

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

**II. GEOCHEMISTRY OF TRACE ELEMENTS.**

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**ABSTRACT**

The abundance of the elements Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, Se and Zn in the recent sediment of the Gulf of St. Lawrence were studied. The mineralogical associations of the trace elements, was inferred from the study of the detrital fraction of the sediments. The detrital character of the elements decreases in the order Cr > Co > Zn > Mn > Mo > Ni > Pb > Cu > Sr.

Statistical analysis of the results of the non-detrital fraction suggest that sorption by organic matter is important for Co, Cr, Cu, Ni, Pb and Zn. Precipitation in association with Fe, Mn hydroxide provides major depositional pathways for Cr, Cu, Pb, Zn and Se. Carbonate may contribute to concentration of Co, Pb, Mo, and Sr. Adsorption on the clay particles appear, to be particularly efficient for removal of Mo from sea water.

**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 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 recent years (Goldberg et al., 1971; Brown Jr., 1971; and Turekian, 1971). For the region of the Gulf of St. Lawrence, published information is lacking, except for Mn (Loring and Nota, 1968).

The following discussion on trace elements in the fine fraction of the Gulf sediments, makes use of the distinction between the detrital and non-detrital fractions. 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.

#### **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; and 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, 1962 b). High rates of sedimentation presumably do not allow for trace elements to enter 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 impossible to remove separately carbonates of detrital and biogenous origin (Wangersky, 1970, p.c.), 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; iii) since it is impossible 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: 1) Paleozoic carbonate rocks have been reported elsewhere to contain very small concentrations of various trace elements, and 2) If the samples collected from nearby carbonate sources are excluded, the average  $\text{CaCO}_3$  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; and 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).

### MATERIAL and METHODS

#### a- Material

Core samples were collected from the Gulf of St. Lawrence (See Beltagy and d'Anglejan, 1982 a). Location of the sampling stations are shown in Figure 1 a & b.

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

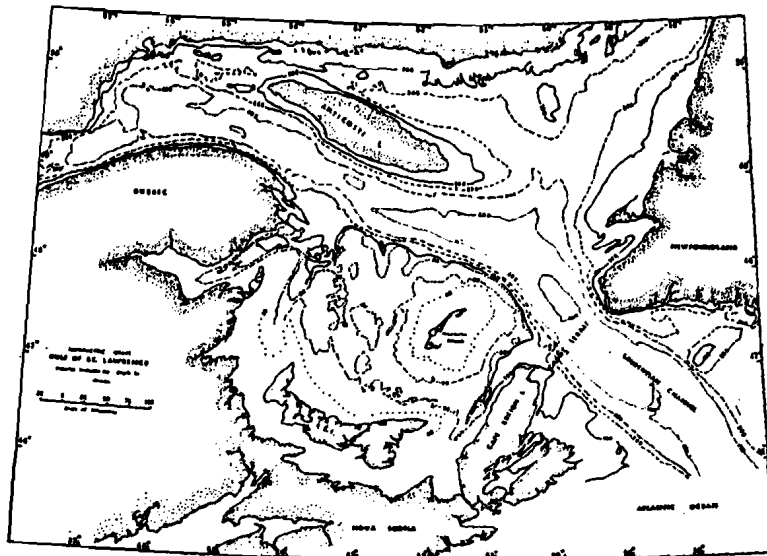


Fig. (1 a)  
Bathymetric chart of the Gulf of St. Lawrence.

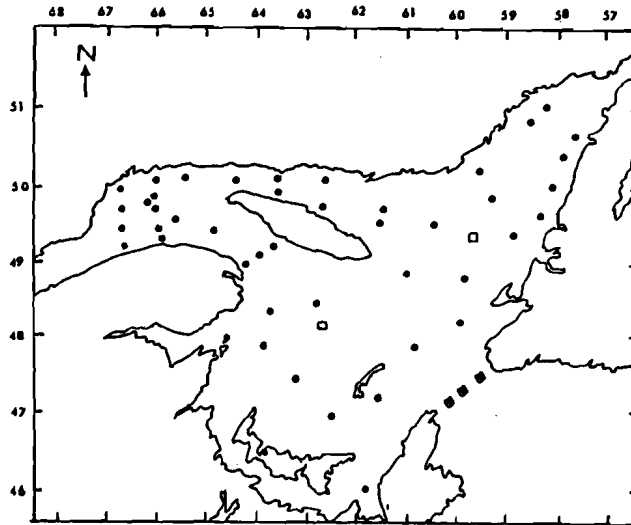


Fig. (1 b)  
Location of sampling stations.

**b- 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 reagents of 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 described elsewhere (Beltagy, 1973).

**RESULTS**

Analytical results for both the non-detrital fraction and the total trace element content of the fine fraction, are given elsewhere, (Beltagy, 1973). In the following discussion the elements are dealt with in alphabetical order, except for some pairs of elements usually treated together in the geochemical literature.

### Chromium

Detrital Cr: the average detrital Cr content of sediments from various depth intervals is given in Table 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 1). The Cr content of the detrital fraction of the deep water samples (> 200m) 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 100m, 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 2, 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.

### 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 analysis show that there is a negative correlation between the element and the carbonate content (-0.33), a positive correlation between Cr and both organic carbon (+0.40) and non-detrital Mn (+0.44).

The negative correlation between Cr and the carbonate content in the Gulf, confirms observations made elsewhere (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.

TABLE I  
 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							Total Cr ppm		
	Cr ppm	0	Cr/Al*	0	Cr/Fe*	0	Cr/Mg*		0	Cr/K*
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. Gulf Sediments.	74.0	14.0	10.1	1.48	23.54	4.50	30.70	6.79	35.75	4.49
55 Argillaceous pelagic sediments (El-Wakeel and Riley, 1961)										59.0 ± 22
12 near shore muds from the Gulf of Paria (Hirst, 1962)										55.0
38 North Atlantic Sediment (Chester and Messiha-Hanna, 1972)										31.0

\* Ratios X 10<sup>4</sup>

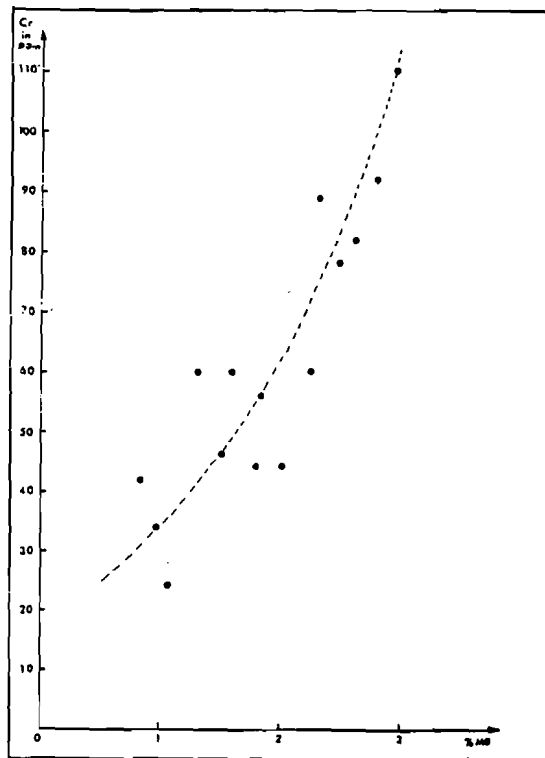


Fig. (2)  
Relationship between detrital Cr and detrital Mg.

### 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 2).

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 of 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 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 3). 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.

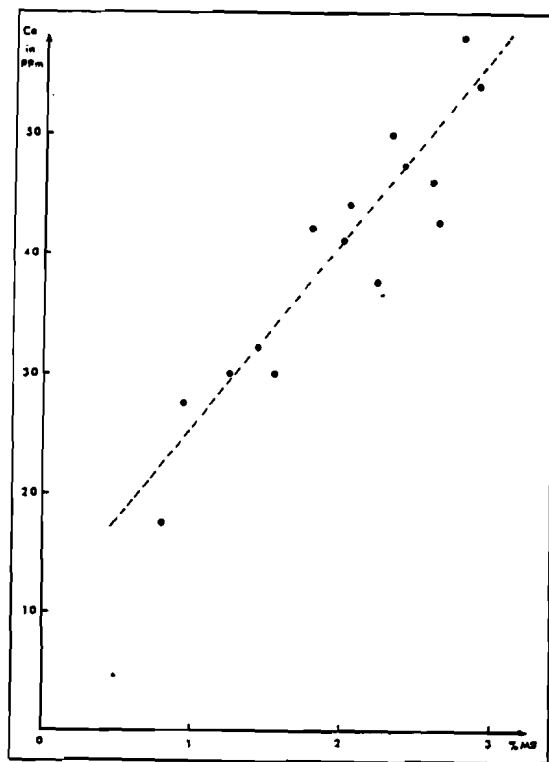


Fig. (3)  
Relationship between Co and Mg contents in the detrital fraction.

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  $\text{Fe}^{+2}$  and  $\text{Mn}^{+2}$  which tend to replace Mg (Grim, 1968). There is no evidence that Ni is associated with any specific clay mineral.

#### 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 were calculated. 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.

Co show a positive correlation with carbonate (0.36) and a negative correlation with organic carbon (-0.51), 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 (-0.36) and positively with organic carbon (+0.32). Here, sorption on organic matter appears to be important.

#### 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 3, 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.

Table (1)  
 Cu and Pb content and their ratios with Al, Fe, Mg and S in the sediments from the Gulf  
 of St. Lawrence, compared with other data from the literature.

Average	Data (1)																		
	Cu	Pb	Cu/Al	Pb/Al	Cu/Mg	Pb/Mg	Cu/Fe	Pb/Fe	Cu/S	Pb/S									
7	17.0	8.0	32.0	16.0	2.52	1.68	6.1	3.05	16.85	8.7	26.85	21.25	7.84	3.95	15.43	9.1	8.21	2.87	16.41
28	16.0	7.1	24.0	9.5	2.26	1.30	2.88	1.35	7.45	3.37	14.9	2.35	4.22	2.29	9.91	2.23	7.22	3.26	12.64
12	23.5	7.9	21.5	22.2	3.54	1.88	4.94	2.82	12.7	6.82	16.21	7.96	8.60	2.79	10.22	5.25	11.26	3.26	17.24
12	36.2	15.1	56.0	31.1	5.26	2.22	7.46	6.45	14.12	3.8	15.26	5.27	11.87	4.41	17.88	11.00	19.20	9.15	27.4
--	70.0																		
--	43.0																		
6	17.0																		
7	50.8																		
--	20.0																		

\* Multiplied by 10<sup>4</sup>

† Total samples

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.

#### Non-Detrital Pb and Cu

Non-detrital 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 (see later).

Non-detrital Pb strongly correlate with non-detrital Mn (+0.42), while there is no correlation between Pb and organic carbon. On the other hand, Cu correlates positively with organic carbon (0.64), and shows a relatively weaker correlation with non-detrital Mn (+0.35).

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.

#### 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 4), 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 contiguous to the Gulf. Contributions from other detrital phases are unlikely, as Mo is not a trace element of calys or other major minerals ( Vlasov, 1966 ).

##### Non-Detrital:

Non-detrital Mo averages 46% of the total Mo content. The degrees of correlation between non-detrital Mo and the reference parameters were calculated. 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 shown elsewhere (Krejci-Graf, 1972) to have Mo content below detection

Table (4)  
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	0	Total sediments	0		
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, 1935 b)					up to 32	
-	Igneous rocks (Sandell and Goldich, (1943)	15.0					
-	Sediments from streams and rivers of Bathuret area, New Brunswick (Boyle et al., 1966)	2-98.0					
-	Soils from Alabama (Clark 1973)						up to 170

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 (Bethel, 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.

### **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 4). 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) ferromanganese 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 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)<sub>3</sub> (Chau and Riley, 1965). As ferromanganese 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 4. Some degree of association between the two elements may be inferred from that figure.

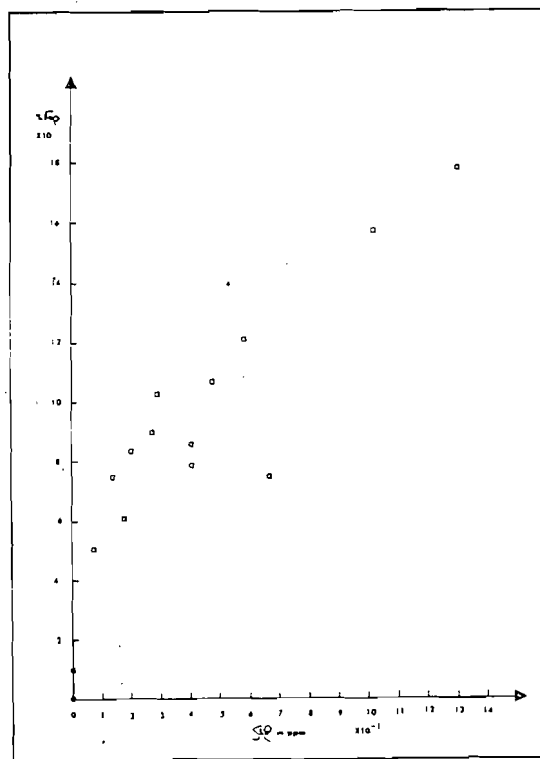


Fig. (4)  
Relationship between total Se and non-detrital Fe in the Gulf sediments.

## 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 ( $\sigma = 338$  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 5.

According to Vlasov (1966), Sr does not enter the clay minerals as an isomorphous inclusion, contrary to its behaviour in igneous aluminosilicates, 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

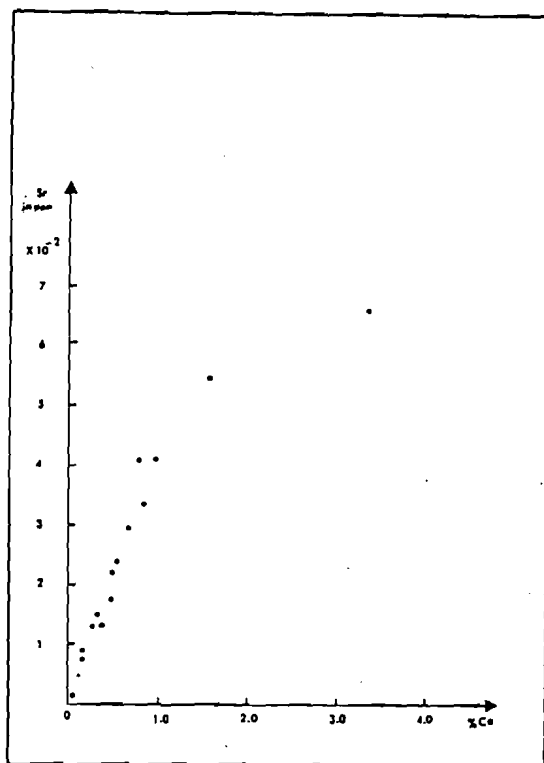


Fig. (5)  
Relationship between Sr and Ca contents in the detrital fraction of the Gulf sediments.

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 granitic rocks from basaltic ones (Wehmiller, 1972).

#### Non-Detrital Sr:

Non-detrital Sr accounts on the average, for 68% of the total Sr, with a range between 40% and 90%.

This fraction may have been interduced in the sediments by either one or both of the following pathways: i) co-precipitation with  $\text{CaCO}_3$  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 (+0.57) 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 accommodate Sr. The remaining may be detrital calcite from local limestones.

## 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 ( $\sigma = 37$  ppm).

Figure 6 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.

## 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 5. The Fe content and Mn/Fe ratios are also indicated. Figure 7 shows the relationship between detrital Mn and Mg in the sediments.

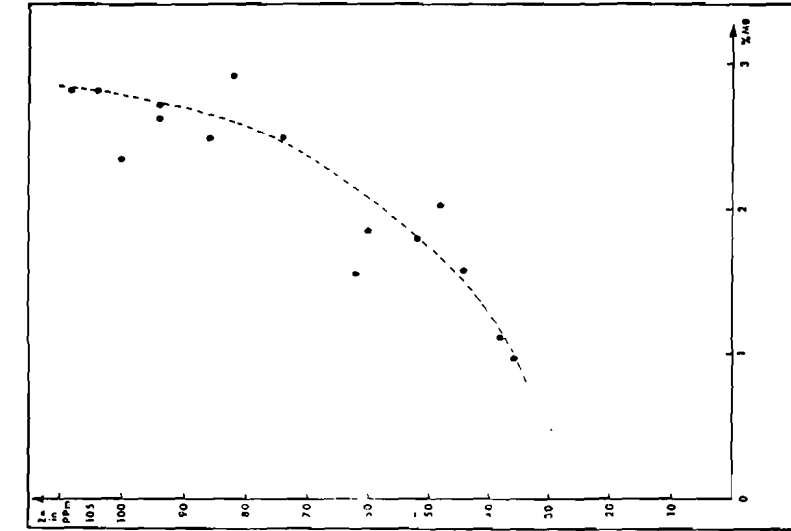


Fig. (6. b)  
Relationship between detrital Zn and detrital Fe

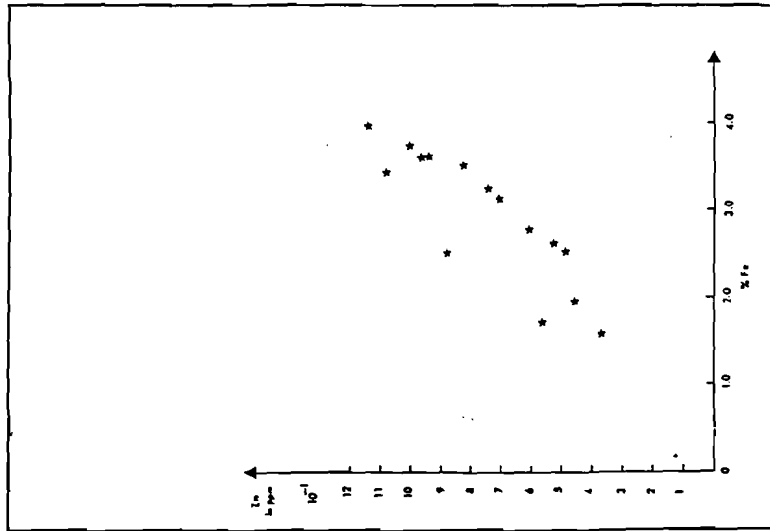


Fig. (6. e)  
Relation between detrital Zn and detrital Mg

Table (5)

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		0	Total sample			
		Fe	Mn		Mn/Fe*	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 Noto, 1968)					4.24	720	170
-	Canadian Shield (Grout, 1938)	3.98	560	140				
-	Delta clays from the Gulf of Paris (Hirst, 1962)	4.21	500	120				
-	Igneous rocks (Goldschmidt, 1937)	5.0		200				
-	Igneous rocks (Clark and Washington, 1924)		1000					
Mn is given ppm	Fe is given %							
								* Ratios X 10 <sup>4</sup>

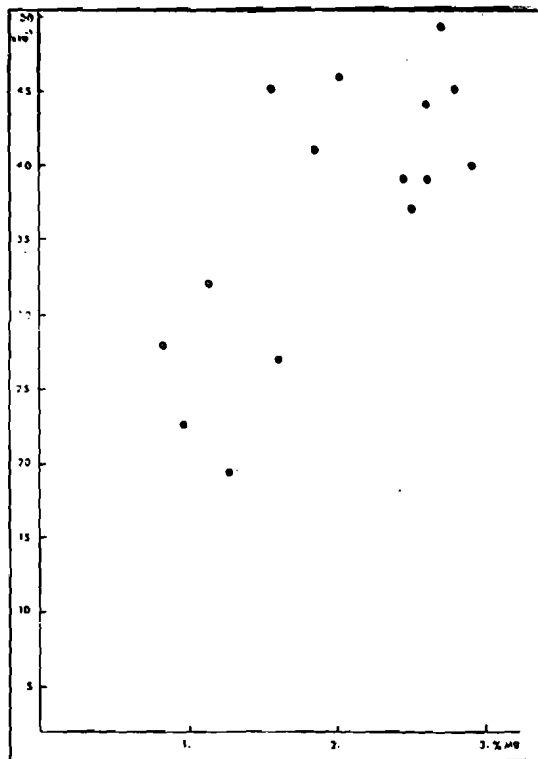


Fig. (7)  
Relationship between Mn and Mg contents in the detrital fraction of the Gulf sediments.

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 7 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 Fe exists (Figure 8).

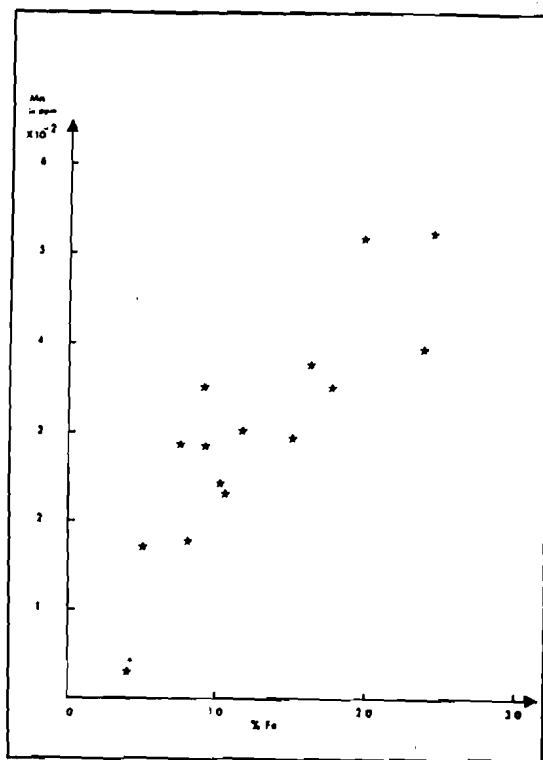


Fig. (8)  
Relationship between non-detrital Mn and  
non-detrital Fe in the Gulf sediments.

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 (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 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).

### DISCUSSION AND CONCLUSION

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 water-sediment interface. This point is illustrated by the variations in elements 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 6). 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.

Table (6)

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

It is difficult to estimate quantitatively 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 6); after normalization to 10.5% CaCO<sub>3</sub>, 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).

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 Co, 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 7), 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

Table (7)  
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 (1962 b)

\*\*\* Beltagy (1969)

\*\* Chester and Messiha-Hanna (1970)

-\* Smith (1973, P.C.)



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.

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