THE GEOCHEMISTRY OF AN ARCTIC WATERSHED

A STUDY OF THE GEOCHEMISTRY OF AN ARCTIC WATERSHED

By

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SCOPE AND CONTENTS: The clay mineralogy and elemental chemistry of soil and sediment samples from a small area of the Canadian Arctic Archipelago were examined. The importance of mineral-water reactions and the distinctive features of the geochemical cycle in polar regions are discussed. New data are presented for Hg, Au and Pd in near-shore sediments. In the case of Au and Pd the study was extended to include pelagic sediments from other oceans, and these results are discussed in an appendix.

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CHAPTER I

INTRODUCTION

The purpose of this study was to investigate the mineralogy and geochemistry of Recent sediments in Fitzwilliam Strait and Marie Bay, and soils from the adjacent source areas. The sampling program employed was designed to allow investigation of the importance of mineral-water reactions in an Arctic watershed, and involved collection of sediment cores and source region soil samples from a restricted area. In the course of the research the determination, by neutron activation, of Au, Pd and Ir in these materials was undertaken. The literature contains few data for the concentrations of these metals in marine sediments in general, and the study was expanded to include pelagic sediments from the Pacific and Antarctic Oceans. The results of these determinations and a discussion of the marine geochemistry of Pd and Au appear in Appendix A.

Fitzwilliam Strait lies between Prince Patrick and Melville Islands in the Canadian Arctic Archipelago, some 650 miles north of the Arctic Circle (Fig. 3). Marie Bay occupies the northwestern corner of Melville Island, and opens into Fitzwilliam Strait to the west (Fig. 4).

The sedimentology and paleontology of Recent sediments from a number of localities on the Canadian polar

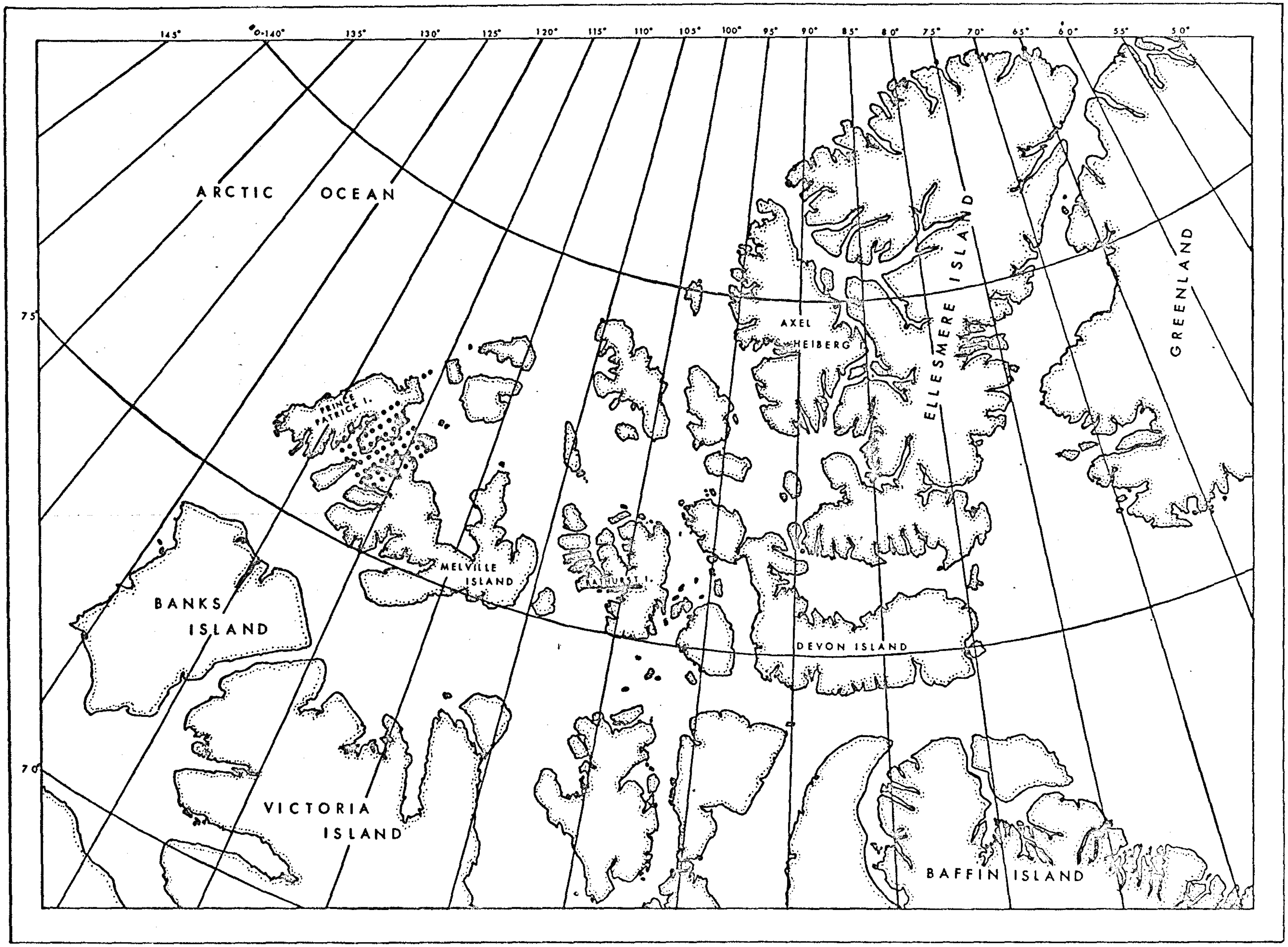

Fig. 3. Location map. Study area dotted

continental shelf have been studied in detail, but, to the writer's knowledge, no extensive chemical investigations have been made. It was thought that analyses of sediment and source region soil samples from a restricted area could contribute toward a better understanding of the geochemical cycle in the unique environment of a polar region.

CHAPTER II

GEOLOGIC SETTING

Provenance of the sediments

The extremely fine-grained nature of the sediments suggests that bottom currents are weak, and that current transport of sediments is not the predominant mode in the area under investigation. Continuous ice cover prevents wave turbulence, so that the fine sediments exist even in shallow waters. It is therefore assumed that the source areas for the sediments in Marie Bay and Fitzwilliam Strait are the land masses immediately bordering the study area, and the chemistry and mineralogy of the sediments support this assumption. The reconnaissance geology of the area has been described by Tozer and Thorsteinsson (1964), and the following summary is derived primarily from their report.

Drainage into Marie Bay is predominantly from the Canrobert Hills to the south. The rocks of this area are paleozoic sediments, consisting of Ordovician and Silurian shales which overlie Cambrian (?) carbonates. Some marine and(?) non-marine sandstones and conglomerates of Middle Devonian and Middle Pennsylvanian age also outcrop in this region.

Rivers entering Fitzwilliam Strait from Melville Island north of Marie Bay, from Prince Patrick Island, and from Eglinton Island drain large areas of Jurassic and Cretaceous sediments. These comprise marine and non-marine sandstone, marine shale, some conglomerate and local coal. An outcrop of tar sand has been reported north of Marie Bay (Trettin and Hills, 1966).

Rate of Sedimentation

Using paleontological evidence from sediments collected a short distance from the present study area, Vilks (1968) has calculated a tentative sedimentation rate of 4.4 cm/1000 yr over the last 8000 years. This is the only estimate available at the present time.

Environmental Conditions

The area of investigation is a "cold desert" region. A compilation by the writer of meteorological data (taken from "Arctic Summary", a semi-annual publication of the Canadian Department of Transport) showed that for the 10 year period 1954 to 1964 the weather station at Mould Bay (see Fig. 4) recorded average January and July temperatures of -27°F and 40°F respectively. Annual precipitation for this period averaged 3.60 inches.

Fitzwilliam Strait has a U-shaped bottom profile, probably the result of glacial gouging. Depths in the central portion of the strait are near 400 meters. Water sampled at

300 meters had a salinity of $34.8^{o}/_{oo}$ and the temperature at the same depth (recorded in July) was 0.00°C.

The extreme climatic conditions strongly affect the erosional and depositional environments, and consequently the geochemistry of the sediments. Some of the most important factors are:

1. Lack of large scale chemical weathering because of permafrost, lack of precipitation and lack of vegetation.
2. Lack of vegetation and frequent strong winds make eolian transport relatively important.
3. Low water temperatures preclude large amounts of precipitated sediment such as $CaCO_3$.
4. There is little evidence of sediment turnover through the action of burrowing or other bottom organisms.

CHAPTER III

METHODS

Collection of the samples

All samples were collected in May, June or July 1967. Sediment cores were obtained using a small piston corer designed at the Bedford Institute of Oceanography, and ranged from 50 cm to almost 2 meters in length. Soil samples were simply scooped into cloth sample bags with a small shovel.

Thick ice cover was present throughout the sampling period, and seal holes or open leads were utilized as sampling stations. Transport from station to station was by motorized toboggan or helicopter. Station positions were determined by fixing three prominent landmarks with a theodolite. However, as maps of the area are probably not precise, and as sightings were often made difficult by weather conditions such as fog banks and mirage phenomena, these locations may not be entirely accurate, although they are adequate for this study. Sample locations are shown in Fig. 4.

Preparation of the samples

Sediments were sealed in their plastic core barrel liners at each station. After transport to the laboratory, the cores were split, described and sampled while still in a plastic state. No deformation due to handling was apparent

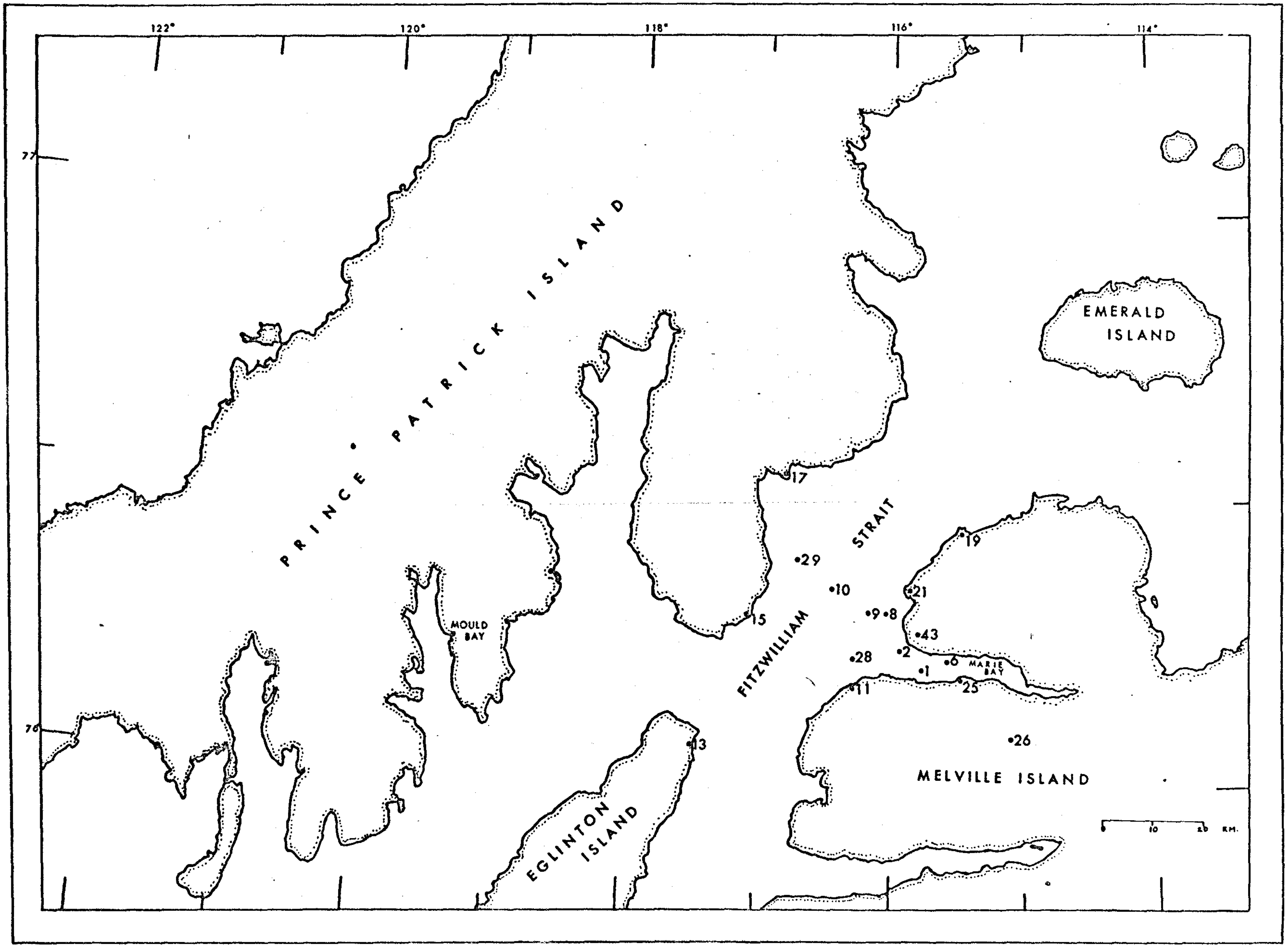

Fig. 4. Sampling station locations

when the cores were opened. Portions of sediment weighing 20 to 25 gm (wet weight) were washed free of soluble salts, then passed through a 0.063 mm sieve to remove sand and larger sized particles. An aliquot of material less than 1/256 mm diameter (approximately 4μ) was obtained by wet fractionation for X-ray analysis. The less than 0.063 mm size fraction was used for all chemical analyses. One less than 4μ fraction was included for comparison (core 1, 144-147 cm), and the differences between it and the less than 0.063 mm size fraction from the same sample appear to result mainly from the greater clay mineral content of the smaller size fraction. The differences, where they appear, are treated in the chapter on elemental geochemistry.

Methods of Analysis

The clay mineralogy of the less than 1/256 mm diameter fraction was examined by X-ray diffraction as described in Appendix B. The bulk soil and sediment samples were analysed for 21 elements. Pd, Au and Ir were determined by neutron activation; SiO_2, Al_2O_3, TiO_2, P_2O_5 and total Fe as Fe_2O_3 colorimetrically; Na_2O, K_2O, Rb_2O, CaO, MgO and MnO by atomic absorption. Detailed descriptions of each of the above analytical methods are contained in Appendix B. A few samples were also sent to Barringer Research Co., Toronto, Ont., for Hg determinations, and to National Spectrographic Co., Cleveland, Ohio, for Cr, Ni, Co, Cu, V and B determinations.

Reproducibility and Accuracy

The reproducibility and accuracy of the X-ray diffraction method used are discussed in Chapter IV. For the chemical analyses, at least one duplicate was analysed by each method, and reproducibility ranged from fair to excellent. The results of typical duplicate analyses may be found in Table 1. It is thought that at least part of the variation between duplicates was caused by the tendancy of some samples to clump, even after powdering. One might expect this factor to introduce the largest differences when major elements are considered, especially if the sample size is small. This was indeed the case for the duplicate included in the colorimentic determination of SiO_2 and Al_2O_3, where the discrepancy was fairly large, considering the usual precision of the method. As the variation in the duplicates was in the opposite sense for the two elements (i.e. the high SiO_2 duplicate gave a low Al_2O_3 value, and vice versa), and as the standards, treated identically, gave excellent standardization curves with no scatter, it was concluded that the discrepancy was due to sampling rather than analytical error.

No direct test of accuracy was carried out. However the techniques used are standard ones and routinely give results comparable with other methods.

Table 1. Results of some duplicate analyses*

1. Colorimetry	Core 10 (50-53 cm)	
Si	28.8	28.2
Al	8.41	8.62
Ti	0.58	0.58
Fe	2.17	2.08
P	.096	.096
2. Atomic Absorption	Core 10 (50-53 cm)	
Na	0.23	0.25
K	2.68	2.66
Ca	0.51	0.48
Mg	1.12	1.10
Mn	.026	.026
Rb	.006	.005
3. Neutron Activation	Core 10 (0-3 cm)	
Au	2.3	2.3
Pd	1.1	1.2
Ir	< .1	< .1
4. Emission Spectrograph	Core 1 (0-3 cm)	
Cr	100	90
Ni	60	60
V	230	240
Co	10	10

(continued next page)

Table 1. (Continued)

Cu	40	70
B	120	140
5. Vapour Detection	Core 9 (0-3 cm)	
Hg	14	12

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*Colorimetric and atomic absorption results in wt %. Neutron activation and vapour detection results in ppb. Emission spectrograph results in ppm. Total Fe was determined as Fe_2O_3. Emission spectrograph analyses by National Spectrographic Co., and vapour detection by Barringer Research Co. Neutron activation results were not always this precise, and other duplicate analyses are reported in Appendix A.

CHAPTER IV

CLAY MINERALOGY

Procedure

The clay-sized aliquot, obtained by wet fractionation, was centrifuged, mixed well, and applied in a thin smear to a frosted glass microscope slide (Gibbs, 1965).

Nickel filtered copper K_α radiation was used for all analyses. Samples were scanned by a Norelco wide range goniometer with a detector slit width of 0.006". The scale factor was adjusted to peak intensities for each sample, but was maintained constant for all scans of a particular slide.

Two slides were prepared for each sample, and scanned from 2° to 40° 2Θ at 1° 2Θ per minute. One slide was also scanned slowly (1/8° 2Θ per minute) from 24° to 26° 2Θ in an attempt to resolve the 3.53 A chlorite peak from the 3.57 A kaolinite peak. Once the data from these untreated samples had been recorded, one slide was treated with ethylene glycol vapour for twelve hours, the second was slowly heated from room temperature to 550°C and air quenched, and both were X-rayed again. Initially K and Mg saturated samples were also prepared in an attempt to determine the nature of the 10A-14A minerals. However, the diffraction records for these showed no change from the untreated samples, and as the entire suite exhibited a marked similarity this step was omitted in later runs. The details of the identification and quantization are given in Appendix B.

Accuracy and Reproducibility

Vemuri (1967) analysed mixtures of pure end member API reference clays, and concluded that slight changes in crystallinity, composition, etc., influence peak heights to such a degree that accurate quantization is almost impossible. He did, however, concede that for a small composition range (i.e. a small area of occurrence) there is some relationship between peak intensity and proportion of mineral present, and it is on this basis that the present quantization was carried out. Reproducibility for duplicates was good in most cases. It should be remembered throughout that this scheme is at best semi-quantitative.

Results

The results of the clay mineral analyses are listed in Table 2. The minerals identified were kaolinite, illite, chlorite and mixed layer lattice minerals of 10A-14A spacing, possibly randomly interlayered illite and vermiculite. Nearly every diffractogram also showed peaks corresponding to quartz. Illite and kaolinite were in all cases the major clay minerals present, comprising 70% to 80% of the total, with kaolinite

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Table 2. Clay mineral abundances[*]

Sample	K	I	Ch	ML
1	40	45	5	15
1 (52-55 cm)	45	35	10	10
1 (144-147 cm)	35	35	5	20
2	55	35	10	5
6	40	40	15	15
8	45	30	10	15
9	45	30	10	20
10	50	25	10	10
10 (16-19 cm)	65	30	5	5
10 (50-53 cm)	40	40	5	15
28	40	30	5	20
29	55	20	10	10
11 (soil)	35	45	10	5
13 (soil)	60	25	5	15
15 (soil)	35	40	5	15
17 (soil)	55	30	5	10
21 (soil)	55	30	5	10
25 (soil)	30	40	10	20
43 (soil)	40	35	10	20

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[*] Abundances are listed to the nearest 5%. K, I, Ch and ML stand for kaolinite, illite, chlorite and mixed-layer clay respectively. Unless otherwise noted, sediment samples are from the top 3 cm of the core.

normally slightly more abundant than illite.

The data show no distinct areal variation in the mineralogy of the sediments within the study area. Van Andel and Postma (1954), Porrenga (1966), and others have found very definite regional mineralogic trends in studies of Recent sediments, and have attributed such trends to differential flocculation. The effect is most pronounced if montmorillonite is present in some abundance, since its rate of flocculation varies markedly with chlorinity. The major minerals found in this study reach maximum flocculation almost instantaneously even at low chlorinities, so that no such effect would be expected.

The clay-sized fractions from various depths within cores 1 and 10 were studied. No significant variations were noted in the clay mineral abundances at different levels in the cores.

The seven soil samples analysed showed the same gross mineralogy as the sediments. It is generally conceded that clays in immediate marine environments (e.g. deltas and bays) differ little from those in source area soils and suspended river load (see review in Weaver, 1959). Furthermore, any possible changes would be minimized in the dominantly physical weathering processes of the Arctic.

Discussion

The close similarity between the mineralogy of the sediments from Fitzwilliam Strait and Marie Bay, and that of the soils from near-by land areas suggests that the marine clays are mainly detrital in origin. Whitehouse and McCarter (1958-59) subjected terrestrial clays to artificial sea water for periods ranging up to five years, and reported no major diagenetic changes in illitic or kaolinitic clays. They did observe changes in alkali and alkali earth concentrations; similar differences appeared in the chemical analyses of soils and sediments for this study, and will be treated in the section on elemental geochemistry. Hurley et al (1959) studied radiogenic argon in illites, and concluded that most marine illite is detrital. Berry and Johns (1966) report that pure illite and chlorite are unstable in the marine environment, and will change to mixed layer expandable clays. No increased in mixed layer minerals for marine compared to terrestrial materials was observed in this study, and, conversely, it appears that illite is reconstituted in the marine environment through uptake of K. Diffractograms typically showed more intense and less diffuse illite peaks for sediment clays compared to soil clays (Fig. 5). Such regrading is simply a reverse weathering process (Jackson et al, 1952).

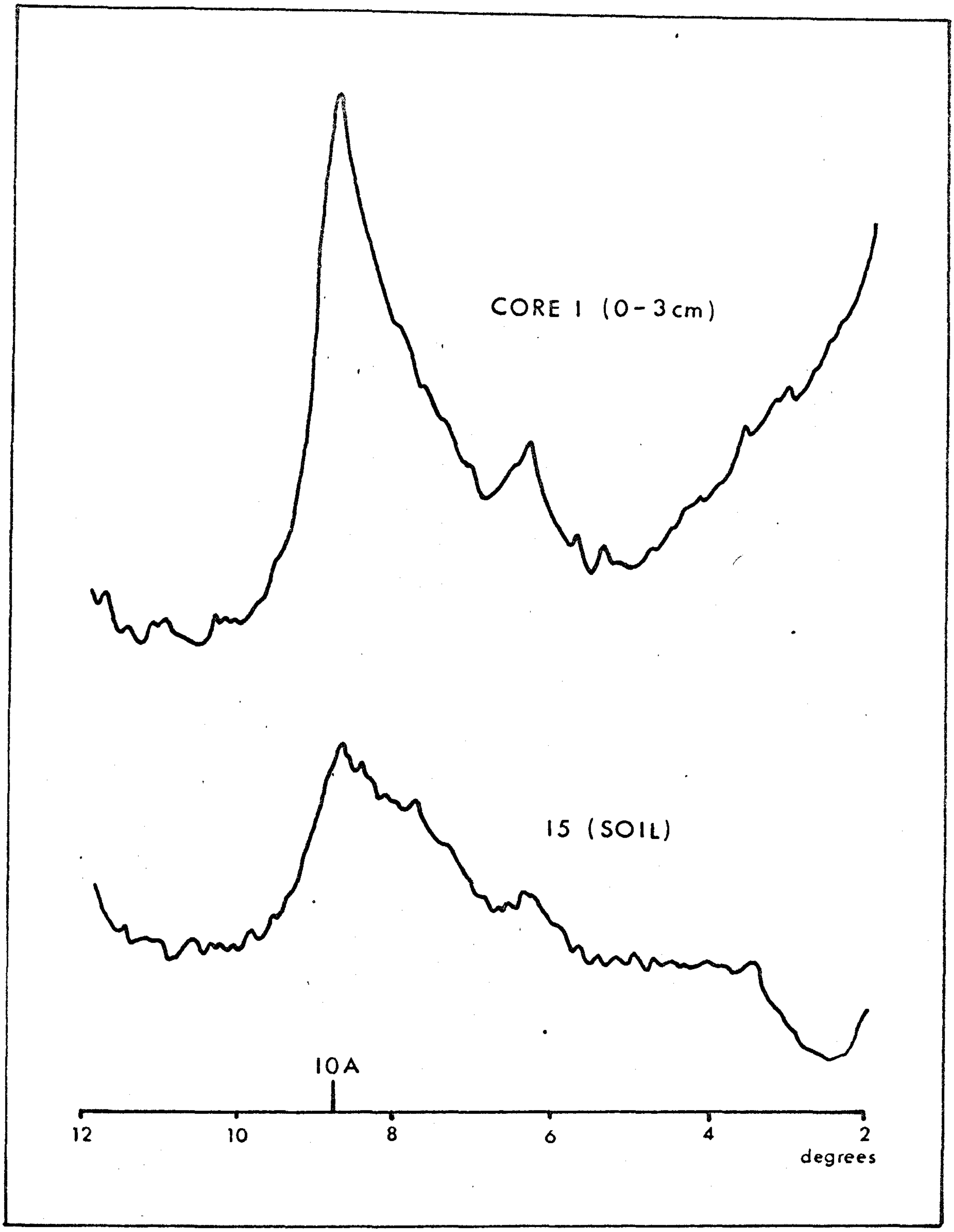

Fig. 5. Diffractograms showing the 10A illite reflection in a soil compared to a sediment

It is likely that the soil clays investigated reflect to a large degree the mineralogy of the underlying rock types, although there is no direct evidence for this. It is well known that kaolinite is a major constituent of soils in tropical regions and lateritic environments, and represents a net enrichment of aluminum in the clay compared with the parent rock (Mohr and Van Baren, 1954; Grim, 1953; and others). Biscaye (1965) found kaolinite enriched in Atlantic muds off the mouths of small tropical rivers. However, soils composed mainly of kaolinite and illite have been described by other workers from widely scattered Arctic regions (Feustel et al, 1939; Tedrow and Hill, 1955). It may be that the parent rock in these cases contained abundant kaolinite; misidentification is also a possibility, particularly for the early work by Feustel et al. In the case of the present study the abundance of kaolinite is thought to indicate disequilibrium between the soil and its environment. The very thin soil cover (where it exists at all) within the study area, and the lack of characteristic soil profiles provide further evidence of disequilibrium.

In summary, the clay mineralogy serves mainly to emphasize the dominantly physical nature of weathering in Arctic areas. The marine clays are predominantly detrital, and no observable mineral transformation or synthesis occurs from the time of weathering from the parent rock to burial to a few meters depth in the sediment. The clay minerals do respond to changing environments, but the changes that take place are restricted to cation exchange reactions and do not affect the lattice types.

CHAPTER V

ELEMENTAL GEOCHEMISTRY

Previous Work

Numerous investigators have published results of complete or partial elemental analyses for a variety of types of marine sediments. Turekian and Wedepohl (1961) compiled what they felt to be the most accurate data up to 1960. A recent and comprehensive element-by-element review of much of the work up to the present is given by Chester (1965).

There has been some controversy regarding the status of dissolved solids in the interstitial water. Goldberg and Arrhenius (1958) consider these salts part of the sediment; El Wakeel and Riley (1961) used washed samples for all analyses. In this study the samples were washed free of soluble salts with distilled water prior to analysis. Where the major cations of seawater (Na, K, Mg, and Ca) are concerned, comparison with other workers' results is only valid if the method of sample preparation is identical, or if a correction is made for the removed salts.

Goldberg (1954), in a genetic classification of marine sediments, listed five types: lithogenous, hydrogenous, biogenous, atmogenous and cosmogenous. The Arctic sediments investigated appear to be predominantly lithogenous (derived from terrestrial sources). The chemical data indicate that both biogenous and hydrogenous components are also present, although in small amounts. It is doubtful that any of the constituents can be assigned to atmospheric or cosmic sources.

Samples Analysed

Five cores were selected for analysis: cores 1 and 6 are from Marie Bay; cores 9, 10 and 29 form a traverse across Fitzwilliam strait. For cores 1 and 10, each visibly distinguishable unit within the core was sampled. The analyses showed that chemically the sediments are essentially identical at all levels in the cores, and in Table 5 the averages include samples from different levels. All samples except those from cores 1 and 10 are from the top 3 cm of sediment. Four soils were also analysed: samples 15, 19, 26 and 43.

Results of the chemical analyses are given in Tables 3 and 4. Average values from this study are compared with values by other workers in Table 5. Water depths and descriptions of the samples are tabulated in Appendix C.

Table 3. Major and minor element analyses for some Arctic soils and marine sediments*

	Si	Al	Fe	Ti	Mg	Ca	Na	K	P	Mn
1	30.0	7.52	2.16	0.55	1.04	0.64	0.68	2.29	.092	.092
1 (52-55cm)	30.9	6.72	1.88	0.50	1.19	1.27	0.25	2.09	.087	.056
1 (144-147cm)	30.5	6.61	1.77	0.52	1.02	1.92	0.22	1.84	.070	.038
1 (" (<4μ)	25.2	11.27	2.37	0.48	1.08	0.43	0.17	2.91	.087	.033
6	29.6	6.89	1.95	0.47	1.33	1.86	0.42	2.00	.074	.128
9	33.4	6.11	1.58	0.53	0.84	0.43	0.27	2.18	.074	.047
10	32.9	6.38	1.51	0.53	0.84	0.51	0.28	2.10	.074	.053
10 (16-19 cm)	37.4	3.92	1.08	0.44	0.49	0.37	0.26	1.89	.044	.015
10 (50-53 cm)	29.0	8.51	2.13	0.58	1.11	0.50	0.24	2.67	.096	.026
29	28.6	6.13	1.47	0.56	0.86	0.59	0.32	1.96	.079	.027
15 (soil)	42.0	1.81	0.50	0.55	0.16	0.01	0.06	1.01	tr.	.009
19 (soil)	40.3	2.74	0.59	0.36	0.18	0.06	0.27	1.90	.013	.007
26 (soil)	30.1	5.88	2.05	0.41	0.66	0.62	0.37	2.13	.122	.003
43 (soil)	26.1	4.67	5.18	0.37	0.53	0.45	0.03	1.53	.118	.018

*Values in weight percent.

Table 4. Trace elements in some Arctic soils and sediments*

	Rb	B	Ni	Co	Cr	V	Cu	Hg	Pd	Au
1	60	130	60	10	95	235	55	(44)	2.6	4.2
1 (52-55 cm)	50	nd	nd	nd	nd	nd	nd	nd	nd	nd
1 (144-147 cm)	50	160	50	10	90	222	160	61	2.4	2.9
1 (" (<4μ)	80	220	60	15	130	270	220	nd	2.9	3.4
6	50	nd	nd	nd	nd	nd	nd	nd	2.6	3.2
9	50	115	35	10	90	180	115	13	3.5	2.9
10	40	100	30	10	90	80	100	21	1.2	2.3
10 (16-19 cm)	30	100	30	10	60	80	100	46	1.2	2.9
10 (50-53 cm)	60	100	30	10	70	120	100	40	1.5	1.7
29	40	110	30	10	100	150	110	12	1.5	1.6
15 (soil)	10	110	10	10	110	120	70	28	1.6	1.0
19 (soil)	20	nd	nd	nd	nd	nd	nd	nd	0.7	0.3
26 (soil)	50	nd	nd	nd	nd	nd	nd	nd	nd	nd
43 (soil)	40	100	50	15	150	160	80	(670)	1.1	1.8

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*The values for Hg, Pd and Au are reported in parts per billion. All other results are in parts per million. Brackets indicate questionable values, and the letters "nd" indicate no determination.

Table 5. Comparison of element abundances from this work with some other values

	Si(%)	Al(%)	Fe(%)	Ti(%)	Mg(%)	Ca(%)	Na(%)	K(%)	Rb(%)	Mn(%)
Sediments this work	31.4	6.53	1.73	0.52	0.97	0.90	0.33	2.11	.005	.054
Soils this work	34.6	3.78	2.08*	0.42	0.38	0.29*	0.18	1.64	.003	.009
Glacial marine sediments (Angino, 1965)	-	7.29	3.72	0.36	-	-	-	-	-	.14
Deep sea clays (Turekian and Wedepohl, 1961)	25.0	8.4	6.5	0.46	2.1	2.9	4.0	2.5	.011	.67
Near shore muds (Hirst, 1962)	25.96	8.79	5.15	0.47	1.32	1.70	1.67	1.87	.016	.13
Crustal abundance (Taylor, 1965)	28.15	8.23	5.63	0.57	2.33	4.15	2.36	2.09	.009	.095

*Indicates average with large variations

(continued next page)

Table 5 (continued

	P(%)	B (ppm)	Ni (ppm)	Co (ppm)	Cr (ppm)	V (ppm)	Cu (ppm)	Hg (ppb)	Pd (ppb)	Au (ppb)	Ir (ppb)
Sediments this work	.078	115	38	10*	85	152	106	30	2.1	2.7	<.1
Soils this work	.064*	105	30	13	130	140	85	28*	1.1	1.0	<.1
Glacial marine sediments (Angino, 1965)	-	-	37	27	89	200	137	-	-	-	-
Deep sea clays (Turekian and Wedepohl, 1961)	.15	230	225	74	90	120	250	-	-	-	-
Near shore muds (Hirst, 1962)	.06	81	31	12	93	146	17	-	-	-	-
Crustal abundance (Taylor, 1965)	.105	10	75	25	100	135	55	80	-	-	-

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*indicates average with large variations.

Silicon

The average Si value for the sediments is 31.4 per cent, while the soils give a value of 34.6 per cent. The less than 4μ fraction has a Si content 5.3 per cent lower than the corresponding less than .063 mm size fraction, and 6.2 per cent lower than the average for the sediments. As might be expected for near-shore sediments, these values are considerably higher than those reported for pelagic muds (usually close to 24 per cent), and are similar to the values Turekian and Wedepohl (1961) report for granites. The figure for the clay-sized fraction is close to that reported by Hirst (1962) for muds from the Gulf of Paria, viz., 25.96 per cent Si.

Si in the sediments appears mainly as quartz or in the lattice of clay minerals. The quartz is predominantly detrital. Rex and Goldberg (1958) found no evidence for inorganic SiO_2 precipitation in Pacific sediments, and Biscaye (1965) found that quartz abundance in Atlantic sediments (particularly near-shore deposits) largely reflected the weathering conditions of the adjacent terrestrial sources. Diatoms are absent from the study area, and biological precipitation of SiO_2 is negligible. The analyses show that quartz is more abundant in grain sizes greater than 4 μ, but quartz peaks were observed in the diffractograms of most of the clay-sized aliquots, indicating the presence of some quartz as a very fine dust. The high Si values are probably attributable to the numerous sandstone beds in the source areas.

Aluminum

In the sediments the Al content varies between 3.92 per cent and 7.52 per cent, with an average value of 6.53 per cent. The variations are due to variations in type and amount of clay mineral present. The less than 4 μ sample has an Al content of 11.27 per cent, reflecting the much higher clay mineral content. The Al content of the soils averages 3.78 per cent, indicating that the clay minerals are less abundant than in the sediments.

Goldberg and Arrhenius (1958) reported an average Al content of 9.2 per cent for Pacific pelagic sediments, while El Wakeel and Riley (1961) found Atlantic sediments to be on the average somewhat less rich in Al. Hirst (1962) found that platform sands from the Gulf of Paria contain an average of 3.24 per cent Al, while clays average 8.22 per cent. The crustal abundance (Taylor,1964) is 8.23 per cent.

Al in the sediments is primarily located in the lattices of the aluminosilicates. Goldberg and Arrhenius (1958) found that only a fraction of a percent is exchangeable. These facts make the Al content a useful indicator of the amount of clay mineral present.

Iron

The range of Fe values for the sediments is fairly small, with an average of 1.73 per cent. The soils, on the other hand, vary in Fe content from 0.50 per cent to 5.18 per cent, and an average is not meaningful. The highest Fe value for the soils (5.18 per cent) is from a rusty coloured sandy soil, visibly rich in iron oxide. It is likely that the large variations observed for the soils result from variations in the immediate parent rocks. The sediments represent a better mixed sample of a large source area.

The primary iron phase deposited from sea water is probably hydrated colloidal iron oxide (Goldberg, 1954) which may transform to goethite upon ageing in the sediment. Iron in the sediments can be present as an essential or substituting lattice constituent of the clay minerals, or as an oxide coating on mineral grains. The constancy of the Fe:Al ratio (Table 6) in the sediments, and, with the exception of sample 43, in the soils, suggests an association of Fe with the clay minerals. Neither kaolinite nor illite contain iron as an essential constituent, and Fe must be present as Fe^{2+} or Fe^{3+} substituting for Mg^{2+} or Al^{3+} respectively in the lattice. A minor amount of Fe may be present in heavy mineral particles (e.g. magnetite).

Titanium

The Ti contents of the soils and sediments are quite constant (range 0.36 per cent to 0.58 per cent) with an average value of 0.52 per cent for the sediments and 0.42 per cent for the soils. The figure for the sediments is lower than the value of 0.73 per cent given by Goldberg and Arrhenius (1958) for Pacific pelagic sediments, but higher than the 0.46 per cent that Turekian and Wedepohl (1961) give for both shales and deep sea sediments, and the figure of 0.36 per cent given by Angino (1965) for Antarctic glacial marine sediments. The crustal average of Taylor (1964) is 0.57 per cent.

It has often been suggested that there is a close relationship between iron and titanium in the sedimentary cycle (see Chester, 1965, p. 33). This suggestion is substantiated by a comparison of Fe:Ti ratios of various rock types. The data from Turekian and Wedepohl (1961), for instance, show a maximum variation of slightly more than a factor of two when the Fe:Ti ratio of basalts, granites, shales and deep sea sediments are compared. From the Fe:Ti ratios for the sediments of the present study (Table 6), it appears that Ti follows Fe in a general way. There is a similar relationship between Ti and Al, although again the ratio does have variations. Probably most of the Ti is associated with clay minerals, and the variations in the Fe:Ti

Table 6. Relationships between Al, Fe and Ti in the sediments and soils

Sample	Fe/Al	Fe/Ti	Ti/Al × 10^{-1}
1	0.29	3.9	0.73
1 (52-55 cm)	0.28	3.8	0.74
1 (144-147 cm)	0.27	3.4	0.79
1 " (< 4μ)	0.21	4.9	0.43
6	0.28	4.1	0.68
9	0.26	3.0	0.87
10	0.24	2.8	0.83
10 (16-19 cm)	0.27	2.5	1.1
10 (50-53 cm)	0.25	3.7	0.68
29	0.24	2.6	0.91
15 (soil)	0.28	0.92	2.5
19 (soil)	0.22	1.6	1.3
26 (soil)	0.35	5.0	0.69
43 (soil)	1.11	14.0	0.79

and Ti:Al ratios are caused by the presence of hydrogenous titanium minerals formed from Ti in solution in sea water (Goldberg, 1954), or by variations in detrital minerals such as illmenite. From the wide variation in the Fe:Ti ratios in the soils under investigation, in comparison to the sediments, it appears that the association of Fe and Ti occurs either in the marine environment or during transport to it.

Manganese

The average Mn content of the sediments is 0.054 per cent; of the soils 0.009 per cent. These results are much lower than the figure quoted by Turekian and Wedepohl for deep sea sediments, viz. 0.67 per cent. They are, however, close to values reported for other near-shore sediments (Hirst, 1962; Presley et al, 1967).

Mn is present in sea water predominantly in true solution as the divalent species Mn^{2+} (Goldberg and Arrhenius, 1958) at a concentration of 1 to 3 parts per billion. Presley et al (1967) have pointed out that a large amount of Mn must be removed in near-shore environments, since rivers usually carry about 70 ppb Mn. In a study of interstitial waters from near-shore sediments, they found that Mn was enriched by a factor of about 50 in oxidizing environments off the coast of Southern California. The solid phases from the same cores contained Mn in concentrations similar to those found in this study. The enrichment in Mn in sediments relative to soils found in the present work can be attributed to leaching of Mn in the terrestrial environment, and precipitation of dissolved Mn as a colloid or a colloid adsorbed to clay mineral particles in the marine environment. It has been demonstrated that Fe in the sediments under investigation is primarily present in the clay minerals, and the lack of covariance between Mn and Fe is probably due to variations in the amount of precipitated Mn in each sample. The rather wide range of Mn contents in the sediments (.015 to .128 per cent) supports this conclusion. There is no evidence that ferromanganese oxide minerals are present in any abundance in the sediments. The presence of such minerals in many deep sea sediments accounts for their relatively high Mn contents, although even in pelagic sediments much of the Mn is reportedly associated with clay minerals (Turekian and Schutz, 1965; Bender et al, 1968).

Bender et al (1968) determined Mn accumulation rates in sediments from four oceans, and found them to vary between 0.13 and 4.6 mg/cm^2/1000 yr (average 1.2 mg/cm^2/1000 yr). No data is available for the density of the sediments in the present study; however, by using a value of 0.7 mg/cm^2 (average from Bender et al, 1968), a sedimentation rate of 4.4 cm/1000 yr (Vilks, 1968), and the average Mn concentration of the sediments, 0.054 per cent, the Mn accumulation rate is calculated to be 1.7 mg/cm^2/1000 yr. If the manganese content of the soils (average 0.009 per cent) is subtracted from the value for the sediment before the calculation is made, the Mn accumulation rate is 1.4 mg/cm^2/1000 yr. These figures are higher by a factor of three or more than the Mn accumulation rates in manganese nodules calculated by Bender et al (1968), and, since volcanism is definitely not a Mn source in the study area, support their proposal that volcanic supply is not a necessity for manganese nodule growth.

Sodium and Potassium

The sediments contain 0.32 per cent and 1.96 per cent of Na and K respectively, while the soils contain 0.18 per cent and 1.64 per cent. The values for the sediments are low compared to most other analyses of washed marine samples. For example, El Wakeel and Riley (1961) report 1.14 per cent Na and 2.71 per cent K in 12 argillaceous sediments from all oceans.

The depletion in Na relative to K is especially large in these sediments and soils. Igneous rocks generally have Na:K ratios of near unity, and shales usually exhibit a ratio of 0.3 to 0.4. Using the average Na and K contents for the sediments and soils investigated, the ratios are 0.16 and 0.11 respectively. The sediments are at least second cycle (they are derived from sediments) and Na is probably

Table 7. Mn:Fe ratios in the soils and sediments

Sample	Mn/Fe × 10^{-1}	Sample	Mn/Fe × 10^{-1}
1	.43	10 (16-19 cm)	.14
1 (52-55 cm)	.30	10 (50-53 cm)	.12
1 (144-147 cm)	.21	29	.18
1 " (<4μ)	.14	15 (soil)	.10
6	.65	19 (soil)	.12
9	.30	26 (soil)	.02
10	.35	43 (soil)	.03

increasingly depleted, with respect to K, in each cycle. This would of course to some extent depend on the weathering product formed in each cycle: montmorillonite can have a Na:K ratio of about 4. It is expected that losely bound Na, as well as some K, was removed in the washing process.

The results show a slight increase in both Na and K for the sediments relative to the soils. The uptake of K (and possibly some Na) can be attributed to the regrading of illite in the marine environment, and is reflected in the somewhat sharper diffraction peaks exhibited by the sediments (Figure 5). Whitehouse and McCarter (1958-59) found a similar increase in the K content of illite subjected to artificial sea water, although they report a loss of Na from both kaolinite and illite under the same conditions. The increase in Na in the sediments compared to the soils of the present study is undoubtedly due to ion exchange reactions between sea water and clay minerals, but exact characterization of such reactions cannot be made with the limited data available.

Rubidium

The Rb content of the soils is .003 per cent, while the sediments average .005 per cent. In a general way Rb follows aluminum in the sediments; the Rb:Al ratio ranges from 6.3×10^{-4} to 8.2×10^{-4}. The values for the soils are more erratic.

The Rb contents of the soils and sediments are low compared to many other marine sediments and terrestrial rocks (Table 8), and the K:Rb ratios are correspondingly high. The ratios show a relative increase in Rb in the sediments relative to the soils. This is in agreement with both experimental studies and theoretical considerations (see Degens, 1965, p.22) which indicate that clays have a greater selectivity for Rb than for K.

Table 8. Average Rb and Rb/K values for the sediments and soils of this work, and a comparison with other workers' values.

	Rb (%)	K/Rb
Sediments this work	.005	455
Soils this work	.003	693
Near-shore marine clays (Hirst, 1962)	.0088	145
Granites (Turekian and Wedepohl, 1961)	.017	247
Shales (Turekian and Wedepohl, 1962)	.014	190
Deep Sea Clays (Turekian and Wedepohl, 1961)	.018	228

Calcium and Magnesium

The average Ca contents of the sediments and soils are 0.90 per cent and 0.29 per cent respectively; the average Mg contents are 0.97 per cent and 0.38 per cent. Values reported by other authors vary; Hirst (1962) reports 0.70 per cent Ca and 1.32 per cent Mg for clays from the Gulf of Paria; El Wakeel and Riley (1961) report 0.66 per cent Ca and 2.08 per cent Mg for argillaceous marine sediments, and Turekian and Wedepohl (1961) report 2.5 per cent Ca and 2.1 per cent Mg for deep sea clays.

The constancy of the Mg:Al ratio in the sediments (range .12 to .19, average .14) suggests that most of the Mg is associated with the clay minerals. The Mg:Al ratio for the soils is slightly lower (.09), and the relative increase in Mg in the sediments may derive from adsorption of Mg by the clay minerals in the marine environment, or from Mg incorporated in calcareous organic debris. Calcareous foraminifera are locally abundant in sediments from the area under investigation (see Vilks, 1968) and although entire tests would be removed in the sieving process, some carbonate fragments would remain in the sample to be analysed. It is probable, however, that most of the Mg in the sediments investigated is present either as a structural component of chlorite or mixed layer minerals, or as an adsorbed substituting component in illite or kaolinite. Whitehouse and McCarter (1958-59) found that terrestrial illite and kaolinite both increase in Mg content during treatment with artificial sea water.

In contrast to Mg, Ca shows no correlation with Al, indicating that it is not contained predominantly in the clay minerals. This is also evident from the analysis of the less than 4μ fraction from core 1, which has a Ca content about one-quarter that of the less than 0.063 mm fraction from the same sample. The variations in Ca in the sediments are probably due to variations in the abundance of calcareous foraminifera. The enrichment in Ca in the sediments compared to the soils is also thought to be due to the presence of calcareous foraminifera in the former, rather than uptake of Ca from sea water. Whitehouse and McCarter (1958-59) found that terrestrial illite and kaolinite both lose Ca when subjected to marine conditions. Inorganic precipitation of significant amounts of Ca as calcium carbonate or calcium phosphate is unlikely in the cold waters of the study area. Detrital apatite may be present in the sediments; however, the low P contents limit the amount of Ca that could occur in this manner.

Phosphorous

The P content of the sediments averages .078 per cent, close to the value for shales (.07 per cent) reported by Turekian and Wedepohl (1961). In the soils, P varies from trace amounts to .118 per cent.

It is probable that the P in the sediments is contained in biogenous material or in calcium phosphate, which may be organic or inorganic in nature. Inorganic precipitation of calcium phosphate from sea water is probably not an important process in the area studied. Fixation of P by iron or manganese hydroxides at the sediment-water interface (Chester, 1965) may account for a small part of the P in the sediments, although it has already been shown that most of the Fe is contained in clay mineral lattices, and there is not a close association between Mn and P in the sediments. Some of the P may be present in detrital apatite; if all of the P were contained in this manner approximately 0.3 per cent of the total sediment would have to be apatite. It has been noted by many workers (see Degens, 1965, p. 147) that phosphatization of organic residue such as shells, wood, etc. is common in marine environments, and such matter may account for part of the P content of the sediments.

Boron

The B content of the sediments is 115 parts per million, while the soils average 105 ppm. The less than 4μ fraction from core 1 contains 220 ppm B, considerably more than the less than 0.063 mm fraction from the same sample. Porrenga (1967) found that B uptake by clay minerals and micas is enhanced by grinding, and the increase was attributed to both a decrease in average grain size and a reduction of crystallinity. Similar effects probably account for the increase in B in the less than 4μ size fraction analysed in the present study.

The B content of marine sediments has been intensively investigated (see Degens, 1965, p.40) because of the possible usefulness of boron for the determination of paleosalinity. As a broad generalization (there are frequent exceptions) marine clays contain 100-200 ppm B, while fresh water clays contain 10-50 ppm. The higher content of marine sediments does not appear to be due to a simple adsorption phenomenon since the B is very tightly held in the clay minerals, probably substituting for Al in silica tetrahedra (Goldberg and Arrhenius, 1958). Theoretical considerations (Nicholls, 1963) show that boron-oxygen bonds should be almost as stable against weathering hydrolysis as silicon-oxygen bonds, and if this is the case no B should be lost until the lattice has almost disintegrated.

The similarity of B concentrations in the soils and sediments of this study is surprising in view of the frequently voiced opinion that reworked clays can gain additional B during each exposure to marine conditions (Degens, 1965, p 40). The soils are developed on marine sediments, hence their relatively high B contents, but the Recent sediments exhibit no further enrichment. The results of Harder (1961) show that B uptake by illite is initially quite rapid, but that the rate decreases with increasing B content, even although only a small percentage of the possible sites (assuming B substitutes for Al) are filled. Perhaps near-maximum B concentrations had previously been reached in the sediments under investigation. Regardless, B in these sediments has not been affected by the salinity of the depositional environment, and the results emphasize the increasingly apparent fact that boron content cannot be used indiscriminantly as a paleosalinity indicator.

Boron is one of Rubey's (1951) "excess volatiles"; that is, it is present in sediments and sea water in larger concentrations than can be accounted for by the weathering of igneous rocks. One can assume that the excess B was contained in a hypothetical primitive ocean and has been gradually removed by detrital and authigenic clay minerals; however, Reynolds (1965) has demonstrated that the B content of the ocean has probably remained quite constant over the last 2-3 billion years. Results of chemical mass balance calculations for the B cycle (R.C. Harriss, personal communication) indicate that at the present time extraction of B from sea water exceeds input to the ocean by about one order of magnitude. These calculations were based on the assumption that suspended clays in rivers gain approximately 50 ppm B upon entering the marine environment, and that authigenic clays constitute about 7% of marine aluminosilicates and contain 100 ppm B. Much of the suspended sediment reaching the oceans is recycled marine material, and if the results of the present study can be generalized, at least a part of this material may not gain appreciable B from seawater. This factor may serve to reduce the apparent discrepancy in the boron cycle mass balance.

Chromium and Vanadium

The sediments average 85 parts per million Cr and 152 ppm V. The two soils analysed for these elements average 130 ppm Cr and 140 ppm V. In keeping with the observations of McLaughlin (1958), who found that both Cr and V are concentrated in the clay-sized fraction of illite, the less than 4 μ fraction from core 1 showed higher Cr and V contents than the less than 0.063 mm fraction.

The Cr and V contents of the sediments are similar to those of deep sea clays (Turekian and Wedepohl, 1961) and crustal igneous rocks (Taylor, 1964). Wedepohl (1960), in analyses of Atlantic clays, found little difference for the Cr and V contents of near-shore sediments compared to deep sea clays, in contrast to many other trace metals. The high Cr contents of some pelagic sediments is apparently due to the presence of basaltic pyroclastics (Goldberg and Arrhenius, 1958).

With the exception of a sample from core 10 (50-53 cm), the Cr:Al ratio (Table 9) is quite constant, indicating that Cr is probably mainly associated with the clay minerals. Fröhlich (1960) has determined that Cr in pelitic sediments is concentrated in illitic and chloritic clays, and to some extent in micas. Experiments performed by Krauskopf (1955) indicated that Cr is strongly adsorbed by hydrated MnO_2, although its concentration in manganese nodules is generally quite low. Cr in the sediments under investigation shows no correlation with Mn (Table 9) and it is concluded that Cr is contained largely in illite and chlorite. The data for the soils indicate that no Cr is adsorbed by the clays in the marine environment, in fact the sediments appear to be slightly depleted.

V in the sediments is quite variable (80 to 235 ppm) and differs from Cr in that it is not closely associated with Al (Table 9). This may be due to a variable contribution to the sediment of V associated with organic material, although such a conclusion must be tentative in view of the fact that organic C was not determined. It is well known that V has greater biophilic tendancies than Cr. A part of the organically associated V may be derived from asphaltic material washed into Marie Bay from the bitumen deposits described by Trettin and Hills (1966).

Nickel and Cobalt

The sediments average 38 ppm Ni and 10 ppm Co. The average for Co is an upper limit since several of the Co determinations were reported only as "less than 10 ppm". The two soils analysed average 30 ppm Ni and 13 ppm Co. Un-

Table 9. Cr:Al, V:Al and Cr:Mn ratios in the Arctic sediments

Sample	Cr/Al × 10^{-2}	V/Al × 10^{-2}	Cr/Mn
1	.13	.31	.10
1 (144-147 cm)	.14	.34	.24
1 " (<4μ)	.12	.24	.39
9	.15	.29	.19
10	.14	.13	.17
10 (16-19 cm)	.15	.20	.40
10 (50-53 cm)	.08	.14	.27
29	.16	.24	.38

like Cr and V, Ni and Co do not show marked enrichments in the less than 4 μ fraction from core 1, which again is in agreement with McLaughlin's (1958) findings. The concentrations of Ni and Co in these sediments are similar to those reported by other workers for near-shore sediments (Hirst, 1962; Young, 1954). Glacial marine sediments (Angino, 1965) have similar Ni contents and slightly higher Co contents. It has been pointed out by Wedepohl (1960) that both elements are greatly enriched in deep sea sediments relative to near-shore sediments.

The similarity in Co and Ni contents of the soils compared to the sediments suggests that the concentrations in the sediments are entirely present in detrital material, and probably reflect the concentrations in the parent rocks. These elements likely proxy for major cations in clay mineral lattices, as suggested by Goldberg and Arrhenius (1958).

Angino (1965) has suggested that trace element data may be useful in distinguishing glacial marine sediments from other types. Although the sediments of this study are not strictly glacial, the environment of deposition shares many characteristics with the Antarctic sediments (e.g. low water temperature, little chemical precipitation, etc.), and it is interesting to compare some of the chemical data. Two ratios which Angino deems especially useful for distinguishing glacial marine sediments are Ni:Co and Ni:Al.

It appears that the average Ni:Co ratio for the sediments of this study is different from that reported by Angino, and closer to the ratio for deep sea sediments, although the agreement is not good (Table 10). The Ni:Al ratios, on the other hand, all fall within or close to the range found by Angino for the Antarctic sediments, and are quite different from those for deep sea sediments. The same ratios for 6 greenish muds from the Gulf of Paria (Hirst, 1962) have values more or less similar to those found in this study. It must be concluded that these ratios are not especially useful in determining sedimentary environments. A large number of variables affect the concentration of each element in marine sediments, and it is difficult

Table 10. The average Ni, Co, Ni/Al and Ni/Co values for the Arctic soils and sediments compared with some other works.

	Ni	Co	Ni/Co	Ni/Al × 10^{-3}
sediments this work	38	10	3.8	.60
soils this work	30	13	2.2	.84
glacial marine sediments (Angino, 1965)	37	27	1.4	.50
Paria green muds (Hirst, 1962)	31	12	2.6	.35
deep sea sediments (Turekian and Wedepohl, 1961)	90	225	2.5	2.9

to imagine how a few elemental ratios can unequivocally characterize the environment of deposition.

Copper

The Cu content of the sediments is 106 ppm, while that of the soils is 85 ppm. The less than 4 μ size fraction from core 1 contains 220 ppm Cu. Precision for Cu was not good (Table 1), so that sample to sample variations cannot be given much emphasis. The averages, however, probably represent fairly closely the true values.

Cu is among the metals that Wedepohl (1960) found concentrated in pelagic relative to near-shore sediments. Turekian and Wedepohl (1961) report 250 ppm Cu for deep sea clays; Hirst (1962) reports 17 ppm for near-shore muds from the Gulf of Paria. The sediments of this study fall close to the value for basaltic rocks (87 ppm) and above the figure for shales (45 ppm) given by Turekian and Wedepohl (1961).

At least a part of the Cu must be contained in the lattices of the clay minerals, especially as these are recycled marine sediments. The Cu:Al ratios for the sediments show quite large variations, and this may be due either to inaccurate Cu determinations or to addition (or subtraction) of Cu to the sediment subsequent to deposition. It appears from the average values for the soils compared to the sediments that Cu is slightly enriched in the latter. This may be due to adsorption of Cu by clay minerals in the marine environment (Krauskopf, 1955) or to addition of Cu contained in organic debris. Cu forms very stable complexes with many organic groups. Goldberg and Arrhenius (1958) have pointed out that Cu is concentrated in the skeletal remains of fish after death of the organism. Variable organic addition of Cu to the sediments could account for the variable Cu:Al ratios. Igneous ferromagnesian minerals containing Cu are not expected to be important in these sediments.

Mercury

The precision for one of the duplicate pairs included in the Hg analyses is very poor, and hence these results may not be accurate. However, the range for the sediments is not too great (12 to 61 ppb) and the average value of 30 ppb is certainly indicative of the order of magnitude for this element. Two soils were analysed, and these contain 28 and 670 ppb respectively. The apparently anomalously high figure for soil 43 may result from laboratory contamination as repeated analyses gave similarly high values.

The Hg content of Recent sediments is not well known. Turekian and Wedepohl (1961) give only order of magnitude guesses for deep sea sediments. For sedimentary rocks, they list 400, 30 and 40 ppb respectively for shales, sandstones and carbonates. Two Recent Antarctic sediments contain 21 and 28 ppb Hg (R. C.Harriss, unpublished data).

Hg is present in sea water as chloride complexes, predominantly $HgCl_3^-$ and $HgCl_4^{-2}$. Goldberg (1963) lists the concentration of Hg in sea water as .00003 mg/l (.03 ppb). If this is correct, Hg is enriched in the sediments studied by a factor of 10^3 relative to sea water. If the soil concentration of 28 ppb is meaningful, then Hg is neither enriched nor depleted in the sediments compared to the soils, even though Krauskopf (1955) found that Hg was strongly adsorbed by clay minerals, plankton and to some extent by organic debris such as peat moss. These mechanisms of enrichment are probably more effective for true pelagic clays, for which much slower rates of sedimentation prevail.

Palladium, Gold and Iridium

The average values for these elements in the sediments and soils are shown in Table 11. Ir was not detectable under the experimental conditions used, and its concentration is less than 0.1 ppb in both soils and sediments. Pd and Au exhibit similar concentrations in the soils and the sediments, indicating that they are primarily detrital components in the sediments.

No data for Pd in recent sediments is available in the literature. DeGrazia and Haskin (1964) report that Au ranges from 3.1 to 17.3 ppb in lutite from the Argentine Basin, and from 4.2 to 31 ppb in red clay from the Brazil Basin. Barker and Anders (1967) report that Ir in Pacific pelagic sediments ranges from .057 to .458 ppb. A discussion of the marine geochemistry of Pd and Au is included in Appendix A, and will not be duplicated here.

Table 11. Data for Pd, Au and Ir in the Arctic sediments and soils*

	Pd	Au	Ir
average sediments	2.1	2.7	<.1
average soils	1.1	1.0	<.1

*Concentrations in ppb.

SUMMARY AND CONCLUSIONS

A number of soils and marine sediments from a restricted area in the Canadian Arctic were subjected to mineralogical and elemental chemical studies. X-ray analyses of the less than 4 μ size fraction indicate that there are no major diagenetic changes in the marine environment. The chemical analyses support this conclusion. Changes in the major cation concentrations between soils and sediments indicate the importance of cation exchange reactions.

The general chemistry of the sediments is similar to that of other near-shore marine sediments, and quite distinct from pelagic sediments. Silicon is high in the soils and sediments because of abundant sandstone in the source rocks. Fe follows Al closely, and is present in relatively low concentrations because the major clay minerals do not contain Fe as a major constituent. Among the trace elements, Cu, Ni and Co exhibit small concentrations relative to pelagic clays, while Cr and V concentrations are similar to those of deep sea sediments.

The Mn content of the sediments is low, but the calculated accumulation rate of Mn, 1.7 mg/cm^2/1000 yr, is greater than the accumulation rate in many manganese nodules. The very low Mn content of the soils investigated suggests that most of the Mn in the sediments is hydrogenous. No Mn is supplied to the study area through submarine volcanism, and it is concluded that volcanic contribution of Mn is not essential for nodule growth.

The B contents of the sediments and soils are similar, averaging just over 100 ppm. This suggests that, at least in some environments, recycled marine sediments do not gain additional B each time they are subjected to marine conditions. If this is applicable to a part of the suspended sediment load entering the world oceans, apparent discrepancies in B mass-balance calculations may disappear.

New data are presented for Hg, Pd and Au in nearshore sediments. The values found are 30, 2.1 and 2.7 ppb respectively. Ir was not detectable under the experimental conditions employed, and an upper limit of 0.1 ppb can be set for this element in the sediments and soils.

APPENDIX A

Pd and Au in Marine Sediments

APPENDIX A

Pd and Au IN MARINE SEDIMENTS

Introduction

Neutron activation was used to determine Au and Pd in the Arctic sediments and soils analysed for the main body of this thesis. Because of the dearth of data for these elements in marine sediments in general, the study was extended and a number of pelagic sediments from the Pacific and Antarctic Oceans were also analysed. Some soils, as well as sediments from the Arctic, Pacific and Antarctic Oceans, were analysed for Ir, but this metal was below the limit of detectability under the experimental conditions employed.

In all, 30 samples were analysed, 15 of them in duplicate. These comprise 3 Arctic soils, 9 Arctic near-shore sediments, 1 Pacific calcareous ooze, 14 East Pacific Rise sediments (see Bostrum and Peterson, 1966), and 3 Antarctic sediments. Sample positions are shown in Fig. 6, and the exact locations, as well as water depths at the sampling stations, are tabulated in Appendix C.

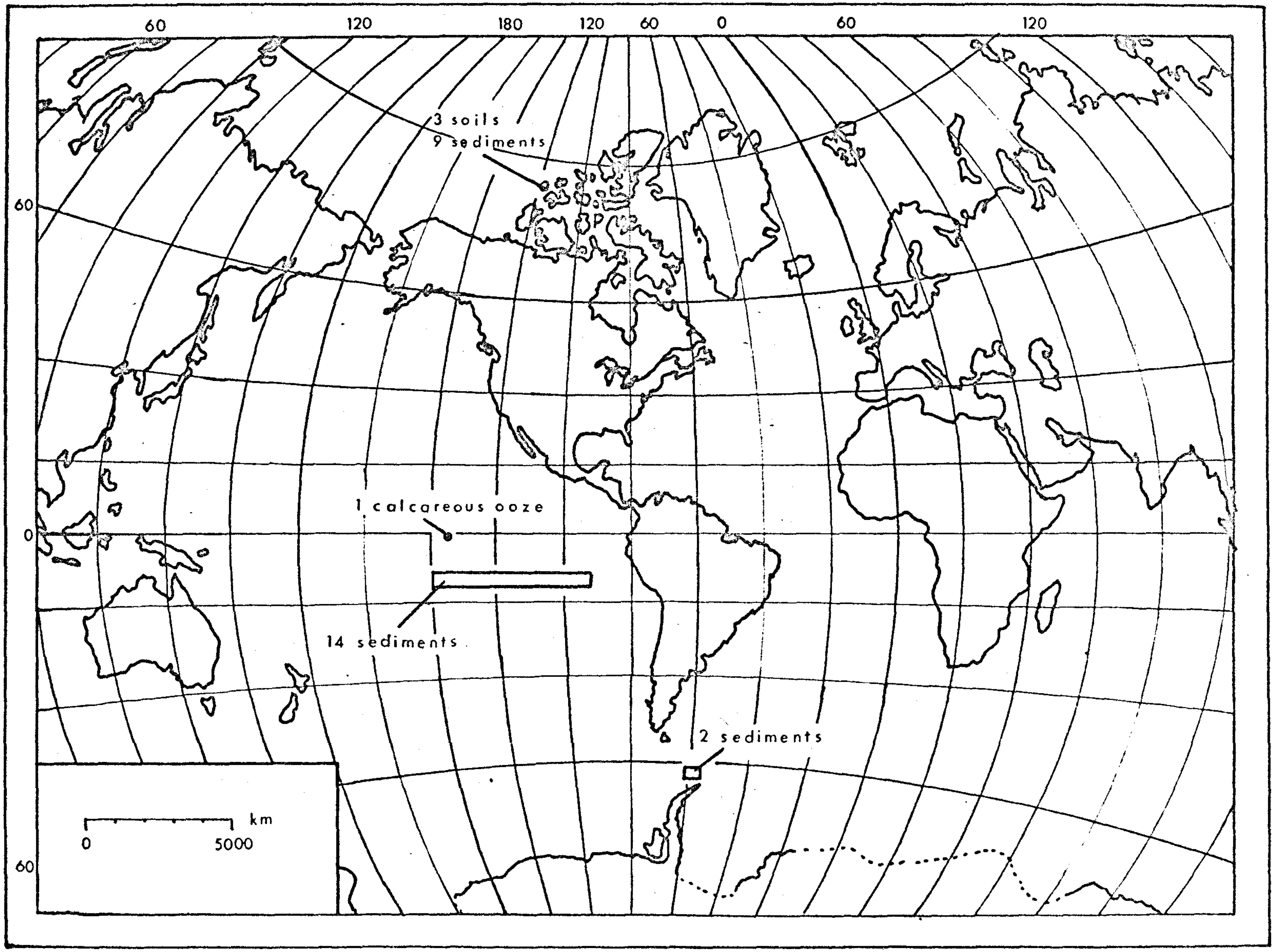

Fig. 6. Locations of samples analysed for Au and Pd

Neutron Activation Analysis

The extremely small concentrations of the precious metals in marine sediments make neutron activation the most reliable method for their determination at the present time. The method is comparative; sample and standard are simultaneously irradiated and their induced activities compared. The addition of an inactive carrier after irradiation permits corrections to be made for loss of the element in question during the radiochemical purification. In this study, the analytical procedure used is essentially that of Crocket et al (1968).

Preparation and Irradiation

Arctic and Antarctic core and grab sample material, sampled while still in a plastic state, was first washed with distilled water, then sieved to remove any sand or larger sized material. After air drying, the samples were powdered in a ceramic mortar. All Pacific sediments were received as fine powders, and no processing was required. Approximately 100 mg of sample were weighed into quartz ampoules for irradiation.

The standard solution used was prepared from "Specpure" chemicals, and contained 0.33, 0.044 and 0.023 μgm/ml of Pd, Ir and Au in 1M HCl. Approximately 25 mg of this solution were weighed into quartz ampoules for irradiation.

Groups of 6 samples with 2 or 3 standards were irradiated for 24 to 36 hours in the McMaster Nuclear Reactor in a flux of 1×10^{13} neutrons/cm^2/sec.

Sample Procedure

Carrier solutions containing 5, 8,and 20 mg of Pd, Ir and Au respectively, were added to a zirconium crucible (one for each sample) and evaporated to dryness. The irradiated sample was transferred to the crucible, mixed with 4 gm of a 1:1 Na_2O_2-NaOH mixture and fused over a meeker burner flame.

After cooling, the fusion cake was dissolved with 10 ml of 2M HCl followed by 10 ml of aqua regia. The contents of the crucible were transferred to a beaker and digested twice with 10 ml of aqua regia. The salts were then converted to chlorides by two digestions with 5 ml of concentrated HCl, and taken up in 30 ml of 0.5M HCl containing 0.004 moles of Ce^{4+} per ml.

The solution was filtered onto a 2 cm (0.8 cm diameter) column of Rexyn 201 200 mesh chromatographic grade anion exchange resin which had been washed with 100 ml of 0.5M HCl, and, immediately prior to loading, treated with 50 ml of 0.5M HCl-Ce^{4+} ion solution. (Note - the Ce^{4+} ion solution is required if Ir is being determined. In many experiments for this study only Au and Pd were determined, and steps involving Ce^{4+} ion solution were omitted.)
The sample solution was passed through the column at the rate

of 1 ml per minute, and after adsorption of the precious metals the resin was washed with 120 ml of 0.5M HCl.

Pd and Au were eluted with 120 ml of 0.1M thiourea-0.1M HCl solution. Following this Ir was eluted with 120 ml of 6M HCl.

The sulfides of Pd and Au were precipitated from the thiourea solution by the addition of 30 ml of concentrated NH_4OH and evaporation to 50 ml on a hot plate. The precipitate was centrifuged, washed, digested in aqua regia, converted to chlorides by two treatments with concentrated HCl, and taken up in 10 ml of 2M HCl. The solution was transferred to a separatory funnel and Au extracted with an equal volume of ethyl acetate. Pd remained in the aqueous phase.

Pd was precipitated from the aqueous phase by addition of 10 ml of 1.5% dimethylglyoxime solution. The precipitate was centrifuged, washed, digested with aqua regia, converted to chlorides with concentrated HCl, and taken up in 10 ml of 1M HCl. The precipitation was repeated, the precipitate centrifuged, washed, slurried with alcohol, and plated out on an aluminum planchet for counting.

The organic phase containing Au was heated gently with an equal volume of 2M HCl until Au had transferred to the aqueous phase. Au° was precipitated from the warm solution by the addition of 0.5 gm of hydroquinone. The precipitate was centrifuged, washed, digested in aqua regia, converted to chlorides with concentrated HCl, and taken up in 10 ml of 1M HCl. The precipitation was repeated, the metal centrifuged, washed, and transferred to a 1 dram glass counting vial.

The Ir solution was evaporated to dryness, treated with aqua regia, converted to chlorides with concentrated HCl, and taken up in 25 ml of 2M HCl. Ir° was precipitated with Zn metal, centrifuged, washed for several minutes with hot aqua regia and finally with water, then transferred to a 1 dram glass vial for counting.

Standard Procedure

The sealed standard ampoule was washed in hot aqua regia, then broken into a beaker containing Pd, Au and Ir carrier solutions. Ten ml of aqua regia were added, and the solution heated to near boiling for 20 minutes. The ampoule was flushed with a capillary pipette and discarded; the solution was taken to dryness, converted to chlorides with concentrated HCl and taken up in 10 ml of 2M HCl.

Au was extracted with ethyl acetate and precipitated with hydroquinone as in the sample procedure. Pd was precipitated from the aqueous phase with DMG as in the sample procedure. The supernatant, containing Ir, was filtered into a beaker, and Ir° was precipitated with Zn metal as in the sample procedure.

Counting

The beta decay of ^{109}Pd was followed for several half lives using a gas flow geiger tube. Occasionally it was necessary to subtract long-lived contamination from the initial counting rates before comparison with the standards could be made. The three Antarctic samples and a few of the Arctic samples displayed beta half lives of close to 15 hours compared to the ^{109}Pd half life of 13.6 hr. This appears to be due to fission product ^{112}Pd produced in the reaction ^{235}U(n,f)^{112}Pd, ^{109}Pd. The U content of the sediments is not known, but Crocket and Skippen (1964) found that decay curves of this type introduce errors of approximately 10 per cent. Accordingly, the Pd values marked with an asterisk in Table 12 should be viewed as maximum values only.

The Au and Ir gamma radiation spectra were recorded using a 1600 channel analyser with a well type NaI(Tl) detector. The .412 MeV photopeak of ^{198}Au was used for gold determinations. No contamination was ever noted. The .320 MeV photopeak of ^{192}Ir was not detected for any of the sediments analysed for this element.

Results and Discussion

The analytical results and average values for each sample are tabulated in Table 12. For the 27 sediments analysed from 3 widely separated areas, the range of Au

Table 12. Experimental results for Pd and Au in marine sediments and three Arctic soils[1]

	RESULTS		AVERAGES	
Arctic Soils	Au	Pd	Au	Pd
15	1.3,0.7	1.6	1.0	1.6
19	0.3	0.7	0.3	0.7
43	2.9,1.0,1.5	1.1	1.8	1.1*
Arctic Sediments				
1 (0-3 cm)	3.9,4.5	2.6	4.2	2.6
1 (144-147 cm)	3.3,2.5	1.9,2.8	2.9	2.4*
1 (" (< 4μ)	3.1,3.6	2.6,3.2	3.4	2.9*
6 (0-3) cm	2.6,3.6	2.5,2.6	3.2	2.6
9 (0-3 cm)	2.6,3.1	3.5	2.9	3.5
10 (0-3 cm)	2.3,2.3	1.1,1.2	2.3	1.2
10 (16-19 cm)	2.4,3.3	1.0,1.3	2.9	1.2
10 (50-53 cm)	1.6,1.8	1.5	1.7	1.5
29 (0-3 cm)	1.6	1.5	1.6	1.5
Pacific Calcareous Ooze				
320	2.0,1.5	1.4,1.9	1.8	1.7
East Pacific Rise Sediments				
Ris 46	2.9,2.0	4.2,4.3	2.5	4.3
Ris 50	2.5	6.3	2.5	6.3
Ris 56	1.4	5.7	1.4	5.7
Ris 60	2.6	1.0	2.6	1.0
Ris 63	2.0	0.8,0.5	2.0	0.7
Ris 66	1.1,1.4	3.6,4.0	1.3	3.8

(continued next page)

Table 12. (continued)

Ris 68	7.6	9.1,9.8	7.6	9.5
Ris 69	2.0	7.9	2.0	7.9
Ris 72	4.9,3.1	2.4,2.2	4.0	2.3
Ris 74	2.4	1.3	2.4	1.3
Ris 76	5.6	1.7	5.6	1.7
Ris 77	5.4	7.2	5.4	7.2
Ris 80	2.2	13.3	2.2	13.3
Ris 82	1.3	7.2	1.3	7.2
<u>Antarctic Sediments</u>				
PG-6-10	2.5	5.4	2.5	5.4*
PG-6-17	1.8	2.1	1.8	2.1*
17-35	2.0	2.2	2.0	2.2*

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[1] Concentrations in ppb

*Indicates maximum value.

is quite narrow (1.3 to 7.6 ppb), while that of Pd is somewhat larger (0.7 to 13.3 ppb). For each area taken individually, the average values are: Arctic near-shore sediments 2.7 ppb Au and 2.1 ppb Pd; Pacific calcareous ooze 1.8 ppb Au and 1.7 ppb Pd; East Pacific Rise sediments 3.1 ppb Au and 5.2 ppb Pd; Antarctic sediments 2.1 ppb Au and 3.2 ppb Pd. The Arctic soils average slightly lower than any of the sediments (1.0 ppb Au and 1.1 ppb Pd).

At the present time the data for Pd and Au in sedimentary rocks and Recent sediments are very scanty. DeGrazia and Haskin (1963) report averages of 2.5 ppb Au for carbonates, 4.7 ppb Au for shales, 6.0 ppb Au for sandstones, and 12 ppb Au for pelagic sediments. The pelagic clay figure is somewhat higher than that of this study, in which the highest gold value recorded was 7.6 ppb. The published literature apparently contains no data for Pd in marine sediments, with the exception of manganese nodules for which Harriss and Crocket (1968) report 5 to 6 ppb Pd and 2 to 3 ppb Au. Ir, which was not detectable under the experimental conditions of this study, is reported to range from .057 to .458 ppb in Pacific pelagic sediments (Barker and Anders, 1967) and averages close to 9 ppb in manganese nodules (Harriss and Crocket, 1968).

The nature of Pd and Au in the sediments is unknown. Sea water is undersaturated with respect to Au (Sillen, 1960) and probably with respect to Pd as well. According to Goldberg (1963), Au has a concentration of .004 ppb in solution in sea water, principally as $AuCl_4^-$. Presumably Pd in solution has a similar or slightly lower value. It is possible that Pd is present as Pd^{2+} and $PdSO_4$, rather than chloride complexes, since Pd is similar to Cu and to some extent Ni in its inorganic chemistry. If this is so, one might expect to find some partitioning of Au and Pd in sediments, with Pd being preferentially adsorbed by negatively charged particles such as clay minerals or manganese oxide colloids. However, there is no correlation between either Pd or Au and Al in the Arctic sediments studied, which indicates that these elements are not strongly associated with the clay minerals. Also, Harriss and Crocket (1968) found no correlation between these metals and Fe, Mn or a number of trace elements in a series of manganese nodules. It is interesting to note that while the Au and Pd contents of the manganese nodules analysed by Harriss and Crocket (1968) differ by no more than a factor of 2 or 3 from the concentrations in the sediments of the present study, Ir is concentrated in the nodules by a factor of 20 to 100. This suggests a mechanism of incorporation for Ir in the nodules radically different from that acting in the sediments. Other trace elements, notably Co, Ni and Cu, are also greatly enriched in manganese nodules relative to pelagic sediments, generally by about the same factor.

It has been suggested that precious metals in marine sediments may be largely due to extraterrestrial contributions. If this is so, one would expect significantly larger concentrations of Pd, Au and Ir in nodules relative to sediments because of the slower growth rates of the nodules (assuming a uniform areal influx of the extraterrestrial material). This does not appear to be the case for Au and Pd. On the other hand, Ir does show a large enrichment in the nodules, which may reflect an extraterrestrial source. There is no doubt that cosmic material does contribute to pelagic sediments since a large amount of such material falls on the earth's surface daily, and in areas of slow sedimentation it is diluted least. However, the results of this study seem to indicate that extraterrestrial material may not be the major source of Pd and Au in pelagic sediments. It is possible that detrital terrestrial material contains much of the Pd and Au found in the sediments, although more data for both terrestrial and marine materials are required before this conclusion can be substantiated. The fact that the calcareous ooze analysed has rather low Pd and Au contents compared to many of the other sediments may be due to the low content of detrital material.

Table 13 lists the values for Pd, Au and Ir in the sediments of this study, and in manganese nodules and some terrestrial rocks (from Tables 1 and 2, Harriss and Crocket, 1968). It is apparent from the data available that terrestrial rocks are potential sources for the elements in question. Adsorption from sea water by charged particles may also occur. The large enrichment in Ir in the manganese nodules relative to the sediments may be due to the fact that this element is supplied to a large extent by extraterrestrial material, and is less diluted in the nodules than the sediments. However, the suggestion that a major portion of the precious metal content of pelagic sediments is extraterrestrial in origin requires an intensive re-examination before any definite conclusions can be reached.

Table 13. A comparison of Pd, Au and Ir contents of various sediments and crustal rocks[*].

	Pd	Au	Ir
3 Antarctic sediments (this work)	3.2	2.1	<0.1
14 East Pacific Rise sediments (this work)	5.2	3.1	<0.1
9 Arctic near-shore sediments (this work)	2.1	2.7	<0.1
1 Pacific calcareous ooze (this work)	1.7	1.8	-
3 Atlantic manganese nodules	5.7	3.0	9.3
7 Pacific manganese nodules	6.0	2.7	9.4
2 Antarctic manganese nodules	3.1	6.5	2.7
Diabase (W-1)	11.5	5.0	0.26
Granite (G-1)	1.6	3.3	.044
Basalts	0.5-29	2.0-14.0	-

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[*] Results in ppb.

APPENDIX B

DESCRIPTIONS OF ANALYTICAL PROCEDURES

APPENDIX B

DESCRIPTIONS OF ANALYTICAL PROCEDURES

Identification and Quantization of Clay Minerals

The literature concerned with identification and quantitative analysis of clay minerals is voluminous; the criteria used here have been selected and modified from the work of Weaver (1958),Vemuri (1967), Johns, Grim and Bradley (1954), Warshaw and Roy (1961) and others. The relative amount of a mineral present has been expressed as the ratio of its first order reflection intensity (except in the case of chlorite where the 002 reflection was used) to the sum of all first order intensities. This gives a rough estimate of the proportions of the various minerals in the sample being studied. The conditions of x-ray diffraction are discussed in the text, and the following is a summary of the criteria used in identification.

1. Illite: Illite is a major component of all samples analysed, and was readily identified from its first order (10 A) and succeeding higher order peaks. These peaks are unaffected by glycolation or heating to 550°C. The 10 A peak intensity was used in the determination of the relative abundance of illite in the sample.

2. Chlorite and Kaolinite: All samples analysed contained a large amount of kaolinite relative to chlorite. The

first order chlorite peak at 14 A is weak and often interfered with by 10A-14A mixed layer minerals; hence it cannot be used as an abundance indicator. The second order chlorite peak coincides with the first order kaolinite peak at 7 A. Where possible, the kaolinite: chlorite ratio was determined from a slow scan past the 3.57 A (kaolinite) and 3.53 A (chlorite) peaks, and the relative contributions of the two minerals to the 7 A peak computed. In cases where these two reflections were not resolved, the chlorite contribution to the 7 A peak was determined from the 4.7 A (003) chlorite reflection, using the assumption that the intensity of this peak represents 80% of the 7 A chlorite intensity (Vemuri,1967).

3. 10A-14A Mixed Layer Minerals: Most samples analysed showed a small but distinct 14 A peak followed by a gradual intensity buildup (but with no apparent peaks) to the 10 A illite peak. The 14 A peak is due mainly to chlorite (verified by the fact that it is retained but shifted to a slightly lower A value upon heating to 550°C). Neither K nor Mg saturation had any effect on the 10A-14A band, which indicates an absence of pure vermiculite or sodium montmorillonite. Glycolation in most cases produced a small shift of part of the 14 A material to about 15 A, indicating some expandable material,

but in no case was a 17 A montmorillonite reflection observed. Heating to 550°C always produced a sharpened 10 A peak of increased intensity, with consequent decrease in the 10A-14A band, and the increase was taken as a measure of the mixed layer expandable component. No exact characterization of this component was made.

4. Quartz: In most cases small amounts of quartz were present, indicated by the 4.26 A first order reflections. As only clay minerals were being investigated, this peak was omitted in the computation of "total mineral intensity".

Preparation of Solution A

Solution A was used for the colorimetric determinations of SiO_2 with molybdenum blue and Al_2O_3 with alizarin red. The procedure used is a modification of that outlined by Shapiro and Brannock (1962).

To a series of dry, 75 ml Ni crucibles was added 10 ml of 15% NaOH solution. The solution was evaporated to dryness in a sand bath. Samples weighing approximately 50 mg were weighed out and sprinkled on the NaOH. Multiples of 7 mg of NBS99 (68.52% SiO_2 and 19.02% Al_2O_3) were weighed out to cover the range of the samples. The crucibles were covered and fused for 15 minutes in a meeker flame adjusted to give a dull red heat. The crucibles were swirled occasionally during the fusion. After the crucibles had cooled to room temperature, 50 ml of H_2O were added, and the crucibles allowed to stand overnight.

Using an acid solution made by adding 430 ml 1+1 HCl to 20 l H_2O, the leach was quantitatively transferred to a 1000 ml flask and made up to volume. The solution was mixed well and transferred to a 250 ml polyethylene bottle. After standing overnight to clear, SiO_2 was determined, followed by Al_2O_3.

Preparation of Solution B

Solution B was used for the colorimetric determinations of TiO_2, P_2O_5 and total Fe as Fe_2O_3. The same solution was used to determine Na_2O, K_2O, CaO, MgO, MnO and Rb_2O by atomic absorption. The procedure used is a modification of that given by Shapiro and Brannock (1962).

Teflon crucibles, rendered anti-static by dipping into liquid hand soap solution, were used to prepare the solution. Approximately 0.5000 gm of sample was weighed out and transferred to a crucible. The sample was wet thoroughly with water, then 2 ml HNO_3 were added and the crucible quickly covered. When the reaction was complete, the cover was removed and the mixture was digested on a steam bath for about 15 minutes. Following this, 20 ml of a 1:3 mixture of $HClO_4$ and HF were added, the solution mixed, covered, and digested at low heat overnight on a steam bath.

The cover was removed and rinsed with water into the crucible. The steam bath heat was increased and the solution evaporated to about 7 ml. The crucible was transferred to a sand bath and evaporated to about 2 ml. Organic matter remaining after this treatment was decomposed by adding more $HClO_4$, replacing the cover, and heating strongly on the sand bath.

After rinsing and drying the crucible, about 20 ml H_2O were added and mixed to dissolve the salts. The solution was quantitatively transferred to a 400 ml Vycor beaker with H_2O. After adding 2 ml HCl and a silica no-bump stirring rod, the beaker was covered and the solution boiled for 5 to 10 minutes. The solution was then transferred to a 100 ml volumetric flask, Li solution was added to make approximately 500 ppm Li, and the solution was made up to volume.

Rb_2O was determined on the first dilution. Two subsequent dilutions (1:5 from the first dilution and 1:10 from the second) were required for the other determinations. Li solution and HCl were added to each dilution to maintain 500 ppm Li and about 0.2 M HCl.

Standards were prepared from "Specpure" chemicals and treated in the same manner as the samples. Fe was determined colorimetrically with orthophenanthroline, Ti with "Tiron" (disodium-1,2-dihydroxybenzene-3,5-disulfonate), and P with molybdivanadate. A Beckman Spectrophotometer was used for the colorimetric determinations.

The atomic absorption determinations were made with a Perkin Elmer Model 303 Atomic ABsorption Spectrophotometer. Conditions for analysis were those given in "Analytical methods for Atomic Absorption Spectrophotometer-Model 303" by Perkin Elmer.

APPENDIX C

SAMPLE DESCRIPTIONS AND LOCATIONS

Sample Descriptions and Locations

Sample	Depth in Core (cm)	Description	Water Depth (m)	Location
1	0-3	dark brown mud	170	Marie Bay
1	52-55	light coloured grey-brown mud	170	Marie Bay
1	144-147	laminated light and dark brown mud	170	Marie Bay
2	0-3	light brown mud	260	Marie Bay
6	0-3	laminated light and dark brown sandy mud	250	Marie Bay
8	0-3	brown clay mud	267	Fitzwilliam Strait
10	0-3	light brown clay mud	190	Fitzwilliam Strait
10	16-19	dark red-brown mud	190	Fitzwilliam Strait
10	50-53	grey-brown sandy mud	190	Fitzwilliam Strait
28	0-3	mottled brown mud	360	Fitzwilliam Strait

(continued next page)

Sample Descriptions and Locations (continued)

Sample	Depth in Core (cm)	Description	Water Depth (m)	Location
29	0-3	light brown mud	172	Fitzwilliam Strait
11	(soil)	dark grey soil	-	Melville Island
13	(soil)	yellow-brown soil	-	Eglinton Island
15	(soil)	grey soil	-	Prince Patrick Island
17	(soil)	brown sandy soil	-	Prince Patrick Island
19	(soil)	grey-brown soil	-	Melville Island
21	(soil)	brown sandy soil	-	Melville Island
25	(soil)	brown sandy delta mud	-	Melville Island

(continued next page)

Sample Descriptions and Locations (continued)

Sample	Depth in Core (cm)	Description	Water Depth (m)	Location
26	(soil)	black soil	-	Melville Island
43	(soil)	red-brown soil	-	Melville Island
320	510	calcareous ooze	4437	0°06'S, 135°58'W
Ris 46	30-60	-	3980	13°43'S, 90°30'W
Ris 50	30-60	-	4120	13°36'S, 96°42'W
Ris 56	33-60	-	3780	13°02'S, 104°41'W
Ris 60	37-70	-	3560	12°48'S, 107°59'W
Ris 63	30-37	-	3135	12°39'S, 110°00'W
Ris 66	30-70	-	3165	12°30'S,112°37'W
Ris 68	30-70	-	2990	13°36'S, 112°42'W
Ris 69	30-70	-	3010	14°41'S, 113°29'W
Ris 72	30-70	-	3250	14°18'S, 115°37'W
Ris 76	30-70	-	3800	13°54'S, 125°21'W
Ris 77	30-67	-	3985	14°02'S, 128°29'W

(continued next page)

Sample Descriptions and Locations (continued)

Sample	Depth in Core (cm)	Description	Water Depth (m)	Location
Ris 80	30-70	-	4250	14°02'S, 134°55'W
Ris 82	30-70	-	3900	14°03'S, 139°35'W
PG-6-10	(grab)	grey-brown mud	802	62°35'S, 57°57'W
PG-6-17	(grab)	grey-brown mud	1115	62°43'S, 59°40'W
17-35	(grab)	grey-brown sandy mud with shell fragments	-	Antarctic Ocean

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