

GEOCHEMISTRY

10. LAKE SEDIMENTS FROM PERMAFROST REGIONS;
Zn, Cu, Ni, Co and Pb CONTENT OF THE SUB-2000
MICRON PARTICLE SIZE RANGES

Project 700046

R. J. Allan and R. T. Crook

Introduction

From December, 1971 to May, 1972, a study was conducted to determine the Zn, Cu, Ni, Co and Pb concentrations in each of eight different particle-size ranges of selected lake sediments from permafrost regions in the Northwest Territories. A search through available literature showed that very few studies of this nature, if any, have been published on lake sediments.

A group of eight samples were chosen for this study (Table 1). These sediments represented five different environmental and geological areas in subarctic and arctic regions of Canada. These areas are underlain by five different rock types (Table 1). The samples had varying trace element concentration, as shown by previous analysis of the total, <80 mesh (<177 μ), sample. The sediments were first sieved to less than 2 mm. Very few, if any, greater than 2 mm particles were encountered during this procedure. The less than 2 mm fraction was then subjected to a procedure of soil leaches, mineral dispersion and fractionation¹. This leaching and dispersion procedure, carried out on the <2 mm fraction first removed all carbonates and exchangeable cations, then organics, then amorphous coatings of Fe and Mn hydroxides, and finally amorphous oxides of Si and Al. These leaches have been stored for future analysis. This "cleansed" sample was then fractionated into eight particle size ranges. Analysis of each size range was made for Zn, Cu, Ni, Co, Pb, Fe and Mn, by atomic absorption spectrophotometry following an HF-HNO₃-HClO₄ total dissolution. The results, in parts per million concentration, are listed in Table 1. Data for certain samples are presented in Figures 1, 2 and 3. All of the samples selected were of medium to high concentrations in one or more elements relative to the average regional concentration levels, so that a readily measurable concentration, above the instrumental detection limit for each element, could be obtained.

Results

The results are given in terms of trace element concentration in each size range. The highest Zn values in the clay fraction were in samples which came from lakes adjacent to known ore deposits containing Zn (Table 1). High Zn concentrations were also found in the <2 μ clays of samples from a lake near a large gossan in an Archean acid volcanic area and also from a lake in an Archean basalt area. The highest copper concentration (8070 ppm Cu) is in the <<2 μ fraction of a sample from a lake adjacent to the High Lake deposit. This known, but undeveloped, deposit in the Northwest Territories consists of 5 million tons Cu-Zn set in an Archean acid volcanic belt. Of the three

TABLE I

Trace element concentrations in particle size ranges
of lake sediments from Arctic Canada

Table 1 (contin

SAMPLE NUMBER	PARTICLE SIZE RANGES							
	SAND				SILT			CLAY
	2000 μ - 500 μ	500 μ - 250 μ	250 μ - 105 μ	105 μ - 53 μ	53 μ - 20 μ	20 μ - 5 μ	5 μ - 2 μ	<2 μ
ZINC	ppm							
1	no sample	68	31	49	96	635	1294	2894
2	216	189	221	347	562	1059	1735	3790
3	50	47	110	187	684	2853	4688	6120
4	40	30	27	29	53	143	395	2495
5	118	79	63	48	91	205	785	3593
6	226	180	143	150	94	88	143	537
7	123	116	132	150	198	258	253	738
8	100	107	88	79	94	168	332	1390
COPPER								
1	no sample	11	5	9	7	35	50	138
2	297	231	237	308	471	975	1583	8070
3	20	9	231	29	40	101	135	221
4	9	7	5	6	6	9	19	122
5	24	20	27	16	19	68	192	672
6	235	249	234	234	169	233	398	2000
7	166	156	161	174	167	156	120	685
8	36	36	33	25	36	23	28	154
NICKEL								
1	no sample	24	15	23	26	69	77	100
2	26	21	21	24	30	38	58	50
3	43	39	45	55	69	112	119	143
4	9	13	6	9	11	17	26	87
5	79	62	52	49	39	89	134	248
6	66	51	49	73	75	41	41	93
7	49	39	47	53	60	67	67	130
8	904	858	583	362	296	214	197	530

COBALT	
1	no sample
2	8
3	10
4	1
5	24
6	45
7	27
8	138
LEAD	
1	no sample
2	20
3	12
4	39
5	17
6	4
7	16
8	4

1. From a lake in the Hacke
2. From a lake deposit in th
3. From a lake Lake area,
4. From a lake on Little Co:
5. From a lake volcanic roc
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7. From a lake basic volcan
8. From a lake (intrusive roc

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Table 1 (continued)

CLAY	
5 μ - 2 μ	<2 μ
1294	2894
1735	3790
4688	6120
395	2495
785	3593
143	537
253	738
332	1390
50	138
1583	8070
135	221
19	122
192	672
398	2000
120	685
28	154
77	100
58	50
119	143
26	87
134	248
41	93
67	130
197	530

COBALT								
1	no sample	5	2	3	5	19	18	20
2	8	5	8	8	10	13	19	21
3	10	6	8	16	23	45	60	70
4	1	1	1	1	1	1	6	20
5	24	19	15	11	15	29	57	109
6	45	31	27	26	16	11	16	58
7	27	24	26	29	35	37	32	72
8	138	107	42	29	19	19	19	59
LEAD								
1	no sample	4	4	4	28	19	4	64
2	20	28	25	34	31	36	87	450
3	12	24	19	31	33	57	71	135
4	39	31	16	17	19	16	30	101
5	17	13	28	17	22	22	34	89
6	4	4	19	4	19	4	4	48
7	16	4	4	4	4	16	22	42
8	4	39	4	4	16	13	13	47

SAMPLE DESCRIPTIONS

1. From a lake (65° 55'N; 108° 22'W) adjacent to a 10-million-ton Zn ore deposit in the Hackett River area, in Archean acid volcanic rocks.
2. From a lake (67° 23'N; 110° 51'W) adjacent to a 5-million-ton Cu-Zn ore deposit in the High Lake area, in Archean acid volcanic rocks.
3. From a lake (67° 28'N; 110° 57'W) adjacent to a large gossan in the High Lake area, in Archean acid volcanic rocks.
4. From a lake (75° 33'N; 96° 09'W) near a 1-million-ton Pb-Zn ore deposit, on Little Cornwallis Island, in Paleozoic carbonate rocks.
5. From a lake (64° 16'N; 115° 25'W) in the Indin Lake area, in Archean basic volcanic rocks.
6. From a lake (67° 24'N; 116° 27'W) adjacent to a 3-million-ton Cu ore deposit, in the Coppermine area, in Proterozoic basic volcanic rocks.
7. From a lake (67° 22'N; 116° 18'W) in the Coppermine area, in Proterozoic basic volcanic rocks.
8. From a lake (66° 54'N; 115° 13'W) in the Muskox Intrusion area, in ultrabasic intrusive rocks.

other relatively high copper values, one came from a lake adjacent to a 3-million-ton Cu deposit in the Hackett River area, N. W. T. The other two were from Archean and Proterozoic basalt areas of regionally higher Cu concentrations. Similarly, the highest Pb (450 ppm Pb) was in the < 2 μ fraction of a sample taken from a lake adjacent to the High Lake Cu-Zn-Pb ore deposit which produced the highest Cu and one of the highest Zn concentrations. The highest Ni concentration (904 ppm Ni) was found in the 2000 μ to 500 μ size fraction of a sample taken from a lake which is found in an ultrabasic intrusive area, the Muskox Intrusion, which is characterized by regionally higher Ni and Co concentrations. The highest Co value (138 ppm Co) was also found in the 2000 μ to 500 μ size fraction of the same sample in which the highest Ni concentration was observed. The one other relatively high Co concentration was found in the < 2 μ fraction of a sediment taken from a lake in an Archean basalt area.

All of the samples had high concentrations of trace elements associated with adjacent ore deposits or the surrounding rock types.

Discussion

Most of the samples showed the highest concentrations in the finer size fractions (Figs. 1, 2 and 3). The highest concentration of every element was, in all cases but two, in the < 2 μ fraction (Table 1). Normally there was a sharp decrease in concentration from the < 2 μ fraction to the 5 μ to 20 μ fraction. However, relatively high concentrations were normally maintained until a particle size range of 50 μ to 100 μ was reached. Few samples had significantly

higher concentrations in the finer size fractions (<50 μ), and for Ni and Co, regionally higher

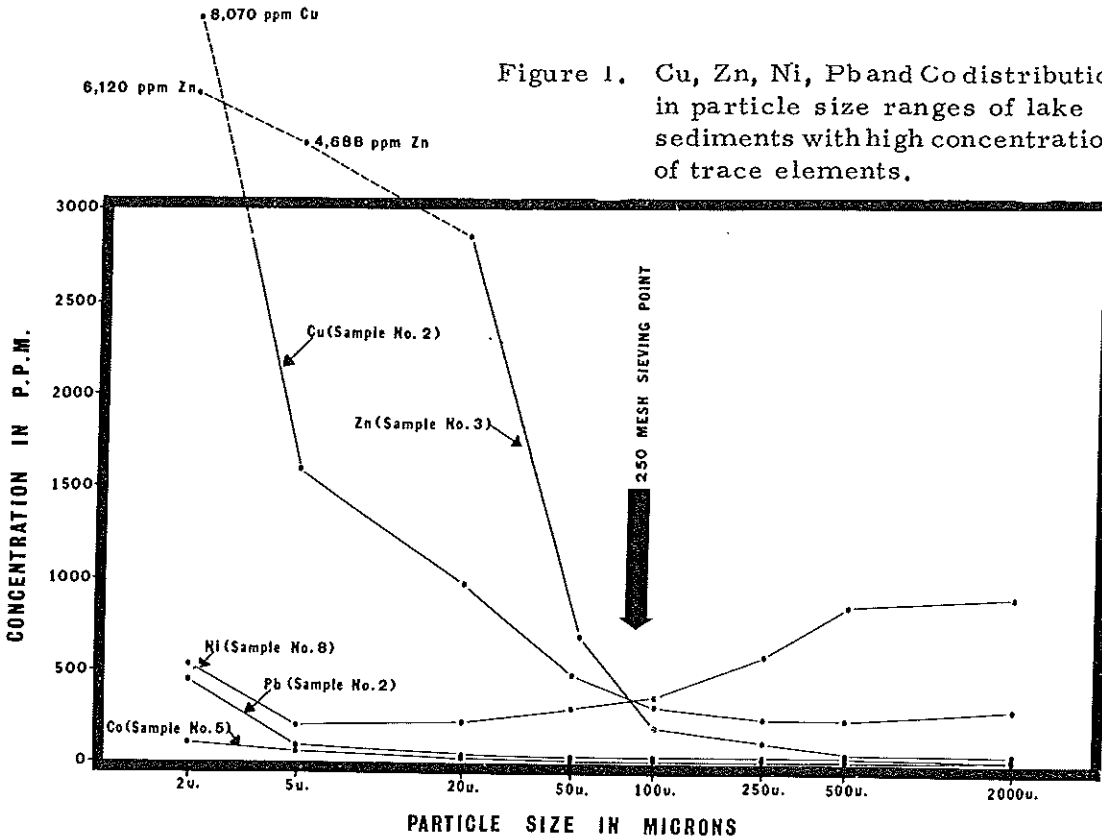


Figure 1. Cu, Zn, Ni, Pb and Co distribution in particle size ranges of lake sediments with high concentrations of trace elements.

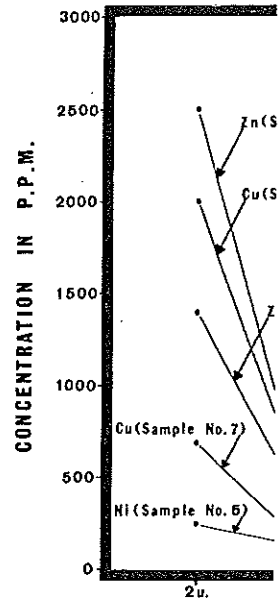


Figure 2. Cu, Zn distribution in sediment.

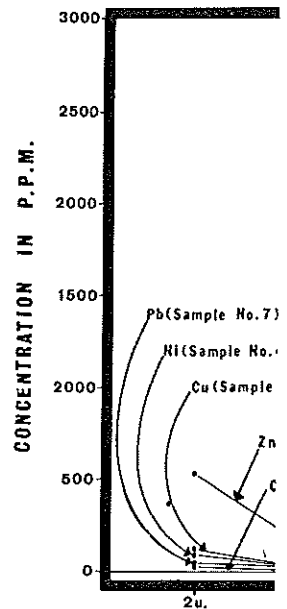


Figure 3. Cu, Zn, Ni, Pb distribution in lake sediments.

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higher concentrations in the coarser fractions (>50μ) compared to the finer fractions (<50μ), as mentioned. The only exception to the rule was sample 8 for Ni and Co. This sample came from an ultrabasic intrusive area of regionally higher Ni and Co background concentrations. In this sample,

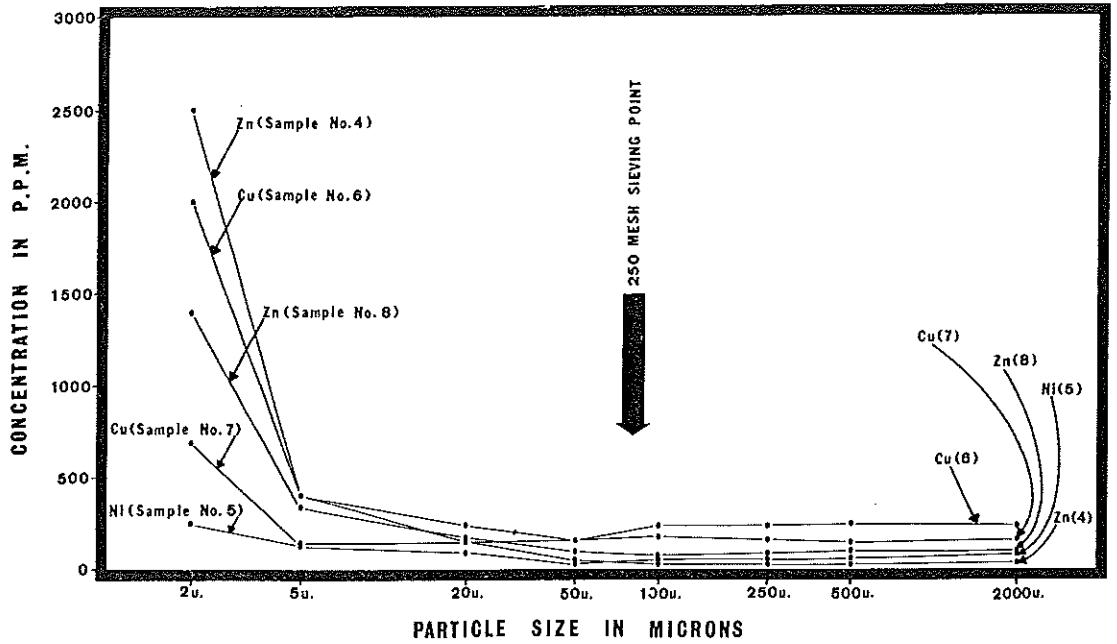


Figure 2. Cu, Zn and Ni distribution in particle size ranges of lake sediments with intermediate concentrations of trace elements.

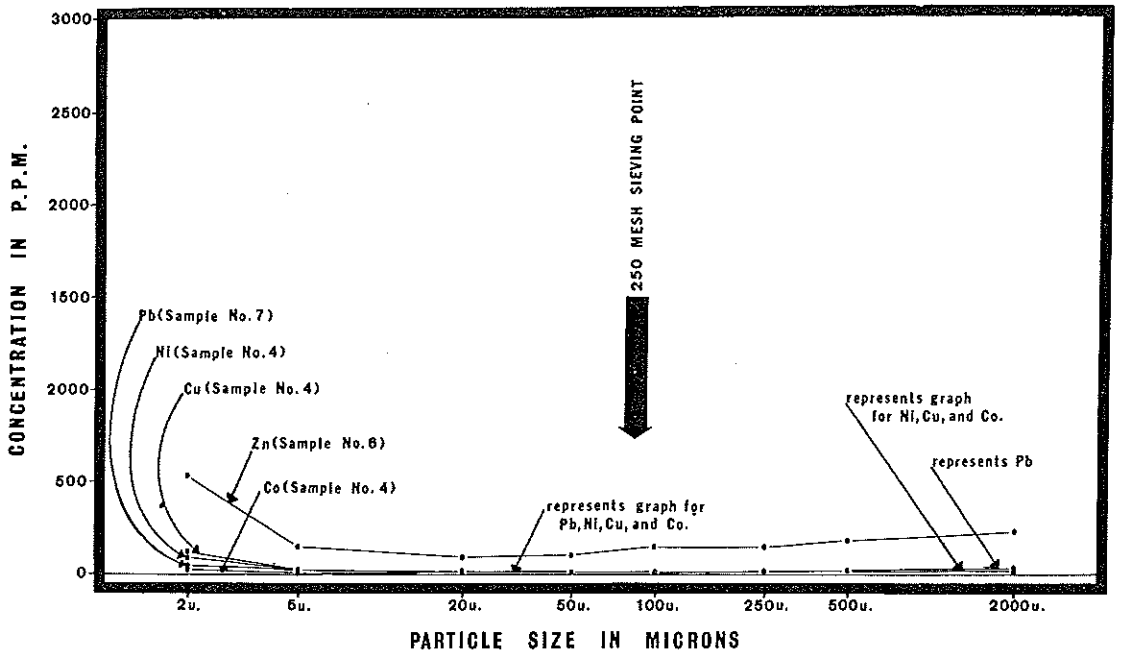
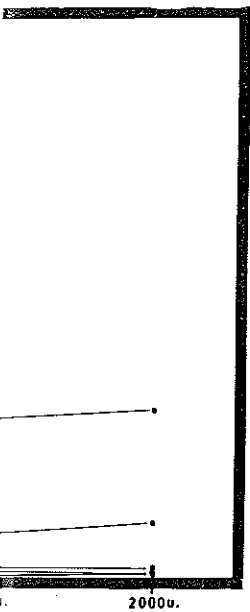


Figure 3. Cu, Zn, Ni, Pb and Co distribution in particle size ranges of lake sediments with low concentrations of trace elements.



the sand fraction had relatively higher concentrations of Ni and Co, with the highest concentrations being in the coarse sands.

In most surficial materials, the 50 μ particle size is the break between the sand and silt fractions. The sand fractions are usually composed of rock fragments or aggregates of several minerals characteristic of the parent rocks. Trace elements in the >50 μ fraction should show a slight increase in concentration as the fraction becomes coarser and so, more closely approaches the parent rock in composition (Table 1, Figs. 1 and 2). The <50 μ portion, consisting of the silt and clay fractions, is normally composed of quartz, feldspars, micas and various secondary layer silicates such as amphiboles and pyroxenes. In this <50 μ fraction we find increasing quantities of trace elements with a decrease in particle size (Figs. 1, 2 and 3).

Because these samples have been leached by several procedures (pH5 NaOAc; H₂O₂; Na-citrate-dithionite) it is unlikely that a very large concentration of trace elements remain in an adsorbed form, that is, in the form of cations sorbed on the surface of fine particles coated by organics or amorphous iron and manganese hydroxides. The increases in concentration of trace elements observed in the finer fractions must then be due to trace element cations in the actual crystal lattices of the minerals in these finer fractions. These can presumably occur in three forms: (1) in the form of minor accessory minerals of high trace element content; (2) in the form of isomorphously substituted elements in the actual lattices of the nonlayer silicate minerals, such as feldspars or in the lattices of layer silicates, such as biotites; or (3) as specifically adsorbed trace elements in the interlayers of secondary layer silicates such as illites or vermiculites. Because sorption processes depend on the total available surface area, we should expect this process to produce greater concentrations of trace elements in the very fine silts and especially in the clays. In the <50 μ fraction, the concentrations in the coarse silt fraction are possibly due to factors (1) and (2) above. In the medium silt fraction, factors (2) and (3) are probably dominant. In the fine silt the nonlayer silicate minerals are replaced by layer silicates so that factor (3) becomes of major importance relative to factor (2). In the clay fraction the high concentrations are possibly due to factors (3) and (2). There may be an effect of the accessory heavy minerals in even the finest size fractions, but this effect possibly decreases with a decrease in particle size. Because of the above effects, the trace element concentrations should increase with a decrease in particle size (Table 1; Figs. 1, 2, and 3).

We should also expect to find high concentrations of trace elements in the leaches themselves. This would be due to the removal and dissolution of the organics and the Fe and Mn hydroxide coatings, and therefore, most of the adsorbed cations, from the surface of the particles.

As seen from the discussion above of the >50 μ and <50 μ fractions, the size range immediately on either side of the 50 μ level should have the lowest concentrations of trace elements. These deductions are substantiated by the results presented in Table 1 and Figures 1, 2 and 3. Because the relative concentrations of the elements can be related (Table 1) to the estimated size of the mineralization which is the source of each trace element, it is then the finer fractions which are responsible for the anomalies due to the nearby presence of oxidation and leaching of sulphides. Also, in areas where unusually high background values for one or more elements are encountered, i. e., sample 8 in the ultrabasic intrusive area, which is regionally higher in Ni and Co, it might be

found that using concentrations of the presence of In prosp the above result better the result the various size must be separat <50 μ size fracti where large nur

11. POTENTIAL

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found that using the finer fractions of the sediment for analysis would give concentrations closer to those desired in discerning anomalous areas due to the presence of sulphides.

In prospecting for sulphide deposits, using inorganic lake sediments, the above results indicate that the finer the fraction selected for analysis, the better the results because trace element contrasts will be increased. However, the various size fractions less than 50μ (approximately 250 mesh) usually must be separated by a wet sedimentation technique. Therefore, the total $<50\mu$ size fraction appears to be the one most economically suited to any survey where large numbers of samples are collected.

11. POTENTIAL OF COMBINED GC-MS AS A SENSITIVE TOOL IN EXPLORATION GEOCHEMISTRY

Project 690091

I. R. Jonasson

The Instrumentation

An integrated GC-MS unit consists of two basically different instruments. The gas chromatograph (GC) is designed to separate and measure a large number of chemical constituents, including those present as trace concentrations, which may occur in either a gas or liquid phase. The obvious application is therefore to direct sampling of planetary or soil atmospheres for trace materials of immediate interest. In many cases, however, the trace material sought may be present in microgram or picogram quantities only, levels which are at the threshold or below the sensitivity limits of conventional GC detectors such as flame ionization gauges or electron capture devices.

The integration of a GC with a mass spectrometer (MS) can offer a method for direct sampling and quantitative analysis of gaseous constituents at picogram levels. With the acquisition of the instrumentation described briefly herein, the Geochemistry Section has undertaken an extensive critical survey of the potential of using such gaseous emanations to detect deeply buried ore deposits. The project both continues the mercury studies initiated three years ago and extends similar investigations to less familiar gases.

Work performed to date on these units has consisted essentially of testing and sample gas analyses. Alkylmercurials can be easily characterized by their mass spectra and can be detected at nanogram levels.

Applications in Geochemistry: 1. Pathfinders to metal deposits

In the immediate vicinity of a buried ore deposit a wide variety of volatile and gaseous materials occur which are either derived from the ore-body by slow chemical processes or owe their origins to the same processes that originally formed the ore deposit. In both cases, however, such vapours are directly indicative of the presence of what may be economic mineralization.

The vapours are quite mobile and generally can permeate covering rock and soil to reach the surface above the deposit. In some instances distance travelled may be around 600 metres. Thus a sampling program designed

to tap soil gases will locate these pathfinder vapours and thereby indicate the presence of mineralization¹. Perhaps the vapour most in the news at present is mercury metal - a species now infamous as a noxious pollutant. From the viewpoint of a geochemist mercury is singularly important as an indicator of polymetallic sulphide deposits (lead, silver, zinc, antimony). Its presence in soil atmosphere (and terrestrial atmosphere) has been utilized extensively to map shallow underground veins of such deposits. Some rather unique physiochemical properties of mercury have enabled it to be detected at nanogram concentrations by conventional atomic spectroscopic techniques. However, detection limits for mercury in soil atmospheres are such that more sensitive detection methods are required to find more deeply buried deposits. GC-MS fulfils these requirements completely and allows potential evaluation of the types of mercury vapours which may exist in the gases sampled. Information gleaned from these studies may then produce data which may help interpret better, exploration methods based on the measurement of soil mercury ions.

Other vapours and gases are potentially just as useful as mercury but usually their concentrations in soil gases are two to three orders of magnitude lower or higher. Examples of such vapours are sulphur-dioxide, hydrogen sulphide, carbon dioxide, iodine, bromine which are associated with deposits of heavy metals, copper, uranium, iron, gold, tin, nickel and rare metals. The presence of iodine and bromine may also indicate proximity of fossil fuels. Volatile hydrocarbons and carboxylic acids in soil gases may lead to the same type of deposit. The value of seeking such vapours is enhanced in cold climates and permafrost regions since lower temperatures and frozen (immobile) conditions allow for increased accumulation of these pathfinder materials in the soils and soil gases. There is sufficient data available in the foreign literature to support this contention. The supporting list of references with this essay provides examples of the uses of all the aforementioned vapours. Other vapours of great interest are considered to occur only at picogram concentrations in soil atmospheres. These include various organometallic compounds and hydrides which, in part, owe their origins to bacterial and chemical action within the soils themselves. For example, dimethylmercury and other alkylmercurials, alkylarsines (arsenic) and arsine, alkylstibines (antimony) and stibine, selenium and tellurium hydrides and various organic derivatives may occur in the presence of copper and base metal mineralization. Moreover, these rarer trace elements are very sensitive indicators of specific types of deposits and the mere presence of say, tellurium compounds may be regarded as a valuable piece of geochemical information since these compounds would only reach significant and detectable levels if extensive metallic sulphides were nearby. A mass spectrometer is the only analytical tool capable of detecting and identifying the very low concentrations of these vapours.

Applications to Geochemistry: 2. Fluid-gas Inclusions

Fluid inclusion studies are increasingly being used in the search for hydrothermal ore deposits. The Russians are presently leaders in the field of fluid inclusion research and its application to exploration for economic ore deposits. Since these fluids are preserved relics of the hydrothermal solutions that produced the enclosing minerals, their composition should reflect the ore potential of the vein system^{2,3}. Our present knowledge of the chemical

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relationship between solution and precipitated mineral phases is sufficient to allow interpretation of ore potential from the chemistry of hydrothermal solutions as represented by fluid inclusions^{4, 5}.

The method requires the analysis of minute fluid inclusions from quartz, calcite and sphalerite in veins for their dissolved gases and for the isotopic compositions of carbon, oxygen, hydrogen and sulphur³. GC-MS is used to analyze for hydrogen sulphide, sulphur dioxide, hydrogen chloride, hydrogen fluoride, ammonia, carbon dioxide, nitric oxide, hydrogen, oxygen, carbon monoxide and methane⁶. These data along with metal cation ratios can be used to prepare contour maps of vein systems which can be interpreted to define direction and potential of ore occurrence⁷.

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12. AIRBORNE

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ADDENDUM

(May 24, 1972)

37. WINTER WORKS LAKE BOTTOM SEDIMENT SAMPLING
PROGRAM FOR THE TIMMINS - VAL D'OR REGION

Project 710099

E.H.W. Hornbrook

A lake bottom sediment and till sampling project was performed under the Special Employment Plan of the Federal Winter Works Program. Field work was carried out in the Timmins-Val d'Or region of northern Ontario and northwestern Quebec from December, 1971 to early April, 1972. The project was planned and supervised by E.H.W. Hornbrook and conducted, under contract, by C.F. Gleeson and Associates Ltd., Ottawa. The total project provided 95 man-months of employment.

Objectives of the project were to provide winter employment and to evaluate the following aspects of geochemical exploration in the clay belt environment of the region.

- 1) The effectiveness of regional lake bottom sediment sampling in the clay belt to detect meaningful metal dispersion halos.
- 2) The effectiveness of bottom till sampling by overburden drilling to detect anomalous dispersion halos in till.
- 3) The comparison of the element content in lake bottom sediment and till at the same sample site to determine their relative suitability as a sample medium. This includes inspection of the geochemical dispersion halos of the two materials to determine their relationship to each other and to known mineral occurrences.
- 4) The suitability of various selected mesh sizes of lake bottom sediment and till prepared for analysis to enhance the contrast of anomalous metal values.

In the regional lake bottom sediment sampling program: 1327 samples were collected from 6580 square miles in the Val d'Or-Noranda, Quebec area and 1400 samples were collected from 6952 square miles in the Kirkland Lake-Timmins, Ontario area.

The overburden drilling program was carried out on lake ice as follows: Pelletier Lake - 30 sample sites; Macamic Lake - 77 sample sites; Abitibi Lake - 54 sample sites and Night-Hawk Lake - 60 sample sites. Calculated footage required to collect the bottom till samples would be 12,124 feet; however, actual footage, including drilling to determine bedrock depth prior to sampling and occasional multiple attempts to collect a sample, was 30,370 feet. These samples were processed to obtain a heavy mineral separate and a -230 mesh sample. All samples have been analyzed for Cu, Pb, Zn, Mo, Ni, Mn, As and Ag and these results, together with appropriate field data, have undergone key punching, compiling, listing, digitizing and simpler statistical treatment.

Limited access and poor ground mobility combined with adverse winter weather and snow conditions made it impossible to obtain the desired uniform distribution of sample sites throughout the region. Access to sample sites was by vehicles on ploughed secondary roads, Snowmobile travel, and

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snowshoe traversing where necessary. There was no fixed or rotary wing air support. Thus, there are some areas with little or no samples within the region and other areas that appear, relatively, to be oversampled.

Contamination of sample sites by mining and other industrial activity and the resulting high metal concentrations creates a problem in the evaluation and interpretation of the data. At many sample sites, contamination was observed and the type recorded on field cards. However, contamination is not necessarily recognized in winter. Thus, there are possibly many high element concentrations listed for sample sites where contamination was present but not recorded. At all sites samples were collected through holes chipped, cut or augered through ice.

Careful examination of the data showed several areas of interest aside from the obvious ones closely associated with the mining camps of Kirkland Lake, Noranda, etc.

Variable sample density and the contamination mentioned above stress the necessity for a careful consideration of the data. Follow-up work, with resampling as a prerequisite, is recommended before serious exploration in any interesting area is undertaken.

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