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GEOCHEMICAL STUDIES OF RECENT SEDIMENTS FROM THE GULF OF ST. LAWRENCE.

I. DISTRIBUTION OF MAJOR AND MINOR ELEMENTS.

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ABSTRACT

The distribution of the major and minor elements in some recent sediments from the Gulf of St. Lawrence has been determined. In discussing the results, considerations were given to such factors as particle size, clay mineral assemblage and bathymetry of the Gulf. The results underline the importence of settling from suspension as a mode of deposition for fine material in the deep areas of the Gulf. The main mode of occurrence of major elements was indicated. The majority of the elements are already present within the lattices of various minerals when they enter the basin of deposition.

INTRODUCTION

Early work on the Geochemisty of sediments was largely confined to studies of the distribution of one or a limited number of elements through a range of samples having no close geological or environmental relationship. More recent studies, indicated, hoever, that a geochemical study confined to a single stratigraphical horizon could be of great importance (see for ex. Hirst, 1962). In such investigation, the physico-chemical conditions of sedimentation must be deduced, since obviously they can not be directly observed. Some values should therefore attach to a geochemical study of modern sediment accumulating in a restricted basin. The Gulf of St. Lawernce offers possibilities of well controlled studies, as sediment sources are only few and well idintified, also sites of deposition vary, over small distances from shallow shelves and platforms to deeper troughs and basins.

MATERIAL AND METHODS

Geographical Setting

The Gulf of St. Lawrence is an inland sea occupying an area of about 226.7 X 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).

It is bounded by Quebec and Labrador to the north; Newfoundland and



Fig. (1) Bathymetric chart of the Gulf of St. Lawrence.

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, stricty speaking, the St. Lawrence estuary is usually considered as the region extending between Quebec City and Pointe des Monts (Forrester, 1967).

The river is fedy by the Great Lakes, has a total drainge area of 513 X 10^3 sq. km., and a mean yearly discharge at Quebec City of about 10.2 X 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.

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 X 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).

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.

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.

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, grandiorites, syenites, ultrabasics, gneisses and schists of the Canadian Shield. Paleozoic sediments are made up principally of limestones and shales.

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.

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 veines and molybdenum occurrences.

Anticosti, Mingan and Magdalen Islands:

On the Mingan Island, 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 Appal achian 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 cabonate sediments. These thin-out futher 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 limestones outcrop around St. Georges Bay (Figure 1).

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 up-lift have made available large quantities of easily eroded material as potential source of sediments (Karrow, 1961; Prest, 1961).

Samples Collection

Core samples were collected from the Gulf of St. Lawrence, during 4 cruises to the Gulf, using piston and gravity corers. Location of sampling stations as well as water depths are given in Table 1. and are shown a Fig. 2.

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Sample No.	Longitude	Latitude	Water depth	Sample No.	Longitude	Latitude	Water depth
A- 2	60° 06' W	47° 16' N	238	S-17	65°33'W	49° 36' N	410
A- 4	59° 34' W	47° 32' N	468	S- 3	63°08'W	48° 34' N	372
A- 6	58° 31' W	49° 50' N	151	S-21	60° 11' W	48° 17' N	345
A- 7	.59°09 W	50° 03' N	241	S-19	62°27'W	49°49'N	270
A-10	61°30'W	49°51'N	182	A-50	59°43'W	47° 24' N	470
A-13	96° 00' W	50° 02' N	113	A-51	59°52'W	48° 54' A	288
A-14	65°54'W	49°46'A	315	1-6	58°42'W	49°49'N	187
A-15	65°59'W	49°35'N	324	A-53	58° 00' W	50° 04' N	220
A-16	65°48'W	49° 17' N	189	A-58	57°52'W	50° 10' N	157
A-17	64°40'W	49°26'N	369	A-54	59°20'W	50° 22' N	118
A-18	63°41'W	49° 22' N	309	A-55	58° 32' W	50°47'N	131
A-20	64°02'W	49° 04' N	320	A-63	61°35'W	49°37'N	275
A-25	62°46'W	48°47'N	297	1-7	59° 11' W	50° 02' N	205
R- 2	61°39'W	46°36'N	61	A-61	60° 14' W	49° 24' N	275
R-4	62°20'W	47° 04' N	57	A-67a	62°24'W	50° 09' N	202
R-5	63°06'W	47° 46' N	70	A-71	63°25'W	50° 07' N	47
R-6	63°24'W	48°04'N	53	A-72a	63°23'W	49°59'N	148
G- c	61°45'W	45°57'N	31	A-74a	64° 17' W	50° 04' N	124
6-9	63°55'W	45°57'N	377	A-78a	65° 12' W	80°09'N	124
6-11	65°52'W	49° 23' N	335	A-82	66° 36' W	50° 02 'N	170
6-12	66° 02' W	49°41'N	350	A-83	66°50'W	49° 45' N	146
6-21	59°05'W	49°35'N	234	A-84	66° 33' W	49° 34'N	230
6-23	87°39'W	50° 39' N	264	A-85	66° 33' W	49° 19' N	320
6-25	58° 11' W	51° 02' N	197	A-67b	3 miles wes	t of 67a	212
6-30	60°49'W	51°02'N	322	A-72	3 miles wes	t of 72a	149
A-74	5 miles wes	st of 74a	50	A-85b	4 miles sou	ith of 85	113

TABLE 1 Core locations and water depths.

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Location of sampling stations.

The top 3 cm of the cores were used for the present work.

Methods of Analysis

The following parameters were measured CO_3 , C, N, P, Na, K, Ca, Mg, Al, Fe, Ti and Mn. Si was calculated assuming that the tatal oxide of the major elements account for 100% of the composition of the samples.

 CO_3 was determined gasometrically, organic carbon was measured following the method described by El-Wakeel and Riley (1957). Nitrogen was determined by the micro-kjdahl method. Phosphers was measured calerimetrically following the method describel by Murphy and Riley (1962).

Other elements were anlyged on a Perkin Elmer M 403 atomic absorption spectrophotometer. Details of the methods of analysis are described else where (Beltagy, 1973).

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frm 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 occurs 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.

Phosphorus

Total phosphorus (as P_2O_5) shows a nearly uniform distribution in the Gulf sediments. Its content varies between 0.10% 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 contents 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.

Aluminum

In samples collected from depths greater than 300 m, Al was found to vary between 4.45% and 9.80% 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 3 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 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 16.70% Al (Kerr, 1959), as against 10.30% to 13.40% 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 these from 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 3)' supports the idea that these sediments have been mainly transported in suspension from this source.

Titanium

The Ti content of the analyzed sediments varies between 0.26% and 0.88% (average 0.48%). Table 4 shows the Ti values obtained as compared to other values reported in the literature.

Data in Table 4[:] indicate 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 follow the concentration of Al fairly closely, despite marked changes in grain sizes. However, the

TABLE (3)	
Variation of Al with depth in surface sediments of the Gulf an	d
Al values for different geological material reported in the litera	ture.

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Average		A1 2	0
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	7.1	
	estuary, (Smith, 1973, P.C)		
14	deep water pelites, Gulf of St. Lawrence (Nota	7.75	
	and Loring, 1964)		
7	shallow water pelites, Gulf of St. Lawrence (Nota and	7.52	
	Loring, 1964)		
3	up-river pelities, Gulf of St. Lawrence (Nota and	8.92	
	Loring, 1964)		
39	granodiorites, Canadian Shield (modified from	9.05	
	Maxwell et al., 1965; Dresser and Denis, 1944)		
-	lgneous 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	

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Averge		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	1.0	0.16
	St. lawrence		
13	suspended matter from the St. Lawrence	0.84	
	estuary, (Smith, 1973, P.C.)		
-	lgneous 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 (4) Ti content in sediments from the Gulf, together with Ti content in different geological materials, reported by other workers.

data reported in Table 5: do 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. TABLE (5)

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

Average		Ħ	A)	e I	A1/T1	Ð	Fe/I†	0
	shallow water samples < 100 m	0.39	8.63	3.7	22.5	1,95	6'6	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 btween	0.47	7.16	4.13	15.6	4.5	9.4	2.4
	200 and 300 m							
14	samples from water depth > 300 m	0.50	7.23	4.25	14.6	5.6	9.2	2.8
νΩ.	suspended matter samples from all	1.0	8.4	10.0	8,44	10.0	10.0	0.4
	over the Gulf							
13	suspended matter samples from	0.84	7.1	4.80	8.4	'	5.7	,
	St. Lawrence estuary, (Smith, 1973, P.C.)							
	Hydrolyzate sediments (Goldschmidt, 1954)	١	r	ı	25.0		,	t

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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 6 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 which are higher than the average for the Canadian Shield. Fe is covariant with Al, with 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 isomporphous substitution. and (iii) as Fe oxides precipitated or absorbed on the surface of the mineral plates. 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 hematite. 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. and (ii) according to Loring and Nota (1968) Fe occurs in the sediments mainly as Fe^{+2} , which is the from 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 biological derived Fe has also been stressed by several workers, e.g. Clark and Wheeler (1922), Bradley and Bramlette (1942), and Revelle (1944).

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-detrial Fe is mainly incorporated into the sediments as ferro-manganese precipitates.

Iron

TABLE (6)

Variation of Fe content with depth, together with the Fe/Al ratios in

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Average		Fe %	0	Fe/Al	0
1	shallow water samples from water	3.7	0.75	0.43	0.11
50	depth < 100 m. samples from water depth between	3.64	0.85	0.46	0.14
12	100 and 200 m. Semples from water depth between 200 and 300 m.	4.13	0.58	0.60	0.15
14 5	somples from water depth > 300 m. suspended matter samples from the	4.25 10.00	0.30	0.58 1.20	0.07 0.05
13	Gulf. suspended matter samples from the	4.8		0.68	,
	St. Lawrence estuary, (Smith, 1973, P.C.) Canadian Shieid rocks (Grout, 1938)	3.98	•	0.78	•

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 7).

Mg may be present in the amphiboles, pyroxenes or clay minerals (as indicated before, less than 1% of the Mg is associated with carbonates). As the first two components are present only is 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 amtter 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 2μ to 63μ fraction. Chlorite particles may vary considerably in size. Gibbs (1967) found that chlorite particles in a samples from the Amazon River vary in size from less than 1μ to 32μ . Also, Griffin et al (1968), who examined some samples from the Gulf of St. Lawrence, found that chlorite exists in the whole particle size specturm.

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

Calcium

The average Ca content in the fine fraction of the sediments obtained from different depths in the Gulf is summarized in Table 8, together with values reported for different geological materials by other workers.

The results indicate that Ca become more abundant with depth. On the other hand, it is clear that calcareous rocks exert a content on the distribution of Ca (Figure 3). Samples from shallow waters are generally lower in Ca than deep water samples. This is ture for 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 plagiolclase feldspar, which is a dominant mineral in rocks along the north shore. Only minor amounts of Ca could be present as apatite, since phosphorus is very low.

On the average, 63% of the total Ca is associted with acid soluble phase (mainly CaCO₃) of the fine fraction, while Loring (1972, p.c.) working on the whole sediment found 54% of the Ca in the non-detrial component.

TABLE (7)

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		¥ 6¥	0	Mg/Al	0	Mg/Fe	0
~	shallow water samples from	1.4	0.15	0.16	0.02	0.40	0.10
8	water ueptin < 100 m. Samples from water depth between	1.69	0.24	0.22	0.07	0.46	0.15
12	JUU and 2UU m. 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	1.69	0.16	0.24	0.06	0.41	0.06
ъ.	out of the samples from a subjection of the second subjections of the subjections of the second seco	4.1	0.85	0.48	0.04	0.40	0.02
ı	lgneous rocks (Rankama and Sahama, 1950)	1.26					
•	Silts and shales and muds (Goldschmidt, 1954)	0-1:51					
	Argillaceous sediments (Rankama and Sahama, 1950)	68.0					
12	Gulf of Paria clay (Hirst, 1962)	1.32					

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TABLE	(8)
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Average calcium content in the Gulf sediments and in different

rock formations reported in the literature.

Average		Ca 🕱	0
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	1.94	0.70
	A-18 and 20)		
55	samples from the Gulf of St. Lawrence.	2.34	
13	suspended matter samples from St. Lawrence estuary	2.45	
	(Smith, 1973, P.C.)		
-	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	

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 correlated, indicate that carbonate minerals derived from calcareous outcrops in or around the Gulf are low Mg limestones.

Sodium and Potassium

In the geochemical cycle, Na and K become separated during weathering and deposition processes (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 9' 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.



Fig. (3) Distribution of calcium in the analysed samples of the Gulf sediments (wt. %).

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 distirbution 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 divided feldspars are retained in suspension, while K-rich clays tend to settle out. This is to 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.

TABLE
9

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Variatiun of Wa and K with depth in the Gulf sediments, together with the Ma/K ratios and the same for other materials as reported elswhere.

l			Į				
Average		Na X	0	×	•	Na/K	•
2	sedIments from water depth < 100 m	1.52	0.07	1.94	0.05	0.78	0.02
	(Morth Shore)						
σ	sediments samples from water depth	0.72	0.07	2.52	0.14	0.29	0.09
	< 100 m (magdalen Shelf)						
8	samples from water depth between	0.51	0.2	2.42	0.14	0.60	0.10
	100 and 200 m.						
12	samples water depth between	1.32	0.16	2.35	0.35	0.53	0.05
	200 and 300 m.						
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	3.84	0.85	2.6	0.45	0.47	0.09
	over the Gulf.						
13	suspended matter samples from the	2.90		2.57		1.12	
	St. Lawrence estuary, (Simth, 1973, P.C.)						
'	Igneous rocks (Rankama and Sahama.	2.83		2.59		1.09	
	1950)						
•	Argillaceous sediments (Rankama and	0.97		2.70		0.36	
	Sahama, 1950)						

It was pointed out earlie 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 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.

CONCLUSION

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.

Some information is also provided as to the main mode of occurrence of the major elements. Becouse of the high Fe/Al ratio in the sediments and the dominance of illite among the clays, it has been suggested that Fe^{+2} 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 suspensoins 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 organic matter deficient in nitrogen being supplied to the sediments.

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