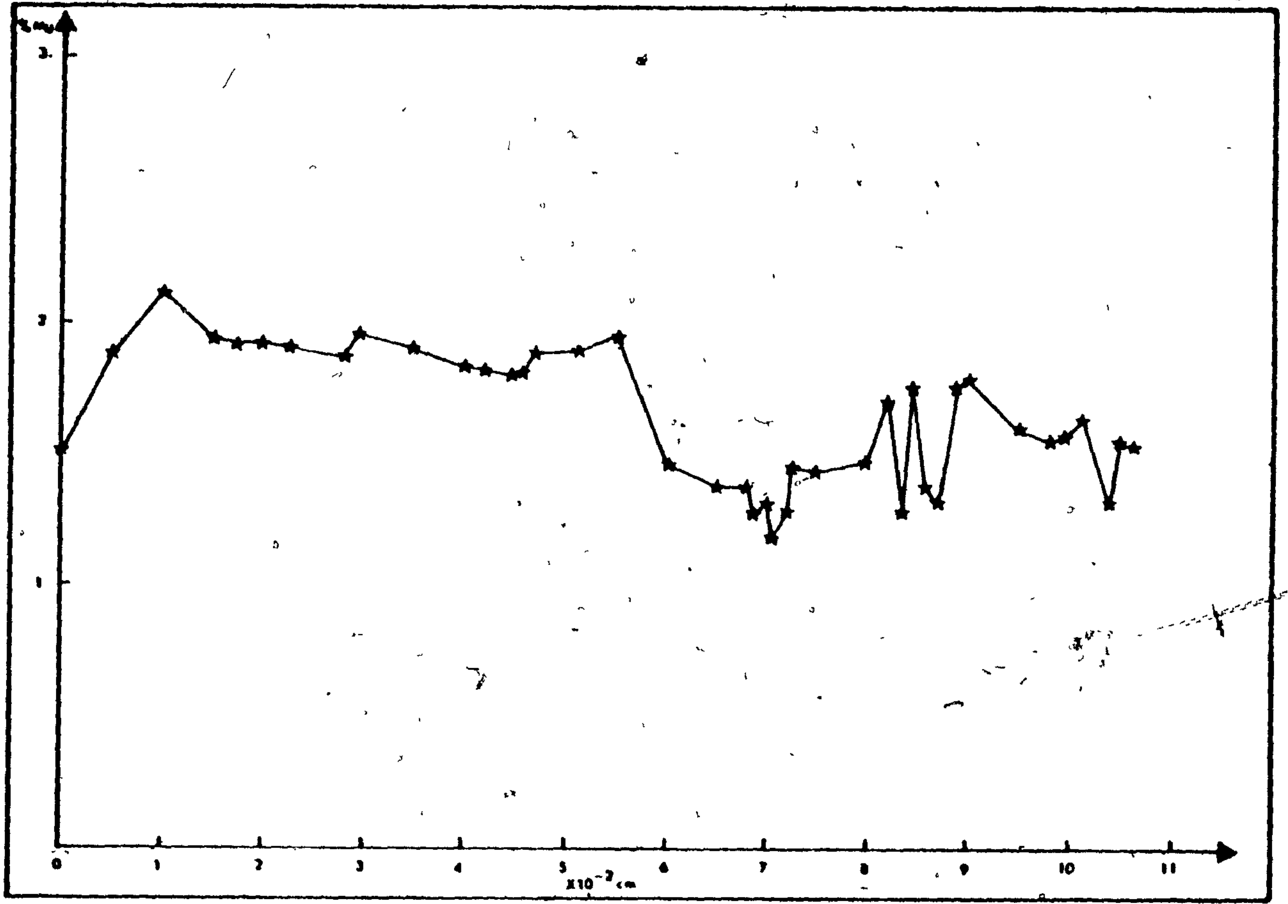

% K
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11

Figure V.10

Variation of Mg content with depth in the core; core BIO 115.

Figure V.11

Variation of Fe content with depth in the core; core BIO 115.


% Mg
3.
2
1
0
1
2
3
4
5
6
7
8
9
10
11
X10⁻² cm

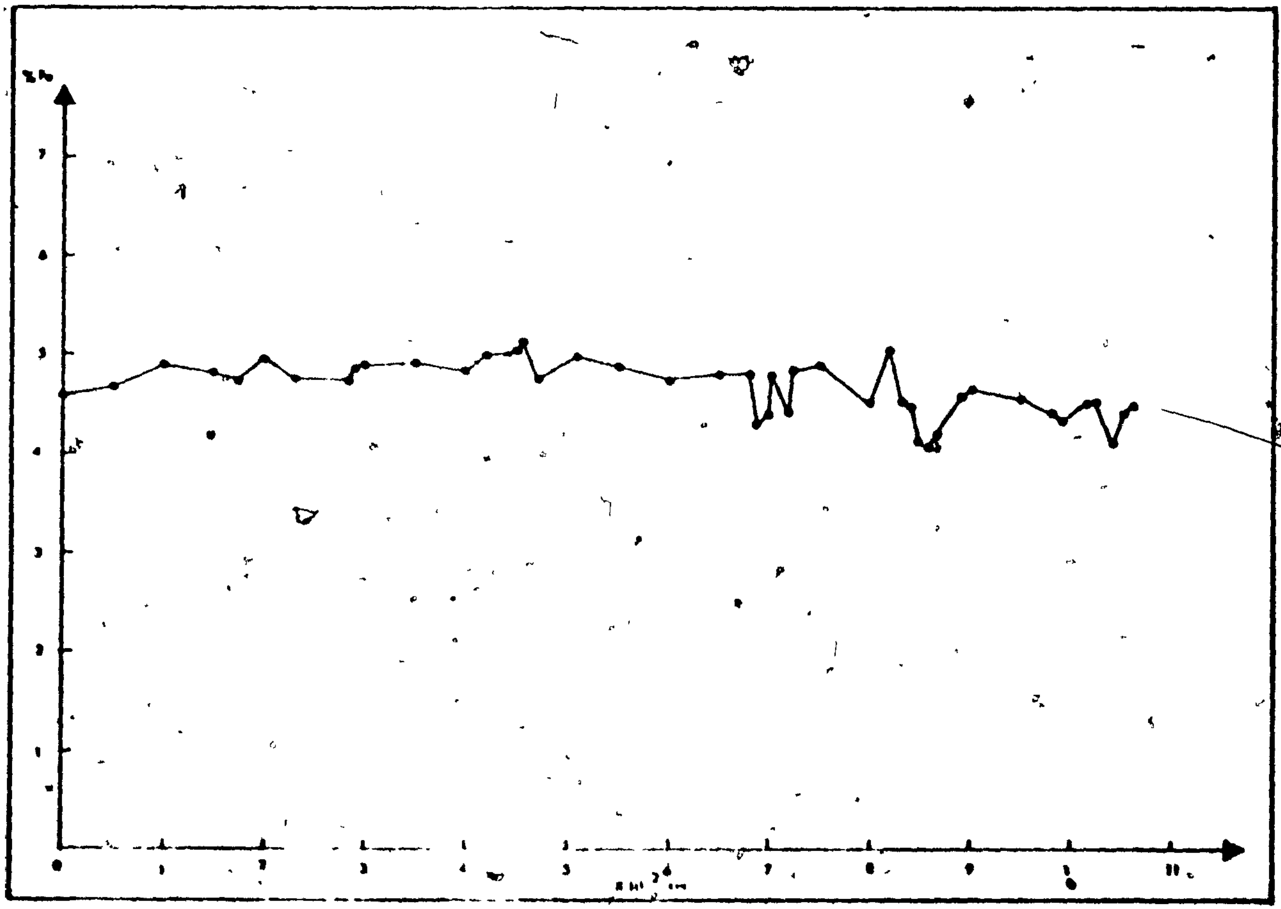
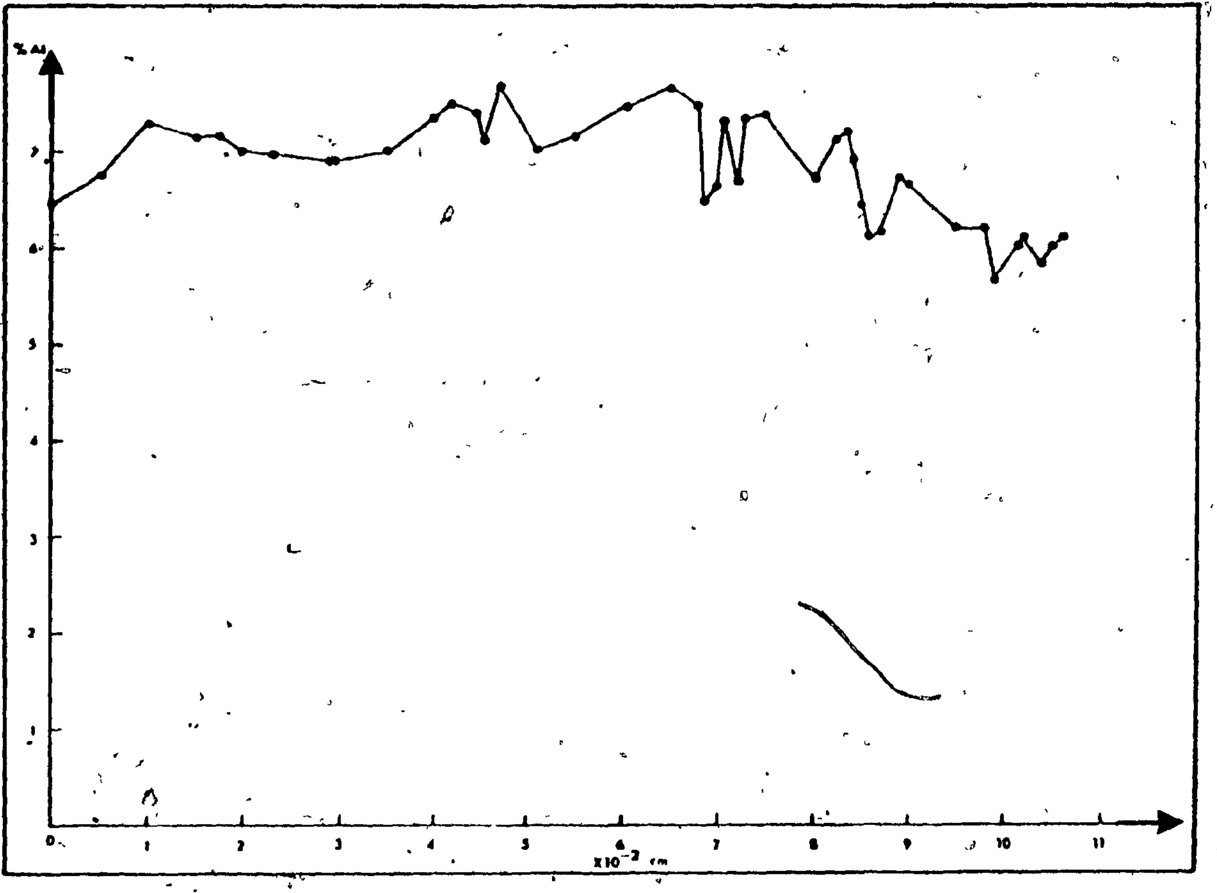

% Fe
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
X 10⁻² cm

Figure V.12

Variation of Al content with depth in the core; core BIO 115

Figure V.13

Variation of Na content with depth in the core; core BIO 115


% Al
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
X10^-2 cm

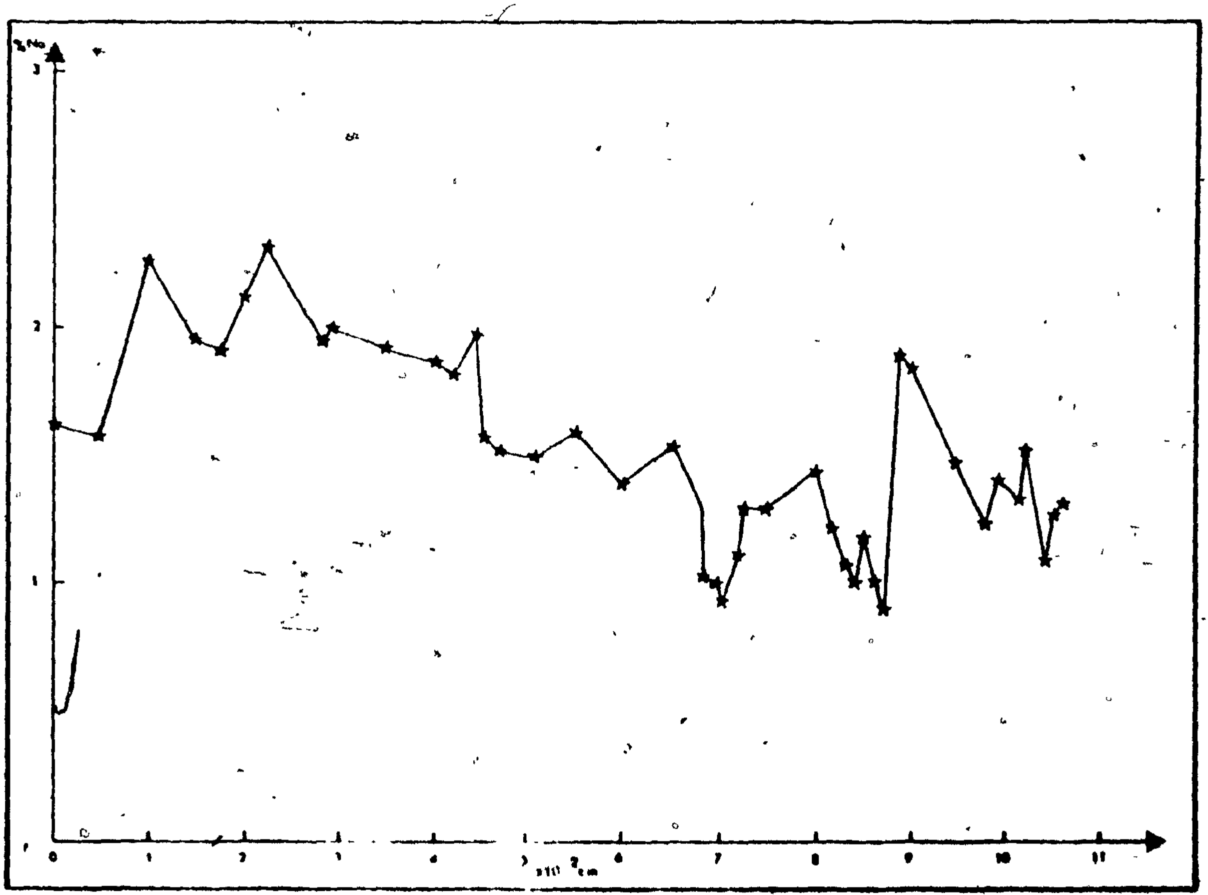
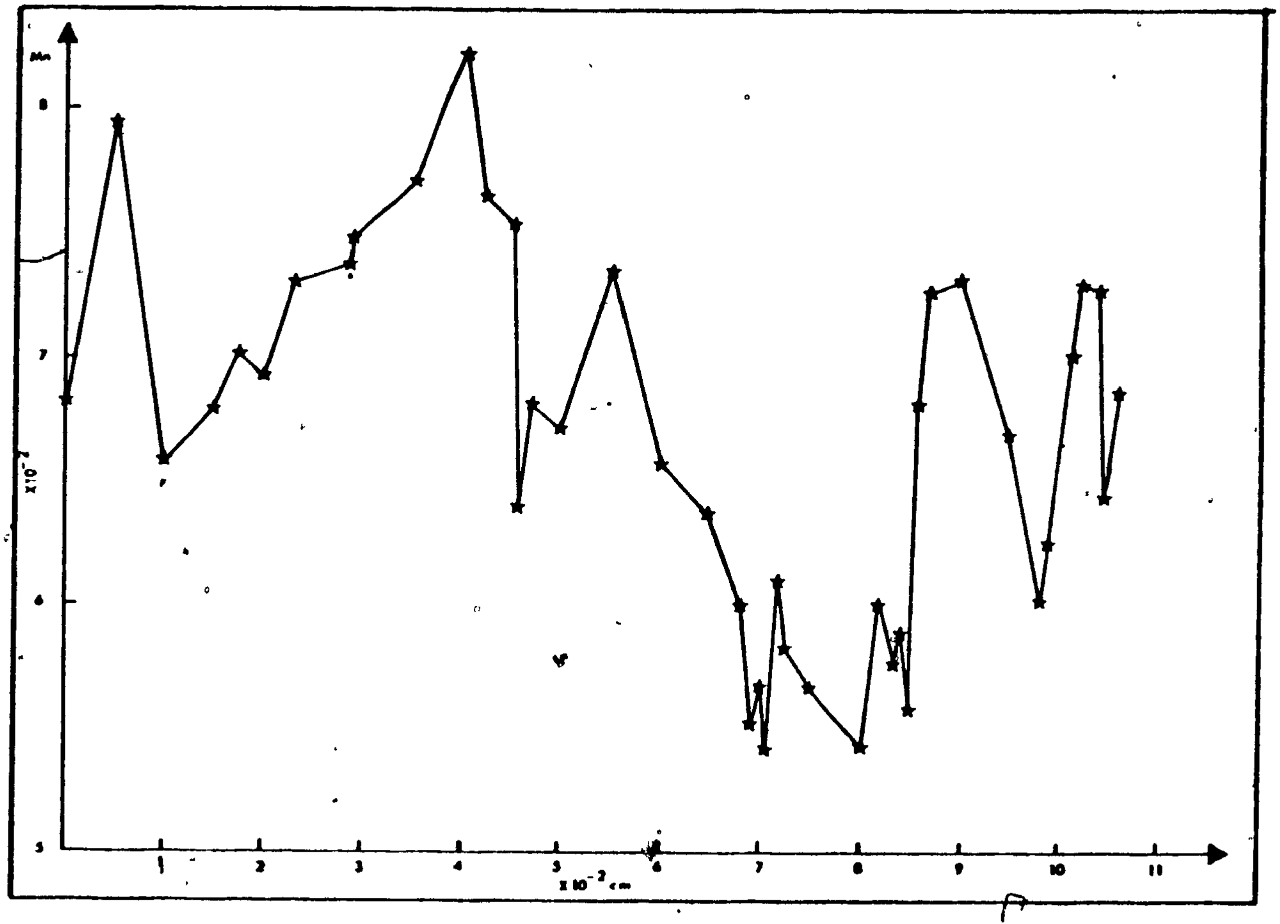

% Na
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
X10^-2 cm

Figure V.14

Variation of Mn content with depth in the core; core BIO 115.

Figure V.15

Variation of Ca content with depth in the core; core BIO 115.


Mn
x10^-2
8
7
6
5
1
2
3
4
5
6
7
8
9
10
11
x 10^-2 cm

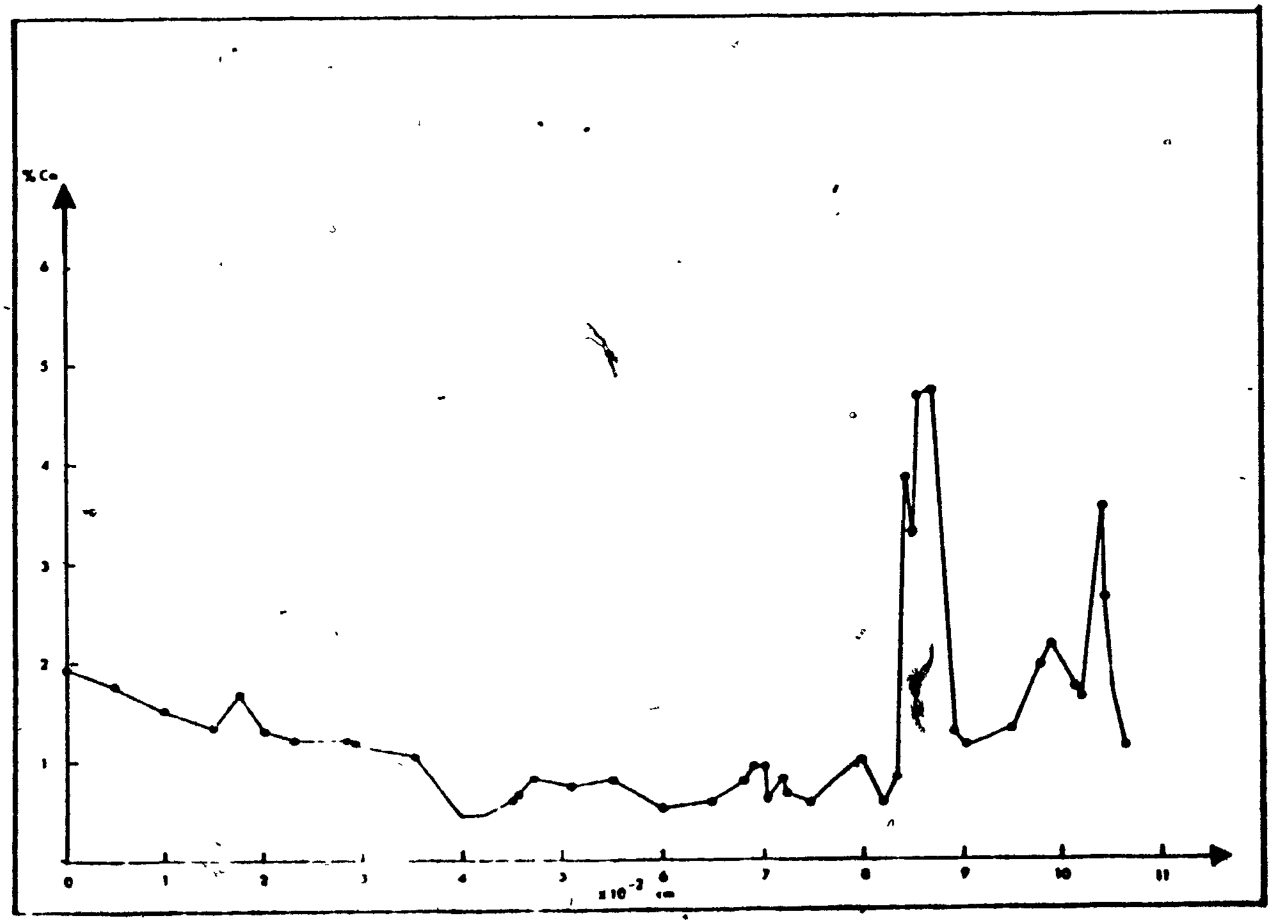
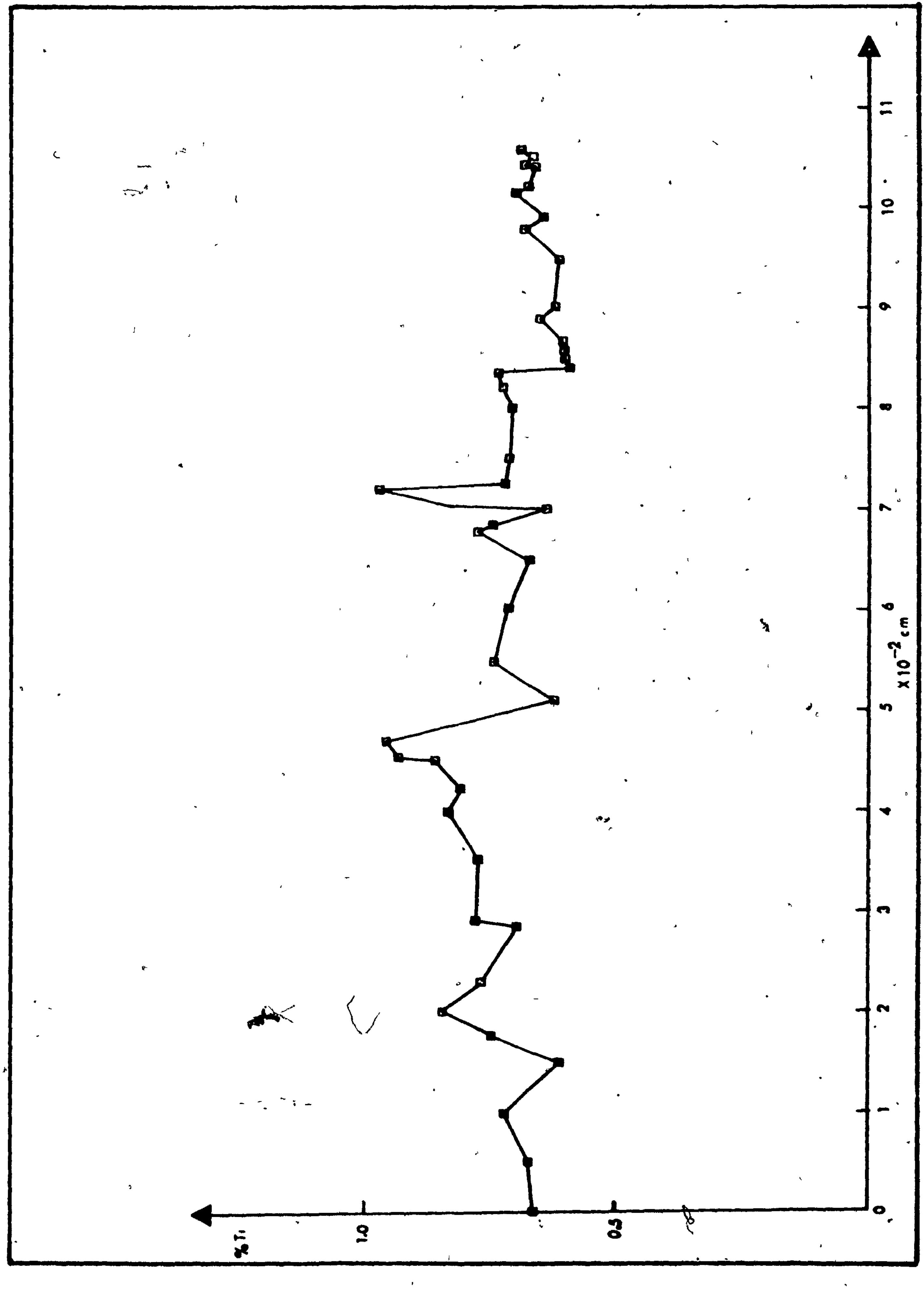

% Ca
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
x 10^-2 cm

Figure V.16

Variation of Ti content with depth in the core; core BIO 115.


% Ti
1.0
0.5
0
1
2
3
4
5
6
7
8
9
10
11
X10^{-2}cm

5.5 Relationships Between the Elements

Sodium and Potassium:

A plot of Na vs. K in the cores is shown in Figure V. 17. The variations of Na/K are similar in the different units of the cores. Both elements tend to decrease in absolute content from the recent sediments (unit 1) to the older ones (units 2 and 3). This may reflect the downward decrease in feldspars abundance which was noted above when dealing with the mineralogy of the coarse fraction.

With the exception of the surface one, all samples from core S 21 are highly deficient in Na, as compared with other cores.

Iron and Magnesium:

Figure V.18 is a scatter diagram of Mg vs. Fe. Samples from core S 21 again lie in a separate region of the graph. A boundary may be drawn arbitrarily between points for the upper unit (unit 1) and the older ones (units 2,3).

It was concluded above, that in the Gulf sediments Mg as well as most of the Fe, occurs mainly in chlorite. The clustering of points in Figure V.18 tend to confirm the fact that they occur in the same mineral.

Although there is some overlapping, sediments of unit 1 have generally higher Mg/Fe than those of units 2 and 3, possibly because of higher content of pyrite, hornblende and garnet in the older units. The presence of these

Figure V. 17

Relationship between Na and K contents in the core samples

☆ Gray olive-green sediments

◻ Reddish brown sediments

● Core S 21

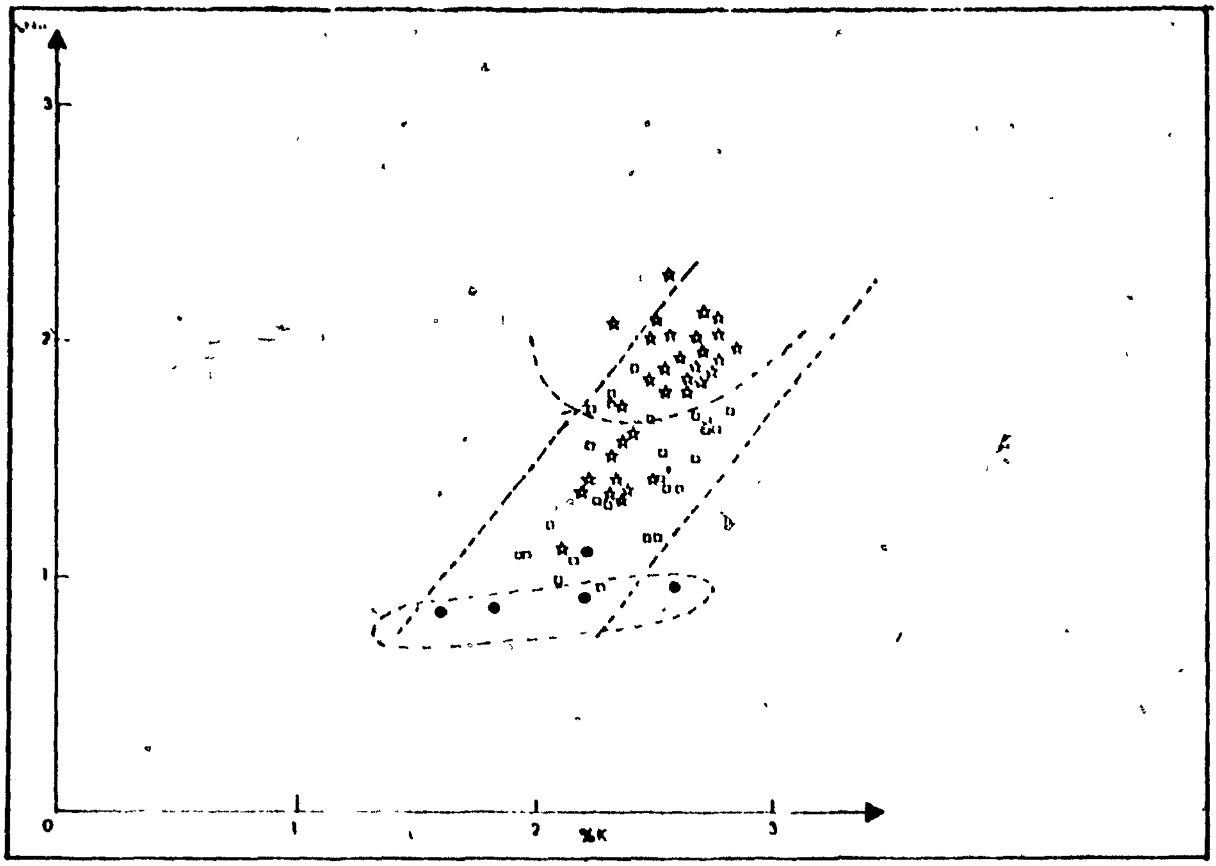
Figure V. 18

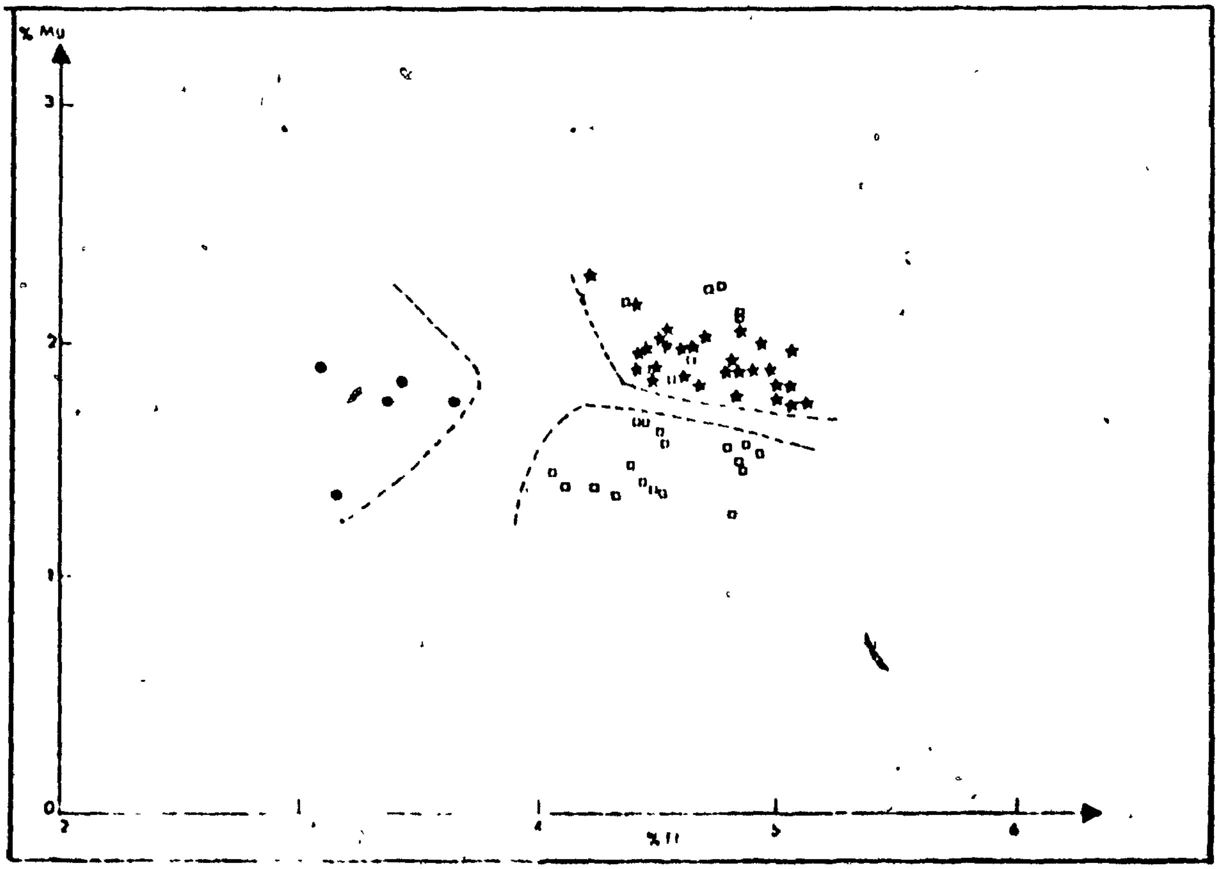
Scatter diagram for the Fe and Mg contents in the core samples

★ Gray olive-green sediments

◻ Reddish brown sediments

● Core S 21


3
2
1
0
1
2
3
%K


% Mu
3
2
1
0
2
4
5
6

minerals results in an increase of the Fe content, thus in a relative decrease of the Mg/Fe ratio.

Titanium:

In surficial sediments, Ti does not show any correlation with either Fe or Al. It does not show either any relative increase or decrease with regard to these two elements in any one of the three units.

As shown above (Chapter III), Ti is mainly incorporated into the Gulf sediments as Ti minerals (chiefly, ilmenite). The lack of any significant trend with depth in the core or colour of the sediments may indicate that Ti minerals were supplied at a constant rate to the fine fraction of the sediments during the deposition of the three units. If Ti minerals are mainly supplied in suspension from the St. Lawrence River (Chapter III); it could mean that this source maintained the same intensity during the complete period of deposition of the cores.

Manganese:

Because of the relatively high proportion of the non-detrital Mn in the sediments of the Gulf, the correlation of total Mn with any other element is expected to be poor. It may then be worthwhile to consider the non-detrital fraction of Mn separately. The results are given in Table 5, Appendix C, and recapitulated in Figure V.19.

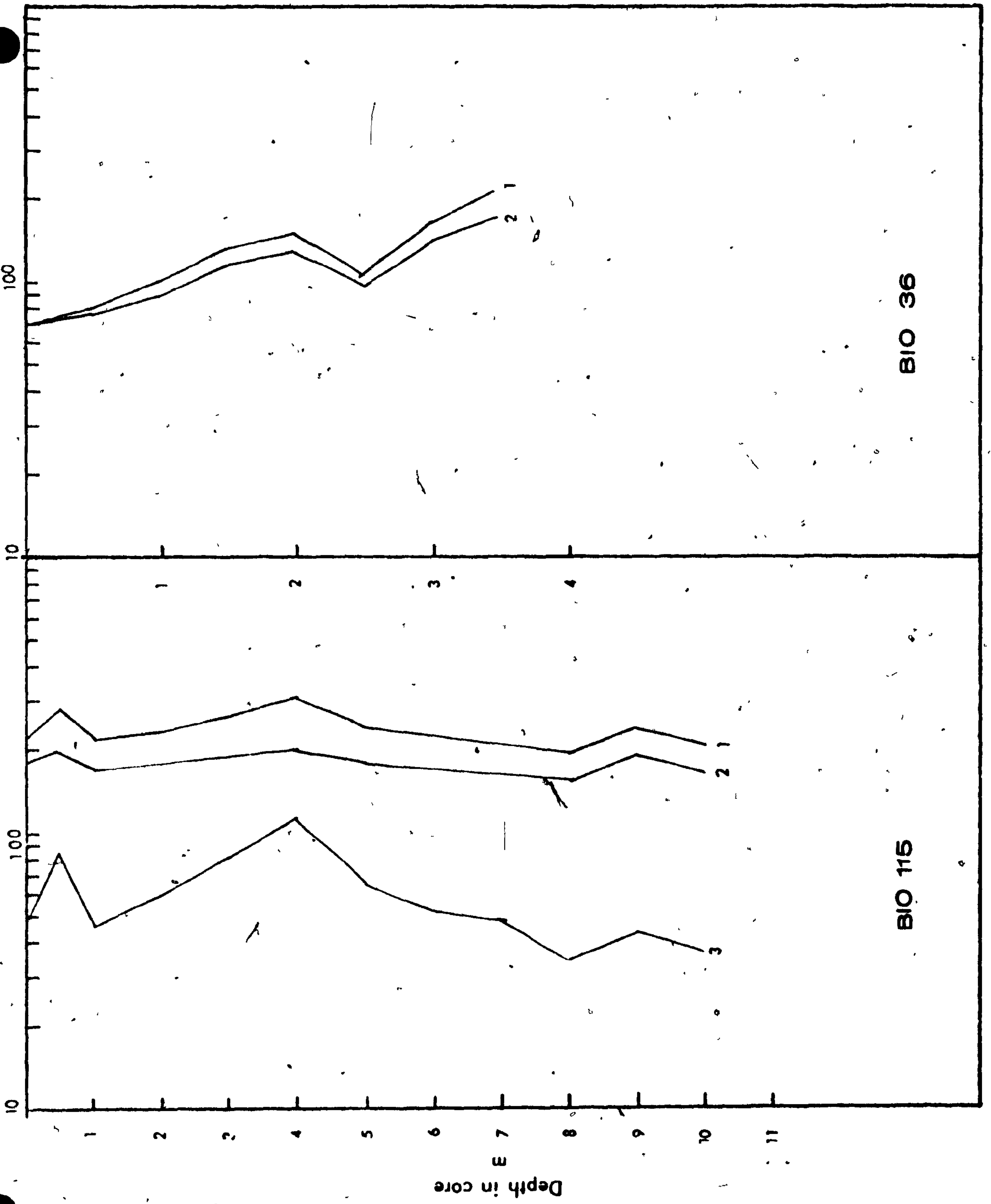
Figure V.19

Variation of non-detrital Mn content with depth in the core; cores BIO 36 and BIO 115.

1 - Acetic acid hydroxylamine mixture extract.

2 - Acetic acid extract.

3 - (1 - 2).


Mn in ppm
10
100
10
100
BIO 36
BIO 115
1
2
3
1
2
3
4
5
6
7
8
9
10
11
Depth in core
m

In core BIO 115, relative maxima in the non-detrital fraction of Mn which is associated with Fe-Mn oxides occur at depths in the core of 50 cm, 400 cm, and 900 cm; and at a depth of 200 cm in core BIO 36.

The presence of authigenic pyrite indicates that reducing conditions may have prevailed in the sediments for some time after their deposition. In these conditions, Mn will be reduced from Mn^{+4} to the soluble Mn^{+2}. The migration of Mn^{+2} in sediments is well documented (Manheim, 1965; Price, 1967). Price (1967) has shown that during burial, the oxidate fraction become reduced, producing metal ions which are either preferentially absorbed by humic acid, or which may form metal amino-acid complexes in true solution. Upward migration of such complexes into more alkaline and oxidizing environments would tend to precipitate Fe-Mn oxides. High pH and Eh values can occur at the sediment-water interface layer as a result of intensive water circulation.

In the present cores, foraminifera is always abundant at the core levels mentioned above; these intervals mark the appearance of the species characteristic of the North Atlantic Slope Waters (Loring, 1972, p.c.). From this we might infer that periods of high Fe-Mn oxides deposition correspond to times of active oceanic circulation, possibly occurring in response to global climatic changes.

The following factors may also lead to increases in the deposition of Fe-Mn oxides: (i) lower rates of sedimentation; (ii) larger inputs of both Fe and Mn from rivers; (iii) higher biological production in the water column.

However, there is no indication that a change in the rates of sedimentation occurred during deposition of the cores. If such changes had taken place, variations in the non-detrital contribution of trace elements other than Mn would be noticeable (Riley and Chester, 1971), which is not the case (Table 5, Appendix C). The last two factors listed may result from climatic modifications, which may affect the weathering processes on land, or may lead to increase in biological production.

5.6 Application of Factor Analysis for the Interpretation of the Geochemical Data from the Gulf of St. Lawrence

To interpret the meaning of the vertical variations in elements content along the cores, the analytical results were subjected to Q-mode factor analysis, as described by Imbrie (1963) with respect to geological studies. This method allows to identify the main factors responsible for the compositional variance of the samples. It is then possible to extract reference vectors which are used to compute the oblique vector projections (Imbrie, 1963). In geochemical surveys, the composition of each vector corresponds to that of a possible single source contributing to regional sediments. By identifying among all the possible sources of sediments to the Gulf, those which fit best the main vectors composition; it is possible to make reasonable interpretation as to the nature of the major sources which have contributed to the sediments and thus establish quantitatively their relative contribution to each sample analyzed. This allows: (i) in dealing with surficial sediments, to define areas of influence for each major source; (ii) in analyzing core samples, to establish time fluctuations in supply from these sources.

The factor analysis indicates that six factors account for the variations in chemical composition of the 55 surficial samples analyzed in the Gulf. 94% of the observed composition can be described in terms of only three factors (Table V.4). The same three factors account again for most of the samples composition when the core data is included. They were extracted and rotated and the oblique vector projections computed. The three vectors extracted were used as reference vectors in interpreting the core data.

The three vectors extracted correspond to samples S-3, A-18 and A-72a. Thus these three samples may be taken as adequately representing three major discrete sources to the sediments.

Sample S-3 comes from a depth of 372 m in the Laurentian Channel. It consists of a very fine-grain sediment with low Al and high Fe contents. Its composition is close to that of the suspended matter in the St. Lawrence estuary. The corresponding vector (vector No. 1) thus may be considered to represent contributions from the suspended load of the St. Lawrence River.

The sample corresponding to vector No. 2 contains the highest calcium carbonate content of all the samples (31% by wt.). It was collected at a depth of 309 m, close to the limestone formations exposed on Anticosti Island. It is assumed then that vector No. 2 represents best the contributions made by calcareous sources to the sediments.

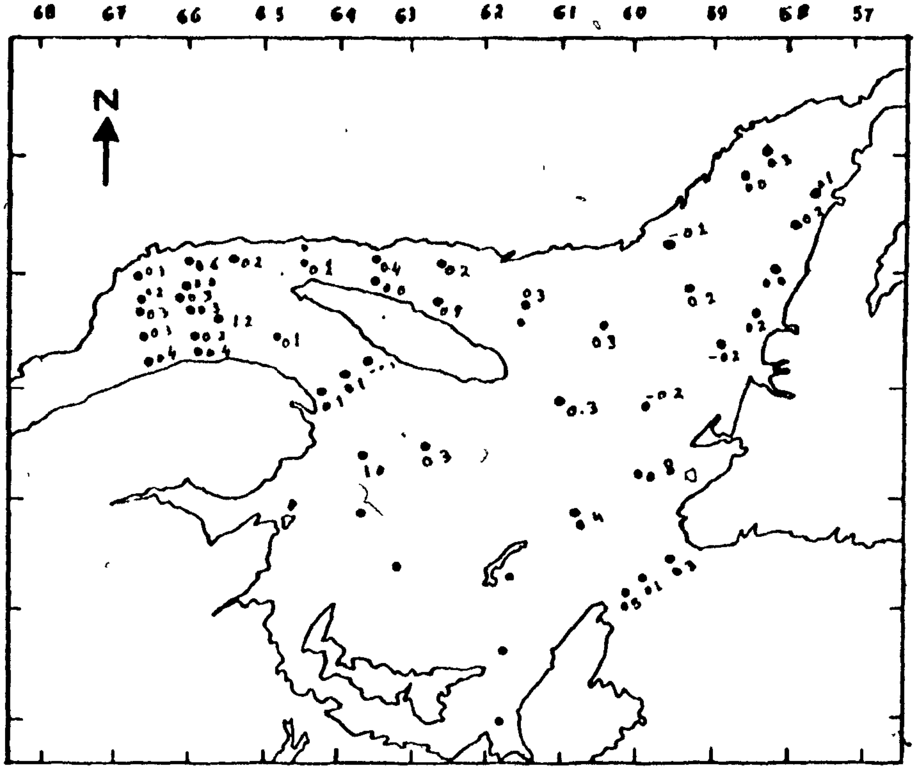
Sample A-72a is a shallow-water sample from the north shore, having a chemical composition similar to the average granodiorite of the Canadian

Figure V. 20

Areal distribtion of vector No. 1 (suspended matter vector)

Figure V-21

Areal distribution of vector No 2 (calcium carbonate vector)


68
67
66
65
64
63
62
61
60
59
58
57
N
51
50
49
48
47
46

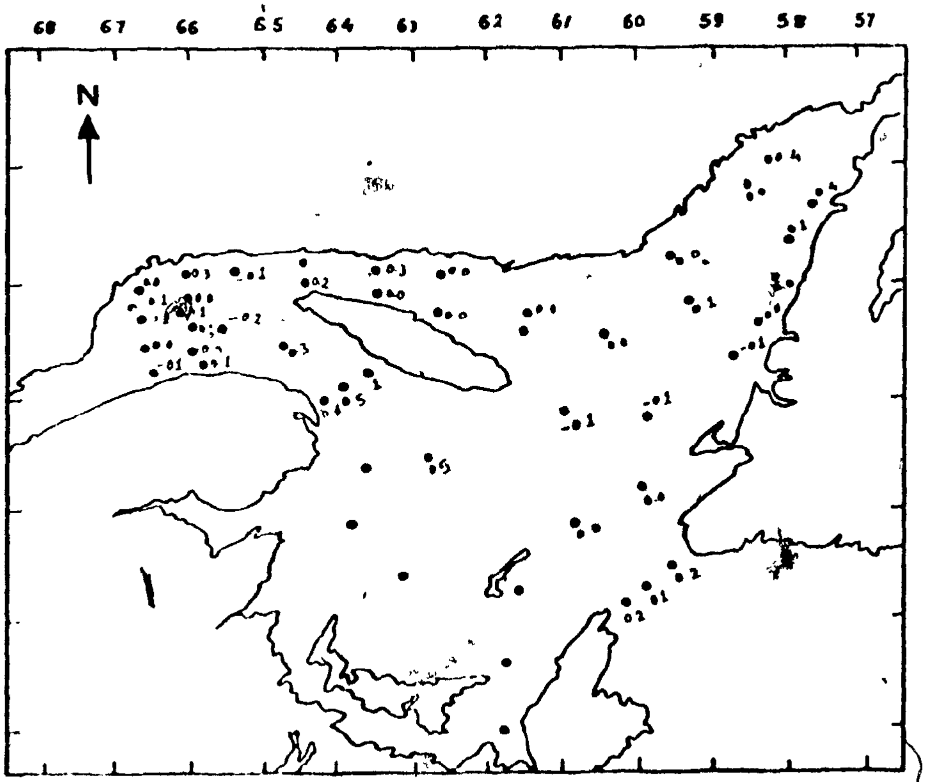
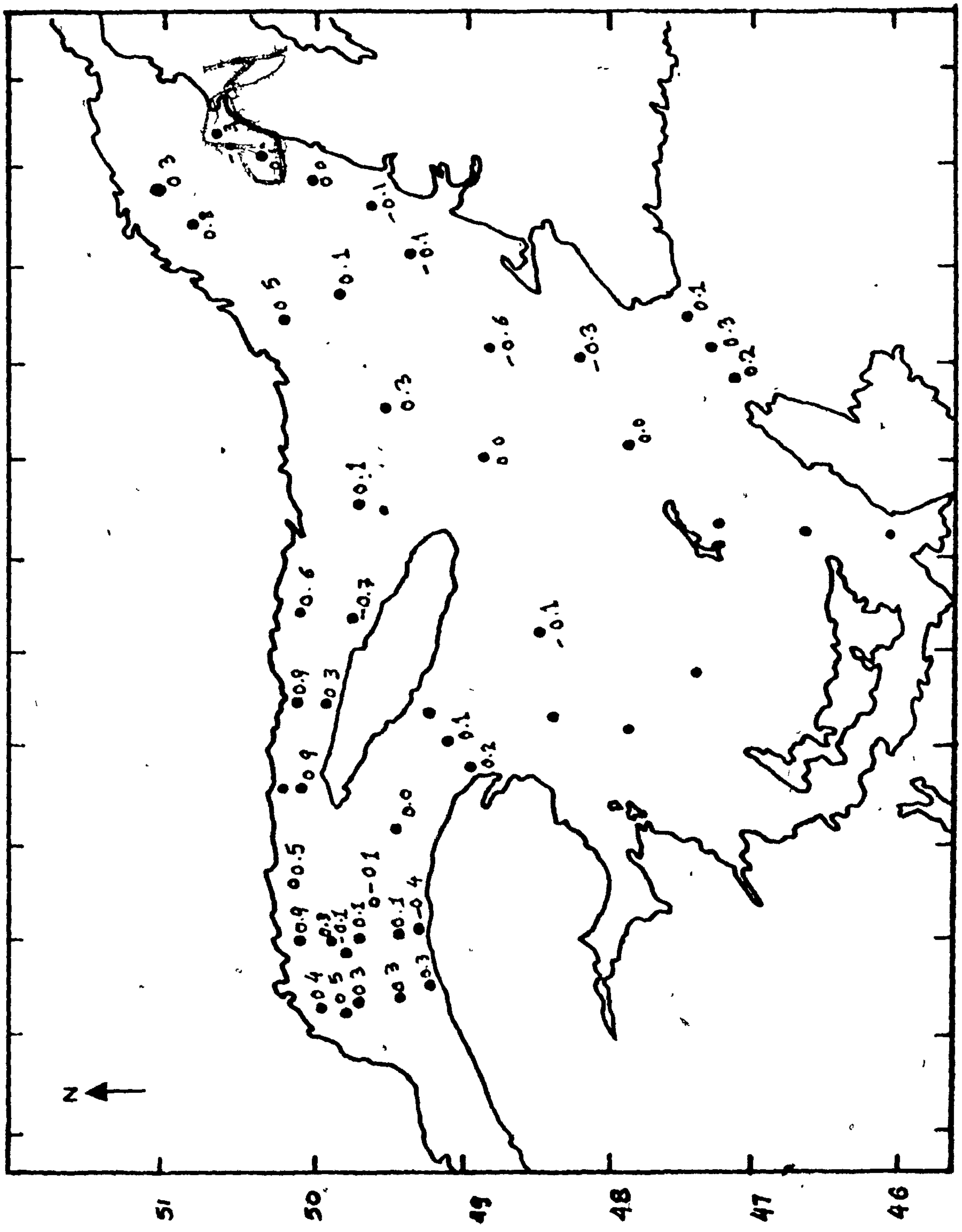

68
67
66
65
64
63
62
61
60
59
58
57
N
51
50
49
48
47
46

Figure V. 22

Areal distribution of vector No. 3 (north shore vector).


57
58
59
60
61
62
63
64
65
66
67
68
51
50
49
48
47
46
N
0.3
0.8
0.0
-0.1
-0.1
0.1
0.5
-0.6
-0.3
0.1
0.3
0.2
0.3
0.0
0.0
0.1
0.6
-0.7
-0.1
0.9
0.3
0.9
0.1
0.2
0.0
0.5
0.9
-0.1
0.1
-0.1
0.1
-0.4
0.4
0.5
0.3
0.3
0.3

Shield as calculated from Maxwell et al. (1965). Vector No. 3 will represent this source.

The correlations between vector No. 1 and the suspended matter in the estuary, and vector No. 3 and the north shore granodiorites are shown in Table V.5 .

Based on the study of surficial samples, it is possible to outline areas of the Gulf where the composition of the sediments is influenced respectively by each one of the three dominant vectors (Figures V.20, 21 and V.22). Vector No. 1 occurs as a major constituent in all samples, particulary in samples from deep-water stations, and in the north western part of the Gulf. This agrees with previous conclusions based on results of the major element analysis, as well as with those of Nota and Loring (1964), that the suspended matter contribution to the sediments in the Gulf increases with the depth of water.

Vector No. 2, the calcium carbonate vector, is more restricted and confined to sediments occurring near carbonate outcrops around or in the Gulf.

Vector No. 3, the north shore vector, controls broad regions of the Gulf. Its influence, however, is more pronounced in the north eastern parts of the Gulf, where there is a corresponding decrease in the contribution made by vector No. 1.

Due to the limited number of samples collected from the Magdalen Shelf, this region was not considered with the rest of the Gulf. It was found,

TABLE V.4

Extract from eigenvalues table

Eigenvalue	Cumulative %
39.12413	71.13
9.14415	87.76
3.14928	93.50

TABLE V.5

*Correlation between extracted vectors and matter from the estuary, and granodiorite

Sample (vector extracted)	S-3	A-72a
Suspended matter	0.95	0.87
Granodiorite	0.84	0.97

* Correlation is based on the cos θ criterion (Imbrie, 1963).

however, that the five samples obtained there are dominated by a particular vector (sample R-4) which accounts for more than 90% of their composition.

Interpretation of the Core Analyses

An examination of the contributions made by the three reference vectors to the sediments during the deposition of the five cores analyzed, indicates that compared to vectors No. 1 and 2, vector No. 3 shows significantly greater variations (Fig. V.23). This may happen for either one of the two following reasons: (i) the contribution made by vector No. 3 is small; hence, even minor fluctuations will become noticeable; (ii) vertical variations in vector No. 3 may occur in response to environmental factors, for instance changes in climatic conditions which may affect the extent of ice cover on the surface of the Canadian Shield and the amount of rock detritus removed.

A definite increase in the relative contribution made by vector No. 3 is observed at a depth of 50 cm in cores S 3, S 17 and to a lesser extent in core BIO 36 (Fig. V.23). As should be expected core S 21, which consists entirely of pre-glacial sediments, does not show the same variations: Vector No. 3 shifts from positive to negative values below about 8 cm. Core BIO 115 shows only a slight inflection in vector No. 3 at the 50 cm. level, but measurable increases appear further down the core at depths of 100 cm, 230 cm, 450 cm and 680 cm.

Again we may speculate that increases in vector No. 3 contributions may be brought about by short periods of warmer temperature with consequent reduction

Figure V.23

Variation in the contribution made by vector No.3 with depth in the core, for the five cores studied.

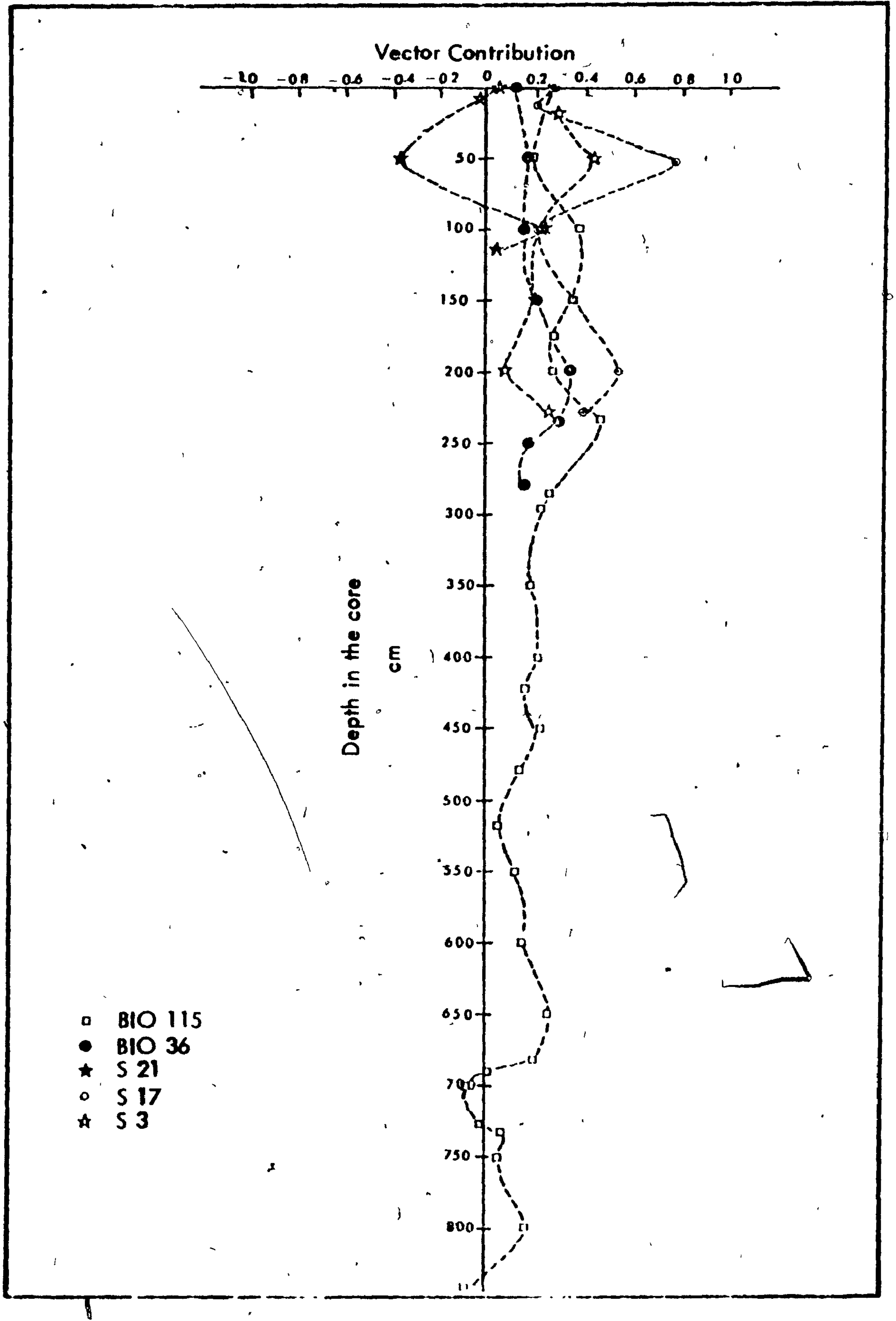
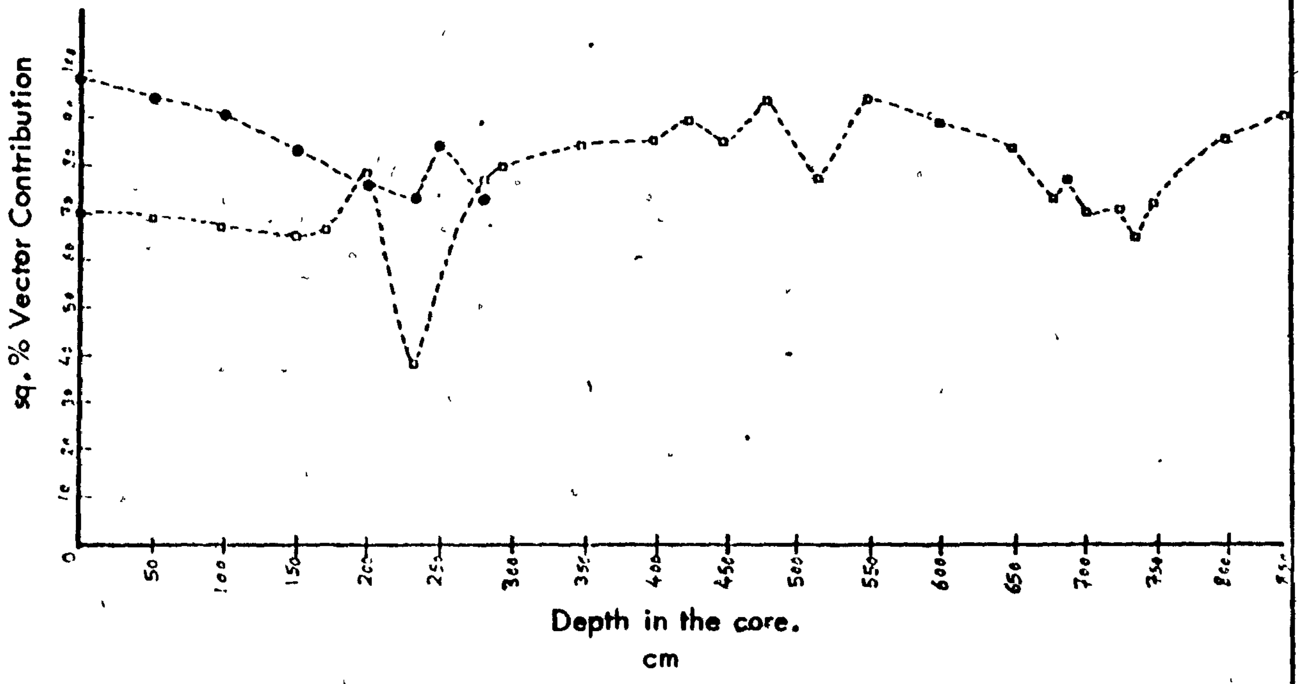

Vector Contribution
-1.0
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1.0
Depth in the core
cm
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
□ BIO 115
● BIO 36
★ S 21
○ S 17
☆ S 3

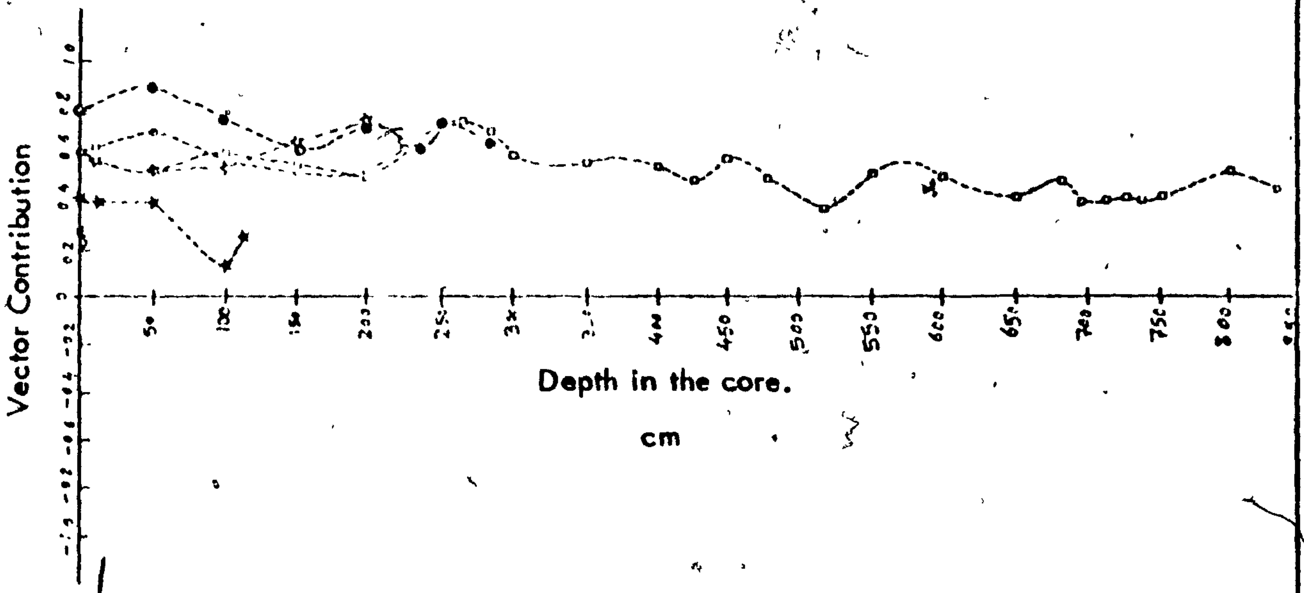
Figure V.24

Variation in the contribution made by vector No. 1 with depth in the core, for the five cores studied.

Figure V.25

Variation of the sq.% vector contribution of vector No. 1 with depth in the core, cores BIO 36 and BIO 115.


sq. % Vector Contribution
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
Depth in the core.
cm


Vector Contribution
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
Depth in the core.
cm

of the ice cover in the source areas to the north of the Gulf. Core BIO 115, which is south and far removed from the north shore than others does not have a pronounced vector No. 3 maximum at 50 cm level, presumably because transport by ice-rafting operates over smaller distances in warmer periods.

This interpretation is supported by the following arguments: (i) levels in core BIO 115 marked by maxima in vector No. 3 coincide with the appearance in the sediments of foraminiferal assemblages characteristic of the North Atlantic Slope Waters (Loring, 1972, p.c.; Fig. V.3). These faunal changes suggest that the major circulation patterns in the Gulf were modified in response to climatic alterations; (ii) if the rate of deposition of 22 cm/1000 year (Nota and Loring, 1964) is taken as an acceptable approximation of the sedimentation rates in the regions where the cores were deposited, the 50 cm level in cores, S 3, S 17 and BIO 36 would be approximately 2400 years old. According to Potzger and Courtemanche (1954), a warm interval occurred during this time. It allowed the terrestrial flora to advance 400 miles north of its present limits in Quebec; (iii) the four vector No. 3 maxima in core BIO 115 and BIO 36 coincide with higher contents of oxides of Fe and Mn (Fig. V.19). The deposition of these oxides may be related to changes in pH and Eh which are both temperature dependent.

Based on a sedimentation rate of 22 cm/1000 year, the lowest three vector No. 3 maxima in BIO 115 would correspond roughly to warm intervals at 10,500 years BP, 20,500 years BP and 31,000 years BP respectively if the above interpretation is correct.

On the other hand, variations along the cores in contributions made by vector No. 1, the suspended matter vector, may indicate fluctuations in water depths, since it has been established above that in present conditions a larger proportion of the sediments comes from suspension as the water depth increases. Variations in the contributions made by vector No. 1 along the cores are shown in Fig. V. 24 and 25. In core BIO 115, relative minima appear at depths of 230 cm, 520 cm and 730 cm; while in core BIO 36 only one minimum occurs at the 230 cm level. According to our previous findings, these would correspond to relatively lower stands in sea level at about 10,500 years BP, 23,500 years BP and 33,000 years BP, and 10,500 years BP respectively.

This application of factor analysis to a small number of cores in a region as broad as the Gulf of St. Lawrence serves only to illustrate the possibilities of this technique in stratigraphic interpretations. The larger the number of cores, the more valid would become the conclusions obtained. The method is useful as it reveals potentially meaningful fluctuations of geochemical properties in core samples which under visual examination appear homogenous. To be entirely meaningful, it would need as supporting evidence, faunal or geochronological studies. In areas like the Gulf where these are difficult to obtain, it may at least allow to raise some questions about recent climatic boundaries, which hopefully could be answered at some later time.

CHAPTER VI

SUMMARY AND CONCLUSIONS

This study has determined and discussed some geochemical characteristics of the Gulf of St. Lawrence Recent sediments based on the composition of a suite of 55 samples. It has attempted to analyse the factors which control the distribution of selected major, minor and trace elements in the fine fraction (63 µ) of these sediments. The major findings and some of their geological implications are now briefly summarized.

The material smaller than 63 microns makes up on the average 79% of the studied sediments. The percentage of clay-size components (< 4 µ) shows an approximately linear increase with water depth, which suggests that settling through the water column of particles delivered to the Gulf in suspension is an important mechanism of sediment accumulation. However, the importance of ice-rafting as a major transport process is evidenced by a complete lack of correlation between the percent coarse fraction in the samples and the depth of water.

The mineral composition of sediments usually provides the best indication as to the nature and relative importance of the various contributing sources. In the Gulf, the dominant fine fraction, which was here analyzed, is a complex mineralogical mixture in which it is difficult to identify all the component minerals. On the other hand, an analysis of the coarse fraction mineralogy provides a convenient simple technique to determine the source areas (Loring and Nota, 1969). It clearly distinguishes between a northern Gulf province, in which sediments originate mainly from the crystalline complexes of the Canadian Shield, and a southern Gulf province, where sediments have their principal sources in the Appalachian regions. This distinction is based on the shape and appearance of the quartz minerals: amphiboles and pyroxenes are particularly abundant in the northern part of the Gulf.

Among the clay minerals in the 2 micron fraction, the order of abundance was found to be illite, chlorite and kaolinite. No montmorillonite was detected. In this very fine fraction, which corresponds to the dimension of particles in suspension, quartz, feldspars and amphiboles are also present in significant quantities. The suspended matter is enriched in chlorite with respect to the sediments. Thus some fractionation appears to take place in the water column during which chlorite is left preferentially in suspension. On the other hand the chlorite content in the clay-size fraction (4 μ) is found to increase with water depth, another indication that the contributions to the sediments made by material in suspension increase toward the central and deeper parts of the Gulf.

In studying the geochemical composition of the sediments, a procedure was used to distinguish for each element between a detrital fraction, which is supplied to the Gulf as component of mineral detritus and a non-detrital fraction, which is introduced in soluble form and accumulate in the sediments by either direct precipitation, surface reaction or biological processes. For both fractions, criteria mineralogy provides a convenient simple technique to determine the source areas (Loring and Nota, 1969). It clearly distinguishes between a northern Gulf province, in which sediments originate mainly from the crystalline complexes of the Canadian Shield, and a southern Gulf province, where sediments have their principal sources in the Appalachian regions. This distinction is based on the shape and appearance of the quartz minerals: amphiboles and pyroxenes are particularly abundant in the northern part of the Gulf.

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In studying the geochemical composition of the sediments, a procedure was used to distinguish for each element between a <u>detrital</u> fraction, which is supplied to the Gulf as component of mineral detritus and a <u>non-detrital</u> fraction, which is introduced in soluble form and accumulate in the sediments by either direct precipitation, surface reaction or biological processes. For both fractions, criteria were defined and correlation tests applied to determine as closely as possible their preferential associations with one or several of the sediment components. The results were discussed in detail in Chapters 3 and 4. They are summarized in the first column of Table VI.1.a.

Locally the nature of the country rocks exposed on shore may affect the composition of the nearby sediments: for instance the distribution of calcium is affected by calcareous outcrops. However, as a rule the distribution of the major elements is mainly a function of the depth of water because of its control on both the texture and the mineralogy of the sediments.

With respect to the <u>detrital</u> fraction of the trace elements, chlorite is found to be responsible for between 65% and 80% of detrital Co, Cr, Mn and Zn. Almost all of the detrital Sr enters the sediments in association with plagioclase feldspars.

On the other hand, partial correlation and multiple regression analyses indicate that organic matter is a major carrier for the <u>non-detrital</u> fraction of the trace elements, which could possibly occur as sorbed ions or organic complexes. Precipitation with iron oxides is important only for Mn and Se, and to a lesser extent for Pb, Cr and Zn. Co, Pb, Mo and Sr are added to the sediments in association with carbonates. Adsorption on clay particles appears to contribute only Mo.

Very high Se values in the sediments analyzed are of particular interest since zones of seleniferous mineralization or soils of high Se content

TABLE VI.1 a

Concentration and partition of elements between mineral components in the Gulf, and comparison with other environments.

Area	Gulf of St. Lawrence*	Low latitude neritic** Sediments	High latitude† Sediments	Deep-sea†† Sediments
Element				
CO_3	2-31% (10.5%) low Mg calcite	30% $CaCO_3$	0-28% $CaCO_3 + MgCO_3$	0-98% $CaCO_3$ Calcite and aragonite
P_2O_5	0.1-0.26% (0.19%) Fe - Mn compounds	(0.14%) ?	0.05-0.07% ?	0.15-0.62 phosphatic nodules + Fe - Mn compounds
C	0.2-3.19% (1.69%) wood fragments	0.17-1.1% ?	0.0-13.0% ?	(0.28%)
Al	4.45-10.31% clay minerals + feldspars	8.7-10.07% clay minerals	(7.29%) ?	0.95-9.38% clay minerals
Ti	0.26-0.88% (0.48%) Ilmenite	0.34-0.55% TiO_2	(0.35%) ?	(0.59%) clay minerals, rutile, anatase
Fe	2.26-5.46% chlorite + Fe oxides	4.21-6.41% Illite + limonite	(3.72%) ?	clay minerals + Fe Mn minerals
Mg	0.85-2.11% Chlorite	0.69-1.78% Montmorillonite	?	(2.18%) Montmorillonite + carbonate + other clays
Ca	0.4-17.0 $CaCO_3$ + Plagioclase feldspars	0.51-0.92% $CaCO_3$	?	(0.75%) Carbonates + Phosphates
Na	0.55-1.94% Soda feldspars	0.76-2.56% Illite + Montmorillonite	?	(1.10%) Montmorillonite + Zeolite
K	1.31-4.45% Illite + chlorite + K feldspars	1.53-2.03% Illite + Chlorite	?	(2.10%) Illites
Co	23-62 ppm Chlorite + Fe	10-13 ppm	9-44 ppm	(39 ppm)
Cr	19-105 ppm Chlorite	59-98 ppm	15-130 ppm Mn nodules + rock fragments	(80 ppm) Illite
Cu	15-169 ppm mostly in association with Organic matter	15-23 ?	9-130 ppm carbonate	(115 ppm) Organic carbon
Mn	415-1597 ppm Chlorite + Fe oxides	2900-4000 Fe-Mn oxides	1250-3000 Mn-Fe nodules	(3982 ppm) Fe-Mn nodules
Mo	0-70 ppm Sulfides + Molybdenite + carbonate	?	?	(27 ppm)
Ni	34-90 ppm no definite minerals	23-34 ppm ?	9-80 ppm Fe-Mn nodules + Carbonates	(79 ppm) Fe-Mn minerals
Pb	25-200 ppm Mainly non-detrital	13-32 ppm ?	?	(52 ppm) ?
Se	0-167 ppm Fe oxides + Sulfides	?	?	0.17-9.0 ppm
Sr	80-199[illegible] ppm Carbonate Ca feldspars	100-480 ppm	580-2300 ppm	180 ppm
Zn	40-[illegible] ppm Chlorite	?	?	(165 ppm)

TABLE VI.1.b

Trace element contribution made by the non-detrital fraction of the sediments in the Gulf as compared to other sediments(1).

% contribution made by the non-detrital fraction	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sr	Zn
* Gulf of St. Lawrence	28	17	61	45	46	48	53	68	36
** Low latitude sediments	58	8	67	--	-	43	4	--	--
† High latitude sediments	11	19	17	13	--	10	--	24	--
†† Deep sea sediments	12	6	11	14	--	9	--	17	--

(1) values normalized to 10.5% $CaCo_3$, which is the average for the Gulf sediment samples used in this study.

TABLE VI.1.c

* Trace element association in the non-detrital fraction

	Elements									
Variable	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sr	Zn	Se
Organic Carbon		X	X			X	X		X	
Fe oxides		X	X	X			X		X	X
Carbonate	X				X		X	X		
Adsorption					X					

* Present work.

** From Hirst (1962 a,b).

† From Angino (1966); Beltagy (1969)

†† Chester and Messiha-Hanna (1970); Van der Weijden et al. (1970); El-Wakeel and Riley (1961).

( )- average values given in parenthesis.

? no information available.

have not been reported anywhere in the drainage basin. The correlation between Se and non-detrital Fe in the sediments would indicate that Se is removed from solution during the precipitation of iron oxides. Whether Se is introduced in the Gulf entirely by natural processes or partly as the results of Man's activities is not known.

The high percentages of non-detrital contributions to the total concentrations of some trace elements, suggest that chemical weathering may be more active in the St. Lawrence basin than is usually expected in subarctic regions. Feldspar particles in the sediments do not show much alterations. On the other hand, there are detectable amounts of kaolinite, a diagnostic product of mineral disintegration. The relatively high organic matter dominantly of terrestrial origin and the numerous peat bogs in marginal areas of the western Gulf suggest that soil-forming processes are active enough to induce partial mobilization of trace elements from parent rocks. Other non-detrital additions of trace elements to the environment may come from, (i) mining and other human activities in the drainage basin (Boyle et al, 1966); (ii) upward migration of some elements, such as Mn, within the sediments followed by redepostion at the interface.

When compared with other regions, broad difference in geochemical characteristics seem to exist between the Recent sediments in the Gulf of St. Lawrence and neritic or shelf sediments in high and low latitudes for which analyses are available. The chemical composition for these various environments and the deep-sea are compared in Table VI.1.a. The main host minerals are also indicated. Differences appear not only in the absolute concentrations of the elements, but also in their relative distribution among the various mineral components of the sediments. Montmorillonite which acts as the host mineral to many elements in low latitude sediments (Hirst, 1962 a,b) is characteristically absent in the Gulf. In contrast chlorite, and to some extent illite are the mineral components which accomodate the largest number of elements. The chlorite comes largely from the physical breakdown or basic igneous and metamorphic rocks, while the illite which is the dominant clay mineral may have been derived mostly from tillite and glacial sediments (Fairbridge, 1965). The element distribution between the detrital and non-detrital fractions differ markedly in the Gulf from that observed in low or high latitude sediments and in deep-sea deposits. After normalization to a constant carbonate content, the non-detrital contribution to the elements Mo, Ni, Pb and Sr is higher in the Gulf than in any other environment (Table VI.1 b). On the other hand non-detrital Co, Cr and Cu are intermediate between low and high latitude sediments.

Since the depth of water appears to be the major factor which indirectly controls the composition of the surface sediments in the Gulf, this raises the possibility of using some aspects of the chemistry of sediments to indicate the depth of deposition, hence changes in sea level. This analysis is delicate and may best be performed using the major and minor elements, as with regard to trace elements complicating factors modify the influence that depth may exert on their distribution. Studies carried out on five cores by means of correlation tests showed that variations in single element composition or in element ratios exist between distinct stratigraphic units. Going one step further, by applying factor analysis it was possible to obtain a theoretical solution which gave the major vector variations as a function of depth in the cores. These variations provide an additional method for core cross-correlation which could be precious in the study of Recent deposits lacking in standard stratigraphic criteria. Also these factor variations may be indicative of recent climatic changes as they can easily be interpreted in terms of short period sea-level fluctuations. Thus geochemical analyses performed systematically on a large number of cores from a given region may provide interesting paleoclimatic information, as long as some independent stratigraphic control is also available.

Finally, the present study may provide a base line for further investigations concerning changes in trace element inputs in the marine environment caused by present industrial activities. Variations in the non-detrital fraction are certainly related to these activities. In fact it has been shown in Chapter IV that the Cu input in the Gulf could be 3 to 4 times that expected for a river having the same annual discharge and comparable drainage area, but without industrial and human contributions. This could also be true for most of the other elements studied.

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APPENDIX A

SELECTION OF SAMPLES AND METHODS OF ANALYSIS

A 1 Selection of Samples

The cores from which the samples were taken were collected during four short cruises to the Gulf of St. Lawrence in the years 1967, 1968, 1969 and 1970. Samples were collected as short cores that varied in length from one foot to twelve feet, depending on the type of sediment and the type of core.

A piston corer as well as simple gravity corer were used in the sampling process.

The positions of the coring stations and the depth of overlying water are given in Table 1. The stations are shown on Figure A.1.

The cores obtained were kept in their plastic tubes under refrigeration until opened for the sampling process at the Marine Sciences Centre laboratories in Montreal. The material used for this study was taken from the first four cms at the top of the core. In order to avoid contamination during sampling, the outer portion of each core section was removed.

Suspended matter samples were collected during a cruise to the Gulf in 1972. A continuous flow centrifuge was used to collect the suspended matter from water samples pumped from ca. 4 m below the sea surface.

TABLE A.1

Core locations and water depths.

Sample No.	Longitude	Latitude	Water depth m
A-2	60° 06' W	47° 16' N	238
A-4	59° 34' W	47° 32' N	468
A-6	58° 31' W	49° 50' N	151
A-7	59° 09' W	50° 03' N	241
A-10	61° 30' W	49° 51' N	182
A-13	66° 00' W	50° 02' N	113
A-14	65° 54' W	49° 46' N	315
A-15	65° 59' W	49° 35' N	324
A-16	65° 48' W	49° 17' N	189
A-17	64° 40' W	49° 26' N	369
A-18	63° 41' W	49° 22' N	309
A-20	64° 02' W	49° 04' N	320
A-25	62° 46' W	48° 47' N	297
R-2	61° 39' W	46° 36' N	61
R-4	62° 20' W	47° 04' N	57
R-5	63° 06' W	47° 46' N	70
R-6	63° 24' W	48° 04' N	53
G-c	61° 45' W	45° 57' N	31
G-9	63° 55' W	45° 57' N	377
G-11	65° 52' W	49° 23' N	335
G-12	66° 02' W	49° 41' N	350
G-21	59° 05' W	49° 35' N	234
G-23	57° 39' W	50° 39' N	264
G-25	58° 11' W	51° 02' N	197
G-30	60° 49' W	51° 02' N	322

TABLE A.1 (cont'd)

Sample No.	Longitude	Latitude	Water depth m
S-17	65° 33' W	49° 36' N	410
S-3	63° 08' W	48° 34' N	372
S-21	60° 11' W	48° 17' N	345
S-19	62° 27' W	49° 49' N	270
A-50	59° 43' W	47° 24' N	470
A-51	59° 52' W	48° 54' N	288
I-6	58° 42' W	49° 49' N	187
A-53	58° 00' W	50° 04' N	220
A-58	57° 52' W	50° 10' N	157
A-54	59° 20' W	50° 22' N	118
A-55	58° 32' W	50° 47' N	131
A-63	61° 35' W	49° 37' N	275
I-7	59° 11' W	50° 02' N	205
A-61	60° 14' W	49° 24' N	275
A-67a	62° 24' W	50° 09' N	202
A-71	63° 25' W	50° 07' N	47
A-72a	63° 23' W	49° 59' N	148
A-74a	64° 17' W	50° 04' N	124
A-78a	65° 12' W	50° 09' N	124
A-82	66° 36' W	50° 02' N	170
A-83	66° 50' W	49° 45' N	146
A-84	66° 33' W	49° 34' N	230
A-85	66° 33' W	49° 19' N	320

TABLE A.1 (cont'd)

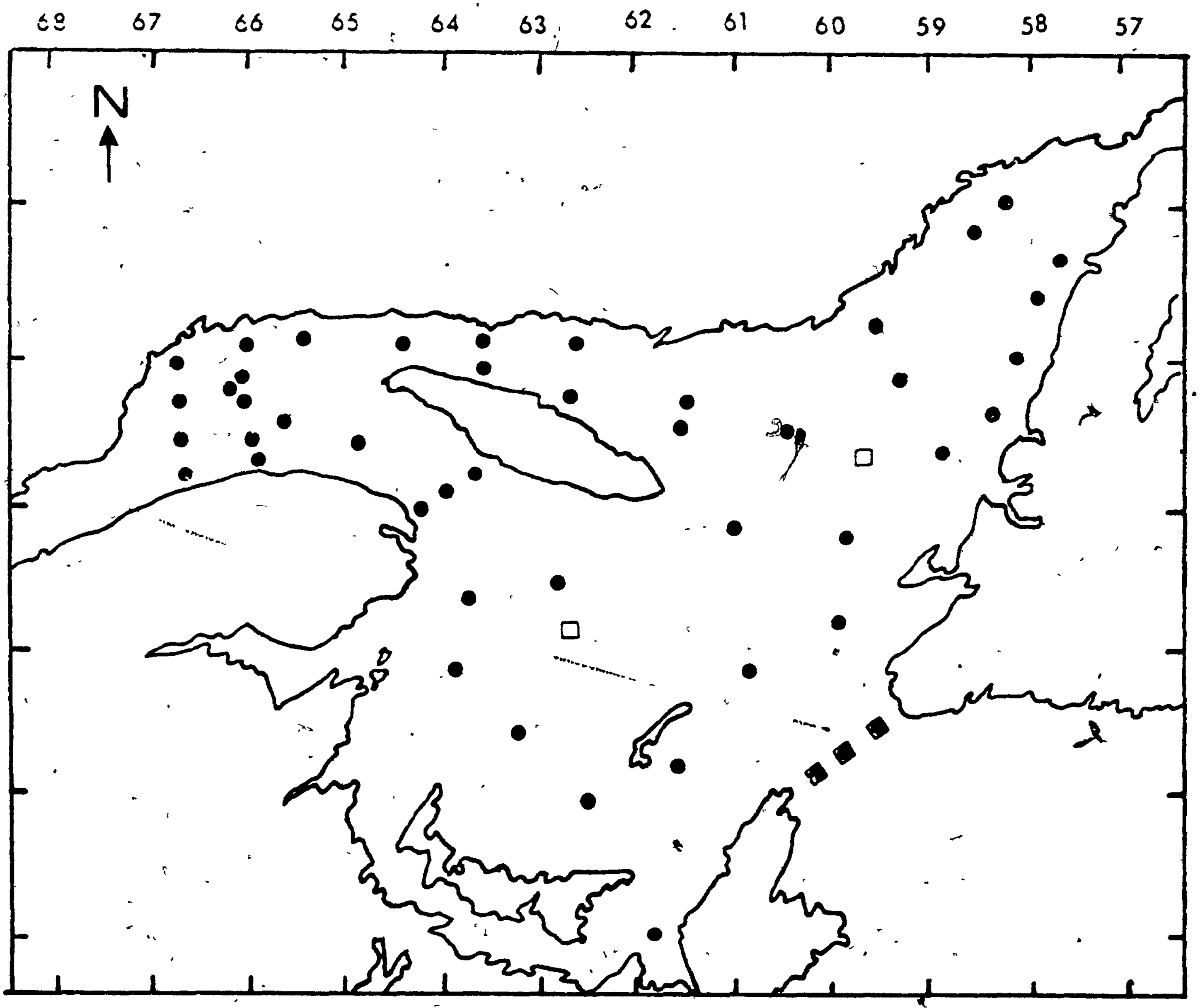
Sample No.	Longitude	Water depth m
A-67b	3 miles west of 67a	212
A-72	3 miles west of 72a	149
A-74	5 miles west of 74a	50
A-85b	4 miles south of 85	113

Figure A.1

Core and Suspended matter samples locations.

● Core sample

☐ Suspended matter sample


68
67
66
65
64
63
62
61
60
59
58
57
N
51
50
49
48
47
46

Samples from 2 long cores (BIO 36 and BIO 115) were kindly supplied by Dr. D.H. Loring. These samples were preserved dry in the open air.

A.2 Methods of Analysis

A.2.1 Sample Preparation

Representative samples were obtained from each core section and were then treated as described below:

1. *ca.* 8 gm of each sample was suspended in 500 ml of deionized water and placed in an ultrasonic bath for *ca.* 20 min.
2. The suspension was passed through a 230 standard mesh, stainless steel seive (0.063 mm). The coarse fraction was dried, weighed, and kept for mineralogical studies.
3. The suspension was filtered and washed with deionized water until Cl^- free, then dried in an air oven at 70°C.
4. The sediment flakes on the filter paper were transferred into an agate mortar. The sediment was ground gently in order to break the aggregates without altering the particle size pattern.
5. The ground samples were kept in glass vials for future analysis.

A.2.2 Particle Size Analysis

Between 2 and 3 gm of the well mixed dry sample was treated as described below:

1. To the weighed sample, 50 ml of 25% acetic acid was added. The sample was then placed in an ultrasonic bath for ca. 30 min to ensure complete dissolution of the carbonate components.

2. The acid washed sample was then centrifuged, washed several times in distilled water and treated with 15 ml of H_2O_2.

3. The sample + H_2O_2 was then placed in a water bath at 85°C until no reaction was visible, then removed, centrifuged, washed and dried in an air oven at 90°C.

4. Each dried, carbonate, organic matter-free sample was then thoroughly mixed, and 1 to 1.5 gm was taken for particle size analysis. Each samples was suspended in 200 ml distilled water and placed in an ultrasonic bath for 20 min. After cooling the sample was transferred to a 1 l graduated cylinder, shaken well, and the sediment allowed to settle.

6. The samples were removed from the cylinder at the 20 cm mark below the water level, at time intervals calculated from Stock's Law and selected to give particles of size ranges given in Table A.2.

7. Samples of each particle size class were collected in a small tube and centrifuged. The liquid was then carefully poured off and the sediment dried at 90°C, cooled and weighed in the tubes, which has previously been weighed dry.

TABLE A.2

Particle Size Ranges

Time min	Time sec	Particle range
1	56	> 31 μ
7	45	16 - 31 μ
30	-	8 - 16 μ
122	-	4 - 8 μ
490	-	2 - 4 μ
*490	-	< 2 μ

* depth - 10 cm

8. The percentage of each particle size class was calculated, and then adjusted to wt% of the total sample, taking the coarse fraction into consideration.

9. Reproducibility of the technique was tested for each size class by carrying out the separation of one sample three times. The results are given in Table A.3, where they are expressed as wt.% of the fine fraction.

TABLE A.3

Reproducibility of the Pipette Analysis

size class	Separation No. 1	2	3
> 31 μ	14.7	15.0	16.3
16 - 21 μ	15.5	14.1	14.4
8 - 16 μ	14.0	14.6	13.6
4 - 8 μ	8.4	10.2	8.1
2 - 4 μ	9.6	8.1	9.4
2 μ	37.8	38.0	38.2

A.2.3 X-ray Diffraction Analysis

X-ray diffraction analyses were carried out on the 2 μ fraction of the sediments and on the suspended matter. Samples chosen for the X-ray studies were treated as described below:

1. Between 1 and 1.5 gm of the dry sample was weighed out and treated with 25 ml of sodium acetate-acetic acid solution at pH 5. The sample was then placed in an ultrasonic bath for ca. 20 min to remove carbonates.

2. The sample was centrifuged, washed with distilled water several times and treated with 10 ml 30% H_2O_2. The sample was then placed in a water bath at 85°C, until reaction ceased to occur, even on the addition of a few fresh drops of H_2O_2.

3. Iron was removed using sodium dithionite-sodium citrate solution, with $NaHCO_3$ as buffer (Mehra and Jackson, 1960), by shaking the sediment with 15 ml portions of the mixture at 80°C three times each for about 5 min.

4. The sample was then washed several times with distilled water, then shaken with 1 N solutions of KCl, $MgCl_2$ and $CaCl_2$ separately.

5. The sample was washed several times with distilled water, suspended in 50 ml of distilled water and placed in an ultrasonic bath for ca. 20 min.

6. The 2 μ fraction was separated by sedimentation, centrifuged and the liquid poured off.

7. The 2 μ fraction was suspended in a minimum of distilled water. Two slides of each sediment sample were prepared by pipetting the

suspension on a 27 x 46 mm microscope glass slide, which was left to dry in a relatively dust free place.

8. A slide of each sample was then glycolated and examined with a Norelco X-ray diffractometer, using the following settings:

Target	Cu
Current	20 mA.
Voltage	35 Kv
Beam slit	1 mm
Filter	monochromator
Time constant	3 sec.
Goniometer speed	1/2 2θ°/ min.
Chart speed	1/2 inch / min.

9. The minerals were identified using the following criteria:

(a) Kaolinite was identified by its 3.58 A° peak; which was used for the calculation of the mineral content.

(b) Illite was identified by its strong peak at 10 A° which is not affected by glycolation or heating.

(c) Chlorite group was identified by its 14 A° peak, which is unchanged by glycolation and not destroyed by heating to 575°C. The fourth order reflection at 3.54 A° was, however, used for the calculation of the mineral content.

(d) Montmorillonite: this group was not identified in any of the samples analysed.

10. The mineral concentration is expressed as a percentage of the sum of the weighted peak areas assuming that the clay minerals account for 100% of the sample mineralogy. From the studies of Johns, Grim and Bradley (1954), Weaver (1961) and Biscaye (1965), the following weighting factors have been used: four times the illite 10 A° peak, the area of montmorillonite peak and twice the area of 7 A° peak which is divided proportionally between kaolinite and chlorite using the ratio of 3.58/3.54 peak areas.

A.3 Methods of Chemical Analysis

A.3.1 Preparation of Sediment Solutions (except for silica and Se)

Sediment solution (A) was prepared by digestion of the sediment sample with HF and $HClO_4$. The solution is used for the determination of all the major elements except silica and all the trace elements, except Se, which need special preparation.

Reagents:
1. Hydrofluoric acid (Fisher certified).
2. Perchloric acid 70% (Fisher certified).

Meth[illegible]

Weigh exactly 0.5 gm of the sample into 20 ml pt crucible. Add 4 ml of $HClO_4$ and from a polyethylene measuring cylinder, add 15 ml of HF. Heat the covered crucible on a water bath overnight. On the following morning remove the lid of the crucible and evaporate the HF on the water bath. When no further fumes of HF are visible, place the crucible under an infra-red lamp and heat until most of the $HClO_4$ is removed (do not allow to dry). Add 2 ml of $HClO_4$ and repeat the evaporation. Add 1 ml of perchloric acid from a pipette and 15 ml of water. Heat the covered crucible on a water bath and stir until the content dissolves. Transfer to a 50 ml volumetric flask and dilute to that volume. A fresh reagent blank solution was prepared each time that a new batch of reagent was used.

Solution (A) was diluted between 10 and 50 times for the determination of the major elements on the AAS, and it was used without dillution for the determination of trace elements.

A.3.2 Atomic Absorption Spectrophotometric Analysis

A.A. spectrophotometer (Perkin Elmer M403) was used for the determination of major as well as trace elements in the sediment solutions.

Standards were prepared from analytical reagent grade chemicals or Fisher certified. They were added to a matrix made also of A.R. chemicals, by mixing them in proportions similar to that given in the literature for near-shore muds. This would give a composition similar to that expected in the sediment samples and hence the background and interference effects are taken into consideration.

The standard solutions, after being mixed in the proper ratios (see Table A.4 a,b) to give the mixed standards, were dried under an infra-red heater and

TABLE A. 4 a,b

*Mixing ratios of different elements used for the preparation of the matrix for the standard solutions.

(a)

Major Elements	Al	Ca	Fe	K	Mg	Mn	Na	Ti	Si
Concn. in ppm, in a final volume of 50 ml.	900	100	500	250	400	30	250	100	3500

(b)

Trace Elements	Co	Cr	Cu	Ni	Mo	Pb	Se	Sr	Zn
Concn. in ppm, in a final volume of 50 ml.	2	5	2	3	1	2	1	10	2

* Ten times dilution of this matrix was used when determining major elements. (Solution B in sediment solution).

the residues were treated in the same manner as the sediment samples. The standards were dissolved in deionized water and made to volume. Standard curves for some elements were drawn using the addition method; the results obtained from the first (artificial rock solutions) and the addition method were compared and found to agree within less than ± 5%. Standard solutions prepared by mixing pure chemicals were used throughout this work.

Sediment samples were analyzed using a Perkin-Elmer Model 403 A.A.S. fitted with digital readout system. Table A.5 gives the analytical conditions applied for each element (Perkin-Elmer Manual, 1969; Robinson, 1966; Buckley and Cranston, 1971).

Reproducibility of the technique was tested by carrying out analysis on six replicates of one sample. The results are given in Table A.6.

A.3.3 Determination of Selenium

Using AAS, selenium was determined in the sediments after being separated from other elements by the method described by Chau and Riley (1965).

(a) Preparation of Sediment Solution (B)

Weight 0.5 gm of the sediment sample in a platinum crucible. Add 10 ml of HF (40%) and 10 ml of concentrated nitric acid. Heat the covered crucible on a waterbath overnight. The next morning, remove the lid

TABLE A.5

Analytical conditions for the A.A. analysis

Element Machine Setting	Al	Ca	Fe	*K	Mg	Mn	Na	Ti
Wave length A°	3247	4227	2483	7665	2852	2975	5890	2768
Burner type	Nitrous oxide	4 inch single slit	4 inch single slit	4 inch single slit	4 inch single slit	4 inch single slit	4 inch single slit	Nitrous oxide
Burner position	parallel	parallel	parallel	--	45° with burner	parallel	45° with burner	parallel
Flame used	acet. + N_2O	acet. + air	acet. + air	acet. + air	acet. + air	acet. + air	acet. + air	acet. + N_2O
Lamp current	Maximum current recommended by the manufacturer.							

Element Machine Setting	Co	Cr	Cu	Ni	Mo	Pb	Se	Sr	Zn
Wave length A°	2425	3579	3247	3415	3133	2833	1961	4607	2139
Burner type	4 inch single slit	4 inch single slit	4 inch single slit	4 inch single slit	Nitrous oxide	4 inch single slit	4 inch single slit	4 inch single slit	4 inch single slit
Burner position	parallel	parallel	parallel	parallel	parallel	parallel	parallel	parallel	parallel
Flame used	acet. + air	acet. + air	acet. + air	acet. + air	acet. + N_2O	acet. + air	acet. + air	acet. + air	acet. + air
Lamp current	Maximum current recommended by the manufacturer.								

* Emission Flame photometry.

TABLE A.6

*Reproducibility of the Atomic Absorption technique.

Run No.

Element	1	2	3	4	5	6
Al	8.34	8.57	8.18	8.61	8.32	8.53
Ca	6.59	6.71	6.74	6.80	6.72	6.75
Fe	6.295	6.46	6.31	6.43	6.30	6.35
Mg	0.113	0.11	0.11	0.111	0.115	0.110
Na	0.875	0.855	0.869	0.855	0.865	0.860
K	1.17	1.19	1.21	1.19	1.18	1.19
Ti	0.555	0.490	0.505	0.565	0.510	0.515
Co	26.5	29.5	28.0	25.5	26.0	27.5
Cr	29.5	30.0	30.0	29.0	29.5	30.5
Cu	45.5	45.5	45.0	46.0	45.0	45.5
Mn	371	369	374	365	365	368
Mo	9.5	9.0	8.5	11.0	9.0	9.5
Ni	20.5	19.5	21.0	21.0	20.0	20.5
Pb	31.5	37.5	33.0	34.5	32.0	33.5
Se	8	12	9	8	9	8
Sr	398	394	385	383	382	385
Zn	57.0	56.0	55.5	58.0	55.0	57.0

* First 7 elements are given in wt.%, the rest in ppm.

and evaporate to dryness on the waterbath. Evaporate to dryness 3 times with concentrated nitric acid to remove fluoride.

Add 25 ml of 4 N hydrochloric acid to the residue and boil gently for 2 minutes in order to dissolve it and reduce to selenite any selenate which might have been formed. Wash and transfer quantitatively to a 4l conical flask.

(b) Separation of Selenium

Co-precipitation with Iron Oxide:

Dilute the sediment solution (B) to ca. 2 l with re-distilled water. Adjust the pH of the solution to ca. 3.5-4 with sodium hydroxide. Dilute to 4 l and add 30 gm of NaCl to assist the coagulation of the Fe^{+3} hydroxide precipitate. Add with shaking, 60 mg Fe^{+3} (as $FeCl_3$ solution) and adjust the pH to 4.5-5.0 with dilute ammonium hydroxide. After 2 hours, add a further 60 mg of Fe^{+3} solution and restore the pH to 4.5-5.0.

Allow the solution to stand for 2 days. Siphon off the supernatant liquid, separate the precipitate by centrifugation, and wash it with 0.5% ammonium nitrate. Dissolve the precipitate by warming with 1 ml of concentrated nitric acid and 0.1 ml concentrated hydrochloric acid. Dilute the solution with enough water to make the acidity 0.2 N.

Ion Exchange Separation:

Pass the resultant solution through an ion exchange column filled with CGS-240 resin (in the form of H^+) to a depth of 10 cm.

Elute with 350 ml of 0.2 N nitric acid. Combine the percolate and eluate, add 1 ml of 2 N sodium hydroxide and evaporate to dryness on a water bath. Dissolve the residue in a minimum of water and dilute to volume (usually 10 ml).

(c) Atomic Absorption Analysis

Se was determined in the resultant solution (step III.b) using the standard settings given in Table. A.5.

Omitting the sample, blank determination and standards were treated in the same manner as described above.

Reproducibility of the method was tested and the results are given in Table A.6.

A.3.4 Separation of Detrital and Non-Detrital Components of the Sediment

There are various ways in which sediments can be subjected to chemical attack in order to examine the partition of trace elements among the component phases. Goldberg and Arrhenius (1958) used EDTA for this purpose. Arrhenius and Korkish (1959) used 1 M hydrochloric acid to separate the Fe oxide fraction of the ferro-manganese nodules. Hirst and Nicholls (1958) used 25% acetic acid to separate the detrital and non-detrital fractions of carbonate sediments. Chester and Hughes (1967) have examined these methods, they concluded that in all the above methods, partial attack of the non-detrital components is likely to occur. They used a mixture of 25% acetic acid and 1 M hydroxyl amine hydrochloride which has the ability to dissolve the carbonate fractions as well as the ferro-manganese minerals. In the present study this latter technique was used.

The non-detrital contribution of the elements was determined in the solution after destroying the organic compounds using perchloric acid as described below. Trace element contribution made by the detrital fraction was calculated by difference, and the trace element content of the detrital phase of the sediment was calculated by multiplying the latter value by 100/100 - % $CaCO_3$.

Reagents:

- 35% (v/v) acetic acid: Dilute 350 ml of glacial acetic acid to 1 l with re-distilled water.

25% (w/v) hydroxyl-amine hydrochloride: Dissolve 25 gm of the A.R. grade reagent in 100 ml of re-distilled water.

Mixed acid reducing reagent: Mix 75 ml of 25% hydroxyl-amine hydrochloride and 175 ml of 35% acetic acid. This solution is equivalent to 1 M hydroxyl-amine hydrochloride and 25% (v/v) acetic acid.

Method:

Place 1 gm of the air dried sediment in a 100 ml conical flask and add 50 ml of the reducing mixture. Put the flask(s) in an ultrasonic bath for 4 hours, centrifuge, and collect the liquid in a separate flask. Wash the sediment and add the washing to the original liquid. Evaporate to near dryness, add 3 ml of perchloric acid and 5 ml of concentrated nitric acid. Continue evaporation with another 2 ml of perchloric acid. Dissolve the white residue in a minimum of water. Make to volume for the elemental analysis on the AAS.

The sediment residues after centrifugation and washing were dried and the detrital fraction (the residue) was treated as described in section A.3.1 and A.3.2 for the total sample.

A.3.5 Determination of Organic Carbon

Organic carbon in the sediments was determined by the wet oxidation method described by El-Wakeel and Riley (1958).

Reagents:

Chromic acid: Dissolve 13 gm of Cr_2O_3 (A.R.) in a minimum of water then add 900 ml of concentrated sulfuric acid. Cool and complete to 1 l.

Ferrous ammonium sulfate 0.2 N: Dissolve 39.2 gm of the A.R. grade salt in 400 ml of distilled water containing 10 ml sulfuric acid and dilute to 500 ml.

Ferrous phenanthrolin indicator (0.025 m): Dissolve 0.337 gm of o-phenanthrolin in 25 ml of 0.69% ferrous sulfate solution.

Method:

Weigh out 0.15-0.3 gm of the washed dry sample into a 100 ml conical flask. Add 10 ml chromic acid reagent. Cover (loose cover), shake, and heat in a waterbath at 100°C for 15 minutes. Cool and pour the contents into 200 ml of distilled water. Add one drop of ferrous phenanthrolin indicator and titrate with 0.2 N ferrous ammonium sulfate until a pink colour just persists.

Blank is carried out by omitting the sample.

1 ml of 0.2 N ferrous ammonium sulfate = 1.15 x 0.6 mg carbon.

A.3.6 Phosphorus Determination

Phosphorus is determined in solution A by a single solution molybdenum blue method, using ascorbic acid as the reducing agent.

Reagents:

Sulfuric acid, 3 N. Dilute 84 ml concentrated sulfuric acid to 1 l.

Ammonium molybdate. Dissolve 5.0 gm of ammonium molybdate A.R. in water, dilute to 250 ml.

Ascorbic acid (0.01 M). Dissolve 4.4 gm of ascorbic acid in water, dilute to 250 ml. The solution should be stored in a refrigerator and made afresh if it becomes yellow.

Reducing solution. Mix 125 ml of 3 N sulfuric acid, 38 ml of ammonium molybdate and 60 ml of ascorbic acid, dilute to 250 ml. The reagent, which has a faint green colour, should be made up immediately before use.

Standard phosphate solution. Prepare a solution of potassium dihydrogen phosphate A.R. (dried at 110°C). Dissolve 0.0959 gm KH_2PO_4 in 1 l. The solution contains the equivalent of 50 g P_2O_5/ml.

Treatment of Flasks:

To obtain accurate results all graduated flasks should be allowed to stand for several hours filled with concentrated sulfuric acid and then washed well with distilled water.

Method:

Pipette 1 ml of solution A into a 50 ml graduated flask, add 20 ml of the reducing solution and dilute to volume. After allowing to stand overnight, measure the optical density at 827 mμ in a cell of an appropriate length (1 or 5 or 10 cm). Carry out a reagent blank determination on a solution treated in the same manner as solution A, omitting the sample. Standardise the method using 1 ml of standard P_2O_5; carry out corresponding blank using distilled water. 50 µg P_2O_2 in a final volume of 50 ml give an optical density (1 cm cell) of *ca.* 0.386 (after deduction of reagent blank, which is *ca.* 0.008). The molybdenum blue colour is stable for at least a week.

Calculate:

$$\% \, P_2O_5 = \frac{\text{optical density of sample} \times 0.25 \times \text{volume of standard}}{\text{optical density of standard}}$$

APPENDIX B

ANALYTICAL RESULTS OF THE SURFICIAL SEDIMENTS

TABLE B.1

Particle size analysis of the sediments.

Sample No. Particle Size Class	R 4	R 2	A 7	A 6	A 25	G 30	G 12	G 25	A 20	A 16	A 17
> 62.5 μ	--	12	9.6	24	22.4	15.2	1.6	16.8	--	14.4	20
62.5-31 μ	15.2	8	16.8	6.4	8.0	3.2	5.6	8.8	7.2	17.6	6.4
31-15 μ	13.6	9.6	17.4	23.2	4.0	0.8	1.6	8.8	12.8	0	4.0
16-8 μ	25.6	17.4	10.4	5.8	1.6	0	4.8	10.4	8.0	6.4	15.2
8-4 μ	10.4	27.2	22.2	0	9.6	2.4	7.2	2.4	4.8	0	12.4
4-2 μ	15.0	11.6	4.2	31.4	13.2	21.6	37.6	24.8	6.4	23.2	7.6
< 2 μ	20.2	13.2	18.4	9.2	41.2	56.8	41.6	28.0	60.8	38.4	34.4

Sample No. Particle Size Class	G 11	R 6	R 5	84	50	G 9	G 21	A 18	A 15	A 14	G 23	51	78a	82
> 62.5 μ	32.0	20.8	16.0	42.4	--	15.3	2.7	57.6	32.8	44.0	--	0	66.4	--
62.5-31 μ	4.0	9.6	--	4.0	2.0	11.4	0.9	9.6	0.8	14.4	--	10.8	4.0	26.3
31-16 μ	0.8	13.6	19.2	2.4	10.0	6.6	20.4	4.8	3.2	3.2	5.6	1.2	4.0	7.5
16-8 μ	1.8	16.0	14.8	3.2	11.3	0.7	9.3	0	1.6	8.0	31.2	19.3	1.6	8.6
8-4 μ	14.4	7.2	14.4	7.2	10.7	18	30.0	2.4	0	1.6	16.8	2.4	6.4	9.0
4-2 μ	7.6	12.8	17.6	13.6	63.2	27	11.7	3.0	20.0	7.6	3.6	19.9	9.6	7.2
< 2 μ	39.6	20.0	28	27.2	2.6	25	25.0	22.6	41.6	21.2	42.8	46.4	8.8	41.2

Figure B.1

Location of samples used for mechanical analysis.

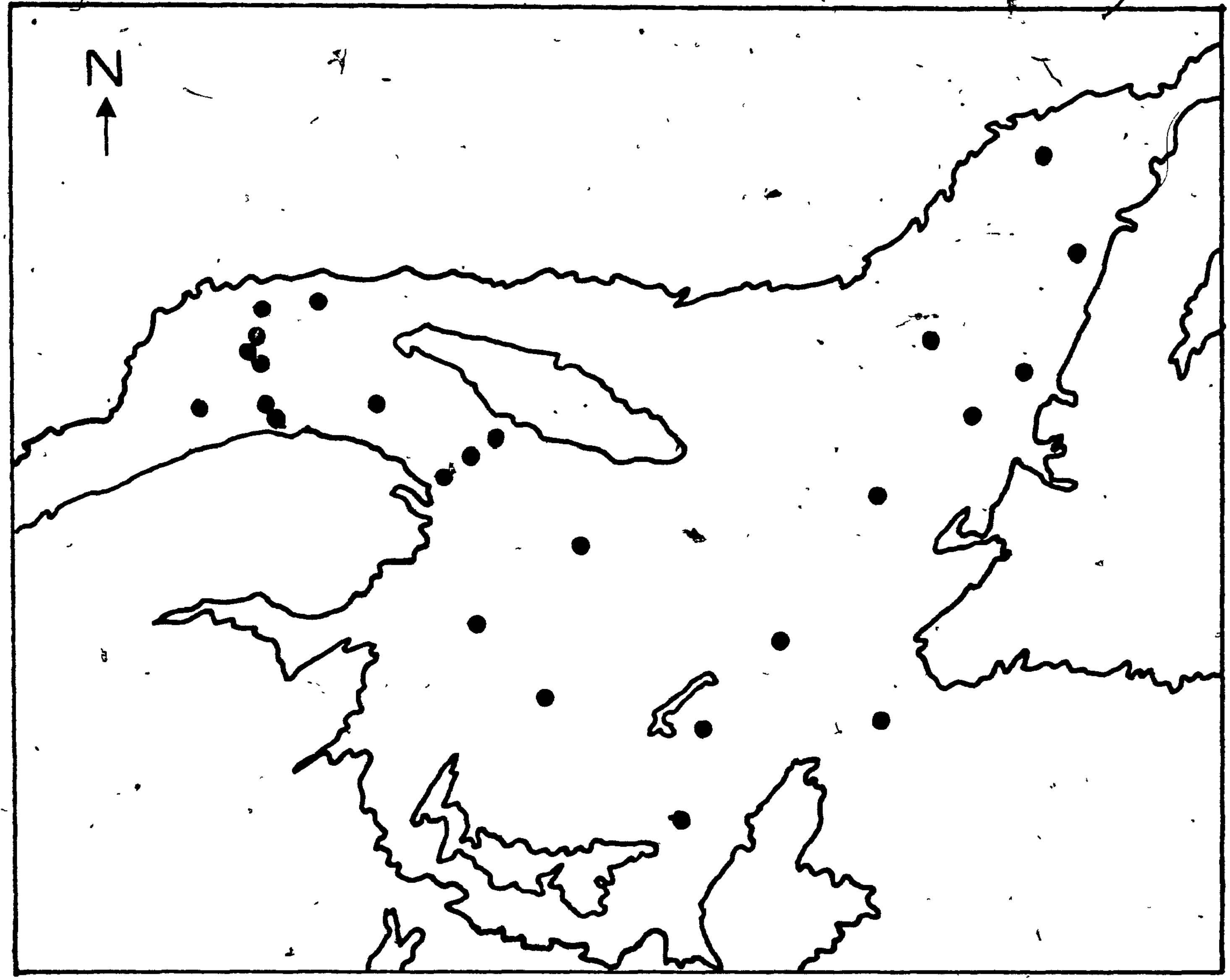

N

TABLE B.2

Mineralogy of the coarse fraction.

% mineral component average		Quartz	K. Feldspar	Plagioclase Feldspar	Horneblende-Augite Garnet-Zircon	Opaque minerals	Sedimentary rock fragments
16	samples from the northern part of the Gulf	35	15	50	7	2	1
9	samples from the southern part of the Gulf	53	10	7	1	5	24

TABLE B.3

Clay mineral composition of the < 2 μ fraction of the sediments and the suspended matter.

Sediment Sample No.	K/C	Chlorite %	Kaolinite %	Illite %
A-50	0.38	25	10	65
A-63	0.58	15	9	76
A-74	0.53	8	7	85
A-85	0.35	15	5	80
A-10	0.35	9	3	73
A-51	0.41	19	8	73
R-5	0.40	7	5	88
A-58	0.40	17	7	76
A-2	0.53	10	5	85
A-61	0.44	10	4	86
I-7	0.37	9	3	88
G-12	0.56	19	11	70
S-17	0.70	29	20	51
A-82	0.32	17	5	78
A-84	0.35	10	4	86
S-3	0.49	22	11	67
A-71	0.15	24	4	72
A-14	0.35	15	5	80
A-25	0.44	21	9	70
R-2	0.67	7	5	88
R-4	0.35	7	2	91
A-17	0.27	14	4	82

TABLE B.3 (cont'd)

Sediment Sample No.	K/C	Chlorite %	Kaolinite %	Illite %
G-9	0.73	15	11	76
G-11	0.47	7	3	90
S-19	0.61	12	7	81
G-30	0.22	15	3	82
G-25	0.36	14	5	81
C-21	0.76	9	6	85

Suspended Matter Sample No.	K/C	Chlorite %	Kaolinite %	Illite %
1	0.17	37	6	57
2	0.15	35	5	60
3	0.23	29	7	64
4	0.35	23	8	69
5	0.27	28	8	64

TABLE B.4

Major elements content of the Gulf sediment in wt%.

Sample Element	G-c	A-71	A-74	R-6	R-4	R-2	R-5	A-13	A-85b	A-54	A-74a	A-78a	A-55	A-83
Si	29.7	20.1	25.4	30.4	28.2	30.2	28.7	30.2	29.6	26.3	26.7	27.5	31.0	27.1
K	2.32	1.88	1.99	2.51	2.71	2.64	2.45	2.23	2.29	2.56	2.17	2.29	2.57	2.43
Na	0.74	1.46	1.59	1.15	0.59	0.55	0.60	1.94	1.66	1.56	1.64	1.64	1.54	1.57
Ca	0.36	2.91	2.85	1.69	0.52	0.42	0.35	3.15	0.84	1.24	2.42	1.63	1.76	1.51
Mg	1.10	1.37	1.54	1.50	1.48	1.55	1.32	1.59	1.49	1.67	1.60	1.59	1.68	1.71
Al	7.37	10.31	9.07	7.75	9.17	8.76	8.00	6.91	8.72	0.71	9.71	9.60	4.80	10.06
Fe	4.04	2.43	2.56	4.19	4.25	4.30	4.09	4.65	3.29	3.59	2.66	3.99	3.49	4.68
Ti	0.35	0.49	0.48	0.30	0.38	0.37	0.37	0.58	0.47	0.46	0.57	0.61	0.45	0.56
MnO_2	0.08	0.08	0.07	0.12	0.17	0.11	0.10	0.13	0.10	0.10	0.08	0.10	0.10	0.12
P_2O_5	0.14	0.17	0.11	0.18	0.20	0.26	0.16	0.26	0.18	0.15	0.10	0.17	0.15	0.21
$^*CO_3^{--}$	8.30	25.0	14.0	4.60	7.50	7.00	9.20	5.00	6.50	10.50	11.5	7.00	8.00	4.00
Org. C	--	1.46	1.56	--	--	0.20	--	--	--	2.30	--	1.30	2.53	2.23
Org. N	--	0.025	0.025	--	--	--	--	--	--	0.06	--	0.02	0.04	0.04

-- not determined

* as Calcium carbonate

TABLE B.4 (cont'd)

Sample Element	A-78a	A-72	A-6	A-58	A-82	A-10	I-6	A-16	G-25	A-82a	A-78b	A-85a	A-83a	A-67a
Si	27.1	30.5	28.7	30.2	29.2	24.0	27.8	31.8	27.9	32.0	27.0	28.4	28.40	29.3
K	2.43	2.49	2.36	2.11	2.51	2.61	2.47	2.44	2.52	2.51	2.51	2.53	2.49	2.57
Na	1.67	1.22	1.18	1.34	1.66	1.47	1.36	1.23	1.67	1.69	1.63	1.45	1.59	1.56
Ca	1.69	2.88	1.52	1.74	1.17	1.52	1.46	1.85	3.88	1.00	1.35	1.25	1.19	1.19
Mg	1.50	2.11	1.88	1.89	1.62	1.65	1.95	1.66	2.04	1.02	1.60	1.73	1.59	1.47
Al	9.20	5.79	7.13	8.80	9.27	8.82	8.54	6.22	6.95	8.85	10.01	8.76	9.37	9.57
Fe	2.28	2.45	4.17	2.26	4.40	4.93	3.78	4.50	3.99	2.76	3.90	4.51	4.10	3.71
Ti	0.54	0.49	0.55	0.44	0.61	0.52	0.57	0.49	0.26	0.52	0.51	0.52	0.44	0.60
MnO_2	0.06	0.09	0.11	0.08	0.14	0.12	0.10	0.15	0.11	0.10	0.11	0.13	0.11	0.10
P_2O_5	0.13	0.16	0.19	0.17	0.25	0.25	0.20	0.23	0.23	0.17	0.19	0.21	0.19	0.17
CO_3^{--}	12.00	10.00	9.00	6.00	2.00	15.00	7.50	4.00	10.0	2.00	8.50	4.00	6.00	2.00
Org. C	--	0.66	--	--	1.85	0.84	1.40	--	--	--	--	2.11	--	1.88
Org. N	--	0.01	--	--	0.03	0.02	0.03	--	--	--	--	0.05	--	0.02

TABLE B.4 (cont'd)

Sample Element	I-7	A-67b	A-53	A-84	G-21	A-2	A-7	G-23	S-19	A-63a	A-61	A-51	A-25	A-18
Si	26.5	29.1	32.1	28.5	27.5	31.9	26.5	23.6	32.1	22.6	28.3	31.4	23.0	21.5
K	2.51	2.53	2.05	2.67	2.40	2.30	2.51	2.29	1.31	2.61	2.64	2.45	2.34	2.27
Na	1.33	1.50	1.20	1.55	1.25	1.13	1.33	1.11	1.51	1.38	1.43	1.09	1.27	1.37
Ca	2.30	1.22	2.47	0.89	1.71	1.30	2.30	3.71	1.00	1.11	1.23	1.52	4.00	9.44
Mg	2.60	1.85	1.94	0.54	0.64	0.85	2.00	1.84	1.39	1.80	1.85	1.80	1.71	1.62
Al	8.28	8.84	4.97	9.12	7.50	5.95	8.28	7.33	4.80	8.75	8.32	4.82	6.75	4.45
Fe	4.34	4.53	2.73	4.49	4.13	3.84	4.34	4.24	4.95	4.98	4.06	3.72	4.44	2.76
Ti	0.55	0.52	0.39	0.49	0.30	0.52	0.55	0.29	0.59	0.56	0.53	0.46	0.43	0.23
MnO_2	0.13	0.13	0.09	0.10	0.11	0.10	0.13	0.11	0.08	0.10	0.10	0.10	0.11	0.07
P_2O_5	0.20	0.21	0.17	0.18	0.20	0.15	0.20	0.21	0.19	0.17	0.20	0.16	0.18	0.10
CO_3^{--}	11.0	4.00	3.00	4.50	11.00	6.50	11.00	19.5	5.00	13.00	6.00	9.00	22.00	31.00
Org. C	--	0.72	3.39	1.43	--	--	--	--	2.16	2.95	2.10	0.91	--	--
Org. N	--	0.01	0.05	0.03	--	--	--	--	0.04	0.08	0.03	0.04	--	--

TABLE B.4 (cont'd)

Sample Element	A-14	A-20	A-85	G-30	A-15	G-11	S-21	G-12	A-17	S-3	G-9	S-17	A-4	A-50
Si	28.6	20.30	31.1	26.9	27.1	26.30	32.5	28.4	28.1	31.2	24.4	30.8	30.8	26.8
K	2.27	2.48	2.60	4.45	2.50	2.46	2.21	2.51	2.34	2.48	2.36	2.33	2.17	2.44
Na	1.37	1.28	1.54	1.28	1.37	1.35	1.12	1.33	0.83	1.66	0.97	1.71	1.32	1.21
Ca	9.44	5.50	1.39	2.10	1.63	2.22	1.54	1.74	3.21	0.75	3.29	1.60	2.22	1.57
Mg	1.96	1.88	1.68	1.70	1.56	1.66	1.71	1.70	1.71	1.79	1.30	1.87	1.46	1.67
Al	6.21	9.80	7.25	7.13	8.20	7.97	5.46	7.10	8.25	6.80	7.50	6.64	6.60	9.14
Fe	4.10	4.68	4.45	4.22	4.69	4.27	3.64	4.33	4.13	4.52	3.90	4.44	3.88	3.97
Ti	0.39	0.49	0.53	0.44	--	0.31	0.74	0.32	0.46	0.88	0.32	0.84	0.52	0.56
MnO_2	0.10	0.13	0.17	0.12	0.14	0.13	0.07	0.25	0.12	0.12	0.11	0.10	0.12	0.13
P_2O_5	0.14	0.19	0.18	0.18	0.20	0.22	0.17	0.23	0.20	0.17	0.15	0.22	0.19	0.19
CO_3^{--}	10.00	21.00	4.00	12.00	10.00	12.00	--	9.00	9.50	2.00	9.00	3.00	7.00	8.50
Org. C	--	--	--	--	--	--	1.40	--	--	1.33	--	1.28	--	2.64
Org. N	--	--	--	--	--	--	0.00	--	--	0.03	--	0.02	--	0.03

TABLE B.5

Total trace element center of the Gulf sediments (in ppm).

Sample Element	G-c	A-71	A-74	R-6	R-4	R-2	R-5	A-13	A-85b	A-54	A-74a	A-78a	A-55	A-83
Co	43	43	48	46	48	40	34	59	50	40	53	52	33	49
Cr	64	26	23	63	73	77	47	55	36	40	19	42	27	61
Cu	169	17	28	80	109	116	73	73	25	44	15	34	29	35
Mn	776	525	415	530	1065	710	648	805	600	605	720	630	605	775
Mo	30	33	71	1	59	27	24	6	62	15	18	19	47	n.d.
Ni	55	44	42	48	70	65	50	55	44	45	45	43	45	61
Pb	117	40	40	70	110	103	85	150	30	30	50	46	35	150
Se	61	6	91	130	120	116	167	116	40	28	79	44	71	120
Sr	225	1997	1582	80	135	115	150	460	249	335	390	446	448	392
Zn	153	48	59	127	133	130	114	109	101	92	117	95	72	122

n.d. = not detected.

-- = not determined.

TABLE B.5 (cont'd)

Sample Element	A-72a	A-72	A-6	A-58	A-82	A-10	I-6	A-16	G-25	A-82a	A-78b	A-85a	A-83a	A-67a
Co	39	36	23	25	59	47	43	55	40	50	48	62	50	44
Cr	23	20	93	92	54	86	64	65	55	29	35	52	52	44
Cu	25	21	72	19	33	70	45	76	48	28	25	40	39	37
Mn	660	555	670	530	865	773	630	915	663	635	720	820	715	585
Mo	24	8	25	70	29	46	12	22	35	49	18	28	21	19
Ni	38	43	69	63	56	72	70	82	49	35	45	62	49	49
Pb	25	45	82	25	40	107	35	250	92	35	50	35	40	45
Se	52	61	60	n.d.	82	84	n.d.	61	20	10	79	65	75	62
Sr	483	606	235	287	365	305	281	320	475	411	390	311	358	353
Zn	79	52	98	56	116	153	108	152	90	85	117	155	112	103

n.d. = not detected.

-- = not determined.

TABLE B.5 (cont'd)

Sample Element	I-7	A-67b	A-53	A-84	G-21	A-2	A-7	G-23	S-19	A-63a	A-61	A-51	A-25	A-18
Co	51	54	28	57	52	44	51	49	38	63	41	46	52	45
Cr	89	52	97	35	70	52	89	98	43	59	49	60	62	33
Cu	100	50	28	39	72	86	100	81	32	55	43	45	97	50
Mn	790	830	565	640	700	600	790	688	484	660	655	660	668	430
Mo	27	68	27	17	24	7	27	24	9	17	58	43	3	9
Ni	81	67	77	79	54	36	81	90	49	67	61	69	71	55
Pb	190	40	30	40	92	70	190	70	28	50	65	35	125	90
Se	47	17	n.d.	78	27	67	47	57	--	36	32	50	45	40
Sr	280	309	491	286	260	190	280	310	533	278	295	185	375	785
Zn	157	163	77	93	190	163	157	133	61	150	123	103	207	85

n.d. = not detected.

-- = not determined.

TABLE B.5 (cont'd)

Sample Element	A-14	A-20	A-85	G-30	A-15	G-11	S-21	G-12	A-17	S-3	G-9	S-17	A-4	A-50
Co	43	54	57	47	46	39	49	57	48	37	31	50	35	50
Cr	46	62	54	93	62	61	78	68	72	95	54	105	66	55
Cu	75	115	37	68	45	84	42	89	76	29	154	41	57	58
Mn	642	820	1065	783	865	805	484	1597	755	641	663	772	750	795
Mo	17	n.d.	27	43	10	19	16	14	41	12	56	n.d.	3	6
Ni	50	76	66	70	58	67	34	70	74	50	47	71	42	69
Pb	120	220	80	92	280	92	36	82	170	48	95	44	65	35
Se	n.d.	114	n.d.	67	n.d.	22	--	41	89	--	20	--	54	47
Sr	1135	390	378	305	380	365	147	325	400	211	220	223	350	278
Zn	189	145	132	122	136	196	109	146	145	152	123	133	164	130

n.d. = not detected.

-- = not determined.

TABLE B.6

Trace element content in the non-detrital fraction of the sediments (in ppm).

Sample Element	G-c	A-71	A-74	R-6	R-4	R-2	R-5	A-13	A-85b	A-54	A-74a	A-78a	A-55
Co	26	12	10	19	20	19	17	23	15	6	21	16	7
Cr	24	8	4	8	15	26	3	n.d.	6	n.d.	3	4	6
Cu	146	8	19	60	54	74	40	21	16	28	n.d.	14	19
Mn	511	171	30	354	769	44	448	339	207	238	137	202	196
Mo	19	21	32	n.d.	47	16	14	n.d.	12	6	31	2	21
Ni	38	26	22	15	47	42	21	23	15	11	17	21	10
Pb	67	13	13	41	66	61	49	84	n.d.	3	6	11	13
Sr	214	1690	1195	67	122	100	135	189	25	118	339	190	232
Zn	106	9	18	46	70	59	43	38	32	38	27	36	24

n.d. = not detected.

-- = not determined.

TABLE B.6 (cont'd)

Sample Element	A-83	A-72a	A-72	A-6	A-58	A-82	A-10	I-6	A-16	G-25	A-67a	I-7	A-67b
Co	7	10	7	8	3	1	13	16	16	6	0.0	20	0.0
Cr	6	7	6	22	19	12	21	0.0	6	1	0.0	9	n.d.
Cu	23	17	39	13	8	n.d.	29	24	32	26	17	56	17
Mn	401	38	141	206	127	522	352	168	425	226	213	283	213
Mo	n.d.	6	4	11	--	6	27	4	10	15	5	14	5
Ni	17	17	23	31	24	13	39	21	40	24	17	39	17
Pb	86	1	16	44	7	22	76	1	n.d.	58	11	135	11
Sr	123	223	327	153	153	n.d.	181	193	195	209	69	178	69
Zn	37	29	18	35	22	78	61	40	49	23	33	58	28

n.d. = not detected.

-- = not determined.

TABLE B.6 (cont'd)

Sample Element	A-53	A-84	G-21	A-2	A-7	G-23	S-19	A-63	A-61	A-51	A-25	A-18	A-14
Co	9	26	24	18	20	16	11	13	9	26	24	22	--
Cr	9	2	12	20	9	29	8	6	8	1	1	3	--
Cu	16	26	49	65	56	46	21	28	26	20	71	31	39
Mn	241	206	356	391	283	296	218	303	255	278	379	173	282
Mo	19	n.d.	7	n.d.	14	8	4	3	36	18	7	2	8
Ni	41	50	14	1	39	51	24	34	24	35	40	38	7
Pb	12	23	60	53	135	38	15	18	28	12	72	9	75
Sr	190	76	144	121	178	179	362	178	192	126	247	546	541
Zn	9	34	106	129	66	76	22	55	34	52	132	18	115

n.d. = not detected.

-- = not determined.

TABLE B.6 (cont'd)

Sample Element	A-20	A-85	G-30	A-15	G-11	S-21	G-12	A-17	S-3	G-4	S-14	A-4	A-50
Co	30	19	7	12	14	14	14	19	--	33	16	18	4
Cr	18	2	21	19	11	14	11	18	--	0.0	17	20	2
Cu	88	20	19	25	33	22	42	45	--	127	25	42	34
Mn	330	597	397	442	321	242	951	348	--	298	400	508	434
Mo	n.d.	12	18	3	12	n.d.	6	25	--	25	n.d.	n.d.	0.0
Ni	39	37	37	27	40	17	35	45	--	28	33	10	49
Pb	100	45	46	n.d.	64	20	48	52	--	68	25	48	16
Sr	256	59	175	250	198	73	202	210	--	81	141	229	196
Zn	49	42	22	45	112	34	112	50	--	46	55	123	40

n.d. = not detected.

-- = not determined.

APPENDIX C

ANALYTICAL RESULTS FOR THE CORE SAMPLES ANALYZED

TABLE C.1

Particle size distribution of selected core samples.

Sample No. Gray olive-green sediment	> 63 μ	16–63 μ	4–16 μ	< 4 μ
S-3.1	--	32	27	41
S-3.2	3	27	38	32
S-3.3	7	20	29	44
S-17.1	1	18	37	44
S-17.2	5	18	32	45
S-17.3	5	19	30	46
BIO 115.1	2	15	39	44
BIO 115.2	1	22	35	42
BIO 115.6	0	10	31	59
BIO 115.13	5	12	28	55
BIO 115.16	--	14	36	50
BIO 115.17	--	18	39	43
BIO 36.1	5	17	20	58
BIO 36.3	--	29	40	31
BIO 36.4	8	18	21	53
BIO 36.7	8	12	27	53
Reddish-brown sediment				
S-21.1	20	22	22	36
S-21.2	26	17	19	41
BIO 115.22	29	20	17	34
BIO 115.23	30	21	15	34
BIO 115.24	40	27	12	21
BIO 115.32	28	18	14	40
BIO 115.38	26	24	14	36
BIO 115.40	25	22	18	35

TABLE C.2

Mineralogy of the coarse fraction in selected core samples. (% number of grains counted).

Component Sample No.	Quartz	Plagioclase feldspar	Potash feldspar	Amphibole pyroxene garnet	Opaque minerals	Granitic rock fragments	Sedimentary rock fragments
S-17.1	52	8	16	3	1	7	13
S-17.3	72	4	9	1	1	2	11
S-3.1	35	15	5	4	4	4	33
S-3.5	56	4	8	1	4	7	20
BIO-36.1	47	8	7	4	2	9	23
BIO 36 (150)	43	7	10	4	2	15	19
BIO 115.2	68	5	1	1	6	1	18
BIO 115 (150)	57	2	8	1	8	2	22
BIO 115 (250)	64	4	5	3	4	2	18
BIO 115 (450)	30	7	7	2	2	12	40
BIO 115 (685)	46	3	8	-	6	1	36
BIO 115 (720)	50	3	4	-	8	1	34
BIO 115 (780)	28	2	6	-	3	4.5	56.5
BIO 115 (823)	46	3	4	-	5	[illegible]	38

TABLE C.2 (cont'd)

Component Sample No.	Quartz	Plagioclase feldspar	Potash feldspar	Amphibole pyroxene garnet	Opaque minerals	Granitic rock fragments	Sedimentary rock fragments
BIO 115 (855)	65	5	6	-	4	-	20
BIO 115 (880)	75	2	4	-	3	-	16
BIO 115 (900)	60	4	5	-	4	-	27
BIO 115 (988)	63	2	6	-	4	-	25
S-21.1	70	3	4	-	9	-	14
S-21.3	70	6	5	-	5	-	14

TABLE C.3

Elemental analysis of the core samples.

Depth in Core	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115	115
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Element	0	50	100	150	175	200	230	285	290	350	400	420	450	455	470	510	550
K	2.23	2.50	2.67	2.62	2.61	2.53	2.55	2.53	2.60	2.68	2.67	2.71	2.75	2.67	2.74	2.70	2.79
Na	1.73	1.68	2.11	16.8	1.83	2.06	2.27	1.88	1.92	1.83	1.79	1.73	1.91	1.67	1.62	1.60	1.70
Ca	1.93	1.77	1.50	1.34	1.66	1.28	1.23	1.21	1.17	1.07	4.41	4.78	0.61	0.65	0.82	0.72	0.81
[illegible]	1.61	1.80	2.05	1.86	1.85	1.84	1.82	1.79	1.87	1.83	1.76	1.74	1.71	1.72	1.80	1.81	1.87
[illegible]	6.49	6.75	7.29	7.15	7.17	7.01	6.99	6.88	6.93	7.02	7.35	7.50	7.43	7.11	7.68	7.00	7.16
Fe	4.53	4.66	4.86	4.83	4.76	4.97	4.78	4.76	4.84	4.89	4.82	4.98	5.06	5.12	4.78	4.99	4.88
Ti	0.66	0.67	0.72	0.61	0.75	0.84	0.77	0.69	0.78	0.77	0.83	0.82	0.86	0.93	0.95	0.62	0.74
Mn/ppm	682	795	657	678	701	692	730	737	747	771	822	764	754	638	681	671	735

TABLE C.3 (cont'd)

Depth in Core	115 18	115 19	115 20	115 21	115 22	115 23	115 24	115 25	115 26	115 27	115 28	115 29	115 30	115 31	115 32	115 33	115 34
Element	600	650	680	686	700	703	720	723	750	800	8	835	843	850	853-74	864-74	?
K	2.57	2.71	2.52	1.95	1.94	2.10	2.06	2.56	2.61	2.21	2.23	2.47	2.50	2.28	2.14	2.25	2.52
Na	1.49	1.64	1.40	1.09	1.07	0.99	1.20	1.38	1.37	1.54	1.30	1.16	1.07	1.27	1.07	0.95	1.53
Ca	0.51	0.59	0.78	0.90	0.923	0.58	0.78	0.65	0.54	1.02	0.57	0.86	3.87	3.32	4.66	4.73	0.86
Mg	[illegible]	1.47	1.47	1.34	1.40	1.25	1.37	1.54	0.52	1.56	1.81	1.35	1.87	1.68	1.45	1.38	1.65
Al	[illegible]	7.54	7.48	6.47	7.64	7.33	6.72	7.33	7.36	6.71	7.13	7.21	6.79	6.44	6.09	6.17	6.76
Fe	4.78	4.83	4.83	4.29	4.42	4.83	4.47	4.85	4.91	4.52	5.04	4.59	4.45	4.13	4.05	4.21	4.69
Ti	0.71	0.67	0.77	0.74	0.64	0.83	0.97	0.72	0.71	0.70	0.72	0.73	0.59	0.60	0.60	0.61	0.64
Mn/ppm	656	637	595	550	565	538	609	583	566	543	600	575	588	557	682	726	755

TABLE C.3 (cont'd)

Depth in Core Element	115 35 890	115 36 900	115 37 950	115 38 980	115 39 992	115 40 1016	115 41 1021	115 42 1040	115 43 1042	115 44 1049	115 45 1060	BIO36 1	BIO36 2	BIO36 3	BIO36 4	BIO36 5	BIO36 6
K	2.47	2.54	2.35	2.34	2.29	2.31	2.38	2.13	2.17	2.18	2.24	2.50	2.49	2.67	2.84	2.76	2.76
Na	1.83	1.77	1.57	1.32	1.50	1.41	1.63	1.16	1.34	1.35	1.41	2.01	2.12	2.04	1.95	2.09	2.02
Ca	1.24	1.13	1.29	1.93	2.18	1.70	1.57	3.55	2.63	1.69	1.13	0.90	1.07	0.29	1.45	0.51	1.69
Mg	1.85	1.89	1.71	1.65	1.67	1.74	1.71	1.39	1.47	1.64	1.62	1.90	1.89	1.96	1.99	1.94	2.04
Al	6.73	6.64	6.43	6.44	6.18	6.51	6.57	6.30	6.48	6.51	6.56	5.67	6.63	6.40	6.73	6.23	6.74
Fe	4.57	4.64	4.39	4.39	4.36	4.51	4.49	4.12	4.37	4.42	4.52	4.78	4.81	5.06	4.92	4.64	4.82
Ti	0.65	0.62	0.61	0.68	0.64	0.70	0.67	0.66	0.68	0.67	0.69	0.64	0.54	0.61	0.68	0.56	0.59
Mn/ppm	730	704	668	601	624	696	728	727	641	655	685	496	501	557	612	644	612

TABLE C. 3 (cont'd)

Depth in Core	BIO36	BIO36	BIO36	BIO36	BIO36	BIO36				S3	S3	S3	S3	S3	S3	S17	S17
	7	8	9	10	11	12	13	?	?	2	3	4	5	6	7	2	3
Element																	
K	2.69	2 62	2.67	2.50	2.31	2.63	2.58	2.26	2.72	2.30	2.38	2.2	2.63	2.27	2.22	2.74	2.30
Na	1.96	1.82	1.79	1.42	1.31	1.18	1.97	1.27	1.12	1.73	1.88	1.74	1.78	1.76	1.71	1.87	2.06
Ca	1 82	2.17	2.16	2.33	2.50	4.05	2.21	2.24	5.09	0.72	0.86	0.79	0.90	0.81	0.80	1.45	0.20
Mg	2.02	1.97	0.95	2.01	2.17	2.28	2.01	2.03	2.32	1.83	1.88	1.86	1.83	1.84	1.80	2.10	1.55
Al	5.76	5.94	6.39	6.62	6.33	5.92	6.32	6.44	5.78	7.04	7.46	7.30	6.26	6.52	6.58	6.76	6.16
Fe	4.67	4.60	4.41	4.50	4.36	4.20	4.64	4.37	4.01	4.54	4.40	4.48	4.60	4.98	4.46	4.82	3.64
Ti	0.59	0.61	0.73	0.64	0.65	0.54	0.65	0.68	0.57	0.88	0.96	0.86	0.91	0.85	0.88	0.88	0.66
Mn/ppm	583	545	542	517	539	578	549	547	526	422	399	472	417	453	408	398	280

TABLE C.3 (cont'd)

Depth in Core Element	S17 4	S17 5	S17 6	S17 7	S21 2	S21 3	S21 4	S21 5
K	2.63	2.74	2.56	2.48	1.60	1.81	2.58	2.19
Na	1.76	1.88	1.98	2.00	0.84	0.86	0.94	0.90
Ca	2.28	1.24	1.84	2.01	1.60	2.47	1.79	1.54
Mg	2.22	2.22	2.16	2.10	1.34	1.74	1.89	1.83
Al	7.00	7.52	7.48	7.60	4.82	4.28	5.90	6.10
Fe	4.76	4.70	4.34	4.82	3.16	3.36	3.08	3.40
Ti	0.83	0.86	0.82	0.87	0.82	0.84	0.72	0.84
Mn/ppm	400	405	343	331	283	269	257	260

TABLE C.4

Trace element content* in the core samples.

Element Sample No.	Co	Cr	Cu	Mo	Ni	Sr	Zn
Core BIO 115 1	61	46	314	21	66	86	311
2	68	77	244	14	72	73	309
3	73	70	151	18	73	74	303
4	74	86	189	22	65	64	310
5	73	79	127	11	70	69	309
6	73	82	107	13	62	63	310
7	74	81	87	3	82	59	300
8	73	82	91	4	67	56	310
9	78	73	130	14	66	53	305
10	77	85	126	n.d.	59	47	311
11	74	84	126	9	65	30	312
12	76	84	133	6	64	33	310
13	76	70	93	8	62	37	175
14	76	79	99	8	62	37	175
15	78	71	103	9	62	44	308
16	71	60	85	9	65	41	310
17	84	85	169	4	79	38	268
18	84	82	112	1	77	27	309
19	82	78	95	1	66	30	123
20	78	83	70	n.d.	68	37	287
21	76	81	118	n.d.	61	29	294
22	75	82	87	n.d.	67	31	306
23	81	89	75	n.d.	75	20	102
24	82	70	58	1	66	20	268

TABLE C.4 (cont'd)

Element Sample No.		Co	Cr	Cu	Mo	Ni	Sr	Zn
Core BIO 115	25	85	81	77	11	74	28	281
	26	94	77	77	5	74	21	228
	27	71	82	48	n.d.	72	45	289
	28	91	163	61	10	126	19	306
	29	77	85	55	n.d.	74	115	254
	30	61	92	68	6	79	112	305
	31	60	70	46	11	65	102	307
	32	61	60	169	2	84	95	309
	33	59	75	46	20	84	95	309
	34	72	80	51	19	65	39	306
	35	71	76	51	9	69	52	240
	36	71	84	45	18	67	54	306
	37	68	76	65	4	73	52	309
	38	63	80	72	7	69	65	307
	39	63	78	64	25	63	70	305
	40	65	68	54	11	68	59	309
	41	67	73	57	12	71	58	269
	42	60	73	47	19	65	84	263
	43	61	82	44	14	63	74	263
	44	68	76	50	22	67	52	302
	45	64	66	48	20	64	50	311
Core BIO 36	1	73	80	66	25	73	52	137
	2	64	77	66	30	69	61	126
	3	67	80	63	28	75	72	127
	4	76	78	58	28	74	79	127

TABLE C.4 (cont'd)

Element Sample No.		Co	Cr	Cu	Mo	Ni	Sr	Zn
Core BIO 36	5	78	68	67	39	66	82	122
	6	76	66	76	26	66	82	117
	7	70	60	71	25	63	81	111
	8	65	69	64	36	63	91	113
	9	67	72	91	27	68	89	113
	10	67	89	99	--	79	67	103
	11	63	127	51	--	87	61	85
	12	58	131	55	--	91	68	75
Core S-3	1	34	40	21	--	38	46	80
	2	37	40	19	--	32	45	69
	3	35	39	16	--	36	54	60
	4	32	40	18	--	35	52	65
	5	33	36	20	--	35	51	67
	6	37	39	18	--	41	49	66
	7	35	35	18	--	31	49	67
Core S-17	1	31	36	19	--	31	69	62
	2	35	41	30	--	36	67	77
	3	33	35	15	--	29	65	47
	4	36	46	17	--	29	65	71
	5	39	50	21	--	37	63	71
	6	33	37	25	--	33	82	65
	7	26	34	--	--	33	98	52
Core S-21	1	27	34	14	--	27	40	28
	2	27	33	16	--	34	30	42

TABLE C.4 (cont'd)

Element Sample No.			Co	Cr	Cu	Mo	Ni	Sr	Zn
Core	S-21	3	31	47	16	--	36	39	45
		4	30	38	18	--	35	41	47
		5	28	39	16	--	40	36	47

* concentrations are given in ppm.

n.d. not detected.

-- not determined.

TABLE C 5

Analyses of the non-detrital trace elements

Sample No		115	115	115	115	115	115	115	115	115	115	115	115	36	36	36	36	36	36	36	36
		1	2	3	6	9	11	16	18	23	27	38	38								
Element		0 cm	50 cm	100 cm	200 cm	290 cm	400 cm	510 cm	600 cm	703 cm	800 cm	890 cm	980 cm	0 cm	50 cm	100 cm	150 cm	200 cm	250 cm	290 cm	350 cm
Fe	A.S(1)	908	865	977	1122	1069	1135	1126	1043	744	1032	1210	1093	827	869	1014	1065	1124	1080	906	1133
	A.H S.(2)	1630	1525	1485	2190	1670	2000	1930	1745	1420	1690	1925	1720	1525	1590	1775	1920	1925	1795	1540	1850
	2-1	722	660	508	1068	601	865	804	702	676	558	715	627	698	721	761	855	801	715	634	717
Mn	1	179	195	173	176	185	200	178	171	160	156	188	163	68	75	88	112	126	96	137	164
	2	226	278	219	235	267	312	243	223	207	190	231	200	71	78	99	129	148	103	162	207
	2-1	47	83	46	59	82	112	65	52	47	34	43	37	3.0	3.0	11.0	17.0	22.0	7.0	25.0	43
Co	1	8.0	7 0	7.7	7 5	6.6	5.1	6.8	4.6	2.9	5.5	5.7	4.8	3.5	4 0	5.1	5 7	9.5	6.8	7.9	9.5
	2	9 0	7 5	7 5	9 0	8 5	6 0	6.5	6.0	4.5	7 0	5 6	5 5	6.5	6.0	7.5	9.0	9.0	6 5	7 7	9 [illegible]
	2-1	1.0	0.5	--	1.5	1 9	0.9	--	1.4	1.6	1.5	--	0.7	3.0	2.0	2 4	3.3	--	--	--	--
Ni	1	25 0	24.0	18.7	17 2	14 5	11.7	11.0	7.9	5.3	8.4	11.7	10.3	10.6	12.1	15 2	12.5	11.2	13.2	14 1	20 [illegible]
	2	30.0	31.0	22.5	25.5	20.5	16.5	19.5	18.5	11.5	16.5	18.5	23 5	22 0	20.5	29.0	27.0	27.5	22.0	25 0	29.5
	2-1	5 0	7.0	3 8	8 3	6 0	4.8	8.5	10.6	6.2	8.1	6.8	13.2	11.4	8.4	13.8	14.5	16.3	8.8	10.9	9 3
Cr	1	4 4	4 2	4 4	4.6	7.3	4.2	4.8	5 9	2.0	3.1	4 6	4 0	4 0	5.3	4.6	5 1	6 2	4.6	3 7	4 0
	2	12 5	24.0	10.5	8.5	7 5	20.5	8 0	7.0	6.0	7.0	7.5	7 0	8 5	5 5	6 5	6 5	6 5	9 5	[illegible] 5	
	2-1	8.1	19.8	6.1	3.9	0.2	16 3	3 2	1.1	4 0	3.9	2.9	3 0	4.5	0 2	1.9	[illegible]	[illegible].3	[illegible] 9	[illegible] 5	-
Cu	1	122.0	134 2	94.6	83 2	86 0	161.7	46.6	62.9	52.6	31.2	38.1	48.8	29 3	30.1	37.0	29 7	109.3	54.6	6[illegible]	29 3
	2	140.5	130	91.0	82.5	90.5	-	57.5	65.5	59.0	33.5	39.5	42.0	31.0	31.5	37.0	36.0	-	53.0	72.5	30 0
	2-1	18.5	-	-	-	4.5	-	10.9	2.6	6.4	2.3	1.4	-	1.7	1.4	-	6.3	-	-	9.1	0.7
Zn	1	128	125	123	123	118	125	123	121	36.0	125	10.6	118	51.0	37.0	47.0	39.0	59.0	22.0	30.0	[illegible]
	2	274	265	266	273	253	277	274	260	47 0	240	160	264	49.0	37.0	29.0	25	35 0	24.0	20.0	[illegible]
	2-1	146	140	143	150	135	152	151	139	11.0	135	54.0	146	-	-	-	-	-	2.0	-	-

1 Acetic acid extract

2 Acetic acid-Hydroxylamin hydrochloride mixture effect.