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GEOCHEMISTRY

BEAR-SLAVE OPERATION

Project 720063

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The Bear-Slave Operation is a reconnaissance geochemical survey of some 40,000 square miles of the central parts of the Bear and Slave geological provinces of the Canadian Shield. Nearshore, inorganic, silty, lake sediment and surface lake water were systematically collected during the past field season at a site density of one per ten square miles. The objectives of the survey are multipurpose:

1. Mineral exploration. To delineate areas of anomalous metal content that may contain mineral deposits.
2. Geochemical mapping. To map regional geochemical variations in the composition of the upper crust.
3. Geochemistry of the environment. To show the natural abundance and amount of variation of several trace elements, some of which are potentially toxic, in a part of the country that has been little influenced by man's activities.

During the last several years work carried out by various members of the Geochemistry Section has indicated that lake sediments are an excellent medium for both reconnaissance and detailed geochemical exploration surveys within permafrost areas of the Canadian Shield. During 1971 a final orientation survey was carried out in the Bear and Slave geological provinces. This

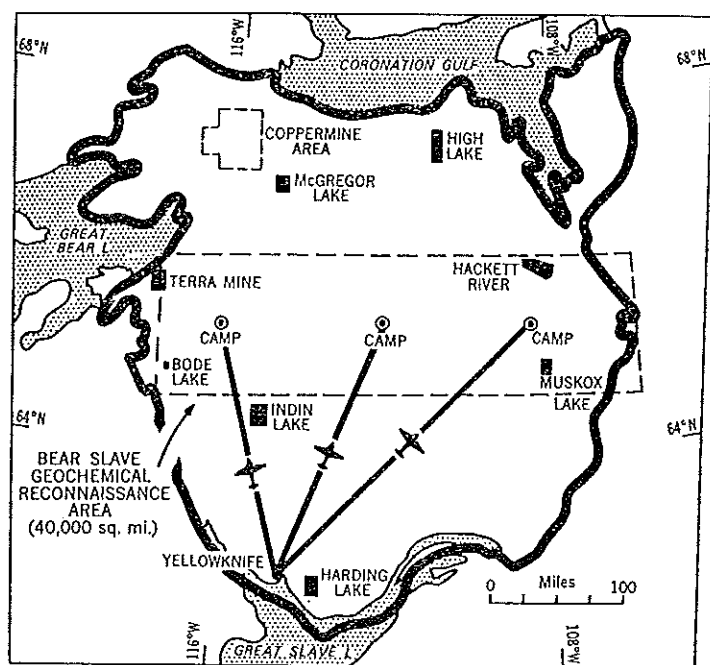


Figure 1.

Area sampled during Bear-Slave reconnaissance geochemical operation. Shows smaller areas sampled during previous orientation surveys.

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Table 1
Publication map-sheets

| Three map-sheets for publication | 1:250,000 scale maps com- prising published sheets |
|-------------------------------------|--|
| Wopmay River* | 86-F, G (complete); 86-B, and C (north half only) |
| Point Lake* | 86-H, 76-E (complete); 86-A, and 76-D (north half only) |
| Beechey Lake* | 76-F, G (complete); 76B, and C (north half only) |

survey involved sampling lake sediments and waters within 8 geologically different and widely separated areas. Rock samples were collected at the same time from these areas. The results¹ of this work showed that the elemental composition of inorganic lake sediments correlated well with that of the surrounding bedrock. The spatial relationship of bedrock composition to lake sediment chemistry does not appear to have been affected by the glaciations that this part of the Shield underwent. Further, the lake sediments are fine grained and are rather uniform in physical composition from lake to lake. As such they are an excellent medium for the sorption of metallic ions released from ore deposits and associated mineralization. Areas containing significant mineralization are thus readily detected by lake sediment analysis.

The Bear-Slave Operation of 1972 is a full-scale test of this type of geochemical survey. As such it was designed to test the feasibility and cost of routine surveys and to measure the benefits of the derived data across a variable geological terrane. The area surveyed extends from 64°30'N to 66°00'N and from 106°00'W to 118°00'W, covering nine 1:250,000 scale map-sheets. Its relation to the smaller areas studied in the orientation survey of the previous year is shown in Figure 1. The field operation extended from June 15th to August 5th, 1972 with sampling carried out every day from June 25th to August 2nd. Three Bell G4A helicopters were used to reach the lakes to be sampled. Water samples were collected in polyethylene bottles from just beneath the lake surface. Sediment samples were collected using extension post-hole soil augers constructed from magnesium-zirconium alloy and stainless steel. A DHC-3 Otter aircraft was used to set out gas caches for the three helicopters such that sample traverses were crudely radial in pattern and so that overflying time was kept to a minimum. All helicopters operated from the same base camp so that three base camps were successively established during the operation.

On certain days, with minimal overflying time, the sample rate per site was as low as 6.5 minutes. The average sample rate for the entire operation was 9.9 minutes per site. Approximately 150 sites (50 per helicopter), equivalent to 1,500 square miles, were sampled each day. Water samples were acidified after pH/Eh measurement at the base camp. Sediment samples were dried at the camp. In total, 4,100 sites were sampled. In the Beechey Lake map-area (see Table 1) an area of 750 square miles enclosing mainly acid volcanic rocks was sampled at a density of one site per 2.5 square miles.

In Ottawa, sediment samples were sieved to less than 250 mesh; sample preparation was completed at the end of September. Analyses by various techniques are being carried out in the laboratories of the Geological Survey,

* Unofficial name.

Geochemistry Section. The sediment samples are being analyzed for the following elements: Cu, Ni, Pb, Zn, Ag, Co, Mn, U, Hg, Mo, Ti, Ba, Cr, Be, V, Sn, Zr, Y, La, Li, Sr, As, Sb, Ca, K, Fe and Mg. Water samples are being analyzed for Cu, Zn and Hg. A measurement of organic content of the sediment samples is being made and these results will also be made available.

For publication purposes the survey area has been divided into three map-sheets, each comprising an area of three 1:250,000 scale maps. For each element the concentration at the sample site and geochemical contours drawn by computer will be superimposed on this background. A handbook, describing the logistics, field operation, analytical methods used, and relevant costs will also be published. The handbook will also indicate procedures for map interpretation, and possible exploration follow-up work.

Preliminary results for the western parts of the surveyed area indicate that the operation will achieve its objectives. The data are coherent; that is anomalous areas are defined by a number of adjacent high results rather than by just one sample point. These anomalous values then pass gradationally to background levels. The sample density chosen is based, in large part, on economic considerations. It now appears that this is sufficiently dense to define the major features of geochemical variations.

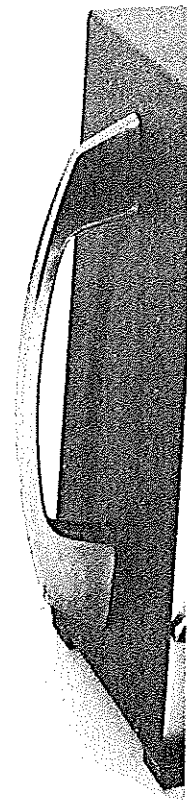
Some of the data give results which can be related to established geological concepts. Thus anomalous areas for U within the Bear Province are associated with high level granites and appear to be structurally controlled, and in the Slave Province relatively higher Zn concentrations occur at the margins of sedimentary-volcanic belts where mineralization associated with acid volcanism might be expected. Other results are completely unpredictable. Thus a large ($\approx 3,000$ square mile) and very distinct Zn anomaly extends for many miles on either side of the Wopmay fault, although the geology on either side of the fault is quite different (high level granites and volcanics to the west, highly metamorphosed eugeosynclinal sediments and migmatites to the east).

¹ Allan, R. J., Cameron, E. M. and Durham, C. C.: Lake geochemistry - a low sample density technique for reconnaissance geochemical exploration and mapping of the Canadian Shield; in *Exploration Geochemistry*, 1972 (Proc. 4th Internat. Geochem. Explor. Symp., London, 1972; Inst. Mining Met., London) (1972).

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19. DEVELOPMENT OF GEOCHEMICAL INSTRUMENTATION

Project 700087

Q. Bristow

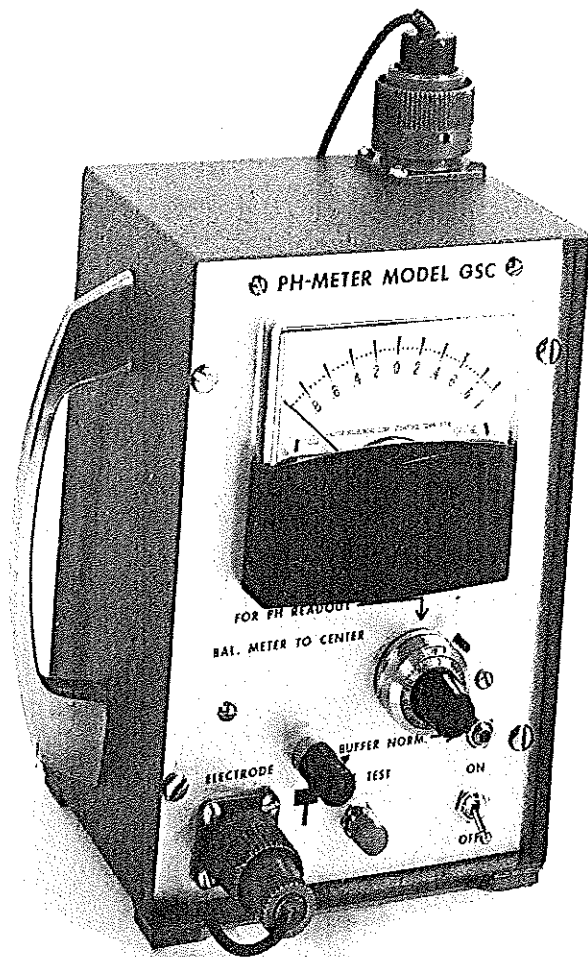
Resource Geophysics and Geochemistry Division, Ottawa

The field staff of the Geochemistry Section have, for some years, felt the need for a compact and very rugged pH meter for field use, including installation in float-equipped helicopters. An instrument filling all of the desired specifications has not been available in Canada.

Advantage was taken of the Special Employment Plan of the federal Winter Works Program to design such an instrument and build models for field trials. The design is available to Canadian companies interested in the manufacture of this instrument. It features rechargeable batteries giving 15 hours continuous operation on one charge, a resolution of 0.01 pH by means of a tenturn dial and null balance meter, wet storage compartment for the standard combination pH electrode built into the instrument case, small size and light weight. Military specification connectors and high insulation coating on the printed circuit board containing the integrated circuitry, ensure that readings are not affected by humidity. State of the art field effect transistors

and operational amplifiers provide ultra high input impedance and excellent gain stability. The unit can be used with specific ion electrodes and for redox measurements. Six instruments were used this summer by Geological Survey field parties in locations from Newfoundland to the subarctic.

The second instrument which has been developed is a mercury vapour detector for use in the analysis of mercury in solid and liquid samples by the well-established Hatch and Ott method. It is basically an atomic absorption device incorporating the most recent advances in solid state technology, for example the conventional photomultiplier tube is replaced by a space-age silicon photodiode coupled with an integrated circuit temperature stabilized preamplifier, the lamp emission at 2537°A (the mercury resonance line) is automatically stabilized by an optical feedback loop and a digital method of calibration is employed to obtain a direct digital readout of mercury



content in nanograms. A unique logarithmic analogue to digital conversion technique, coupled with a digital peak height retrieval circuit, is used to perform the mathematical transformation of the Beers' law absorption signal, which is required in all atomic absorption instruments.

A patent application is being made on the mercury vapour detector and both instruments are being displayed by Canadian Patents and Development Ltd., at a forthcoming manufacturers exhibition in Toronto.

20. THE USE OF VOLATILE COMPOUNDS IN MINERAL EXPLORATION

Project 720067

W. Dyck

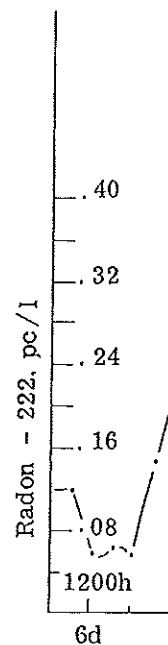
Resource Geophysics and Geochemistry Division, Ottawa

Procedures for taking soil gas samples and analyzing these for He, Ne, Ar, CO_2 , O_2 and N_2 have been developed. The search for methods of detecting H_2S and SO_2 in soil gas is in progress.

Tests with a 300-litre ionization chamber (Fig. 1) have shown that it can be used to monitor continuously the radon content in the atmosphere. The diurnal pattern shown in Figure 2 was obtained by monitoring air from an elevation of 85 feet at the Geological Survey of Canada building in Ottawa. It is characteristic of the daily temperature inversion occurring in the atmosphere near ground level. In general the higher radon levels correspond with hazy quiet atmospheres and lower levels with clear windy or rainy days. If one can assume that the radon emanating from the ground mixes rapidly with atmospheric



Figure 1. Radon monitoring of lake waters using large ionization chamber. Core attached to the side of the boat collects radon that is released from the water. (GSC photo 202086)



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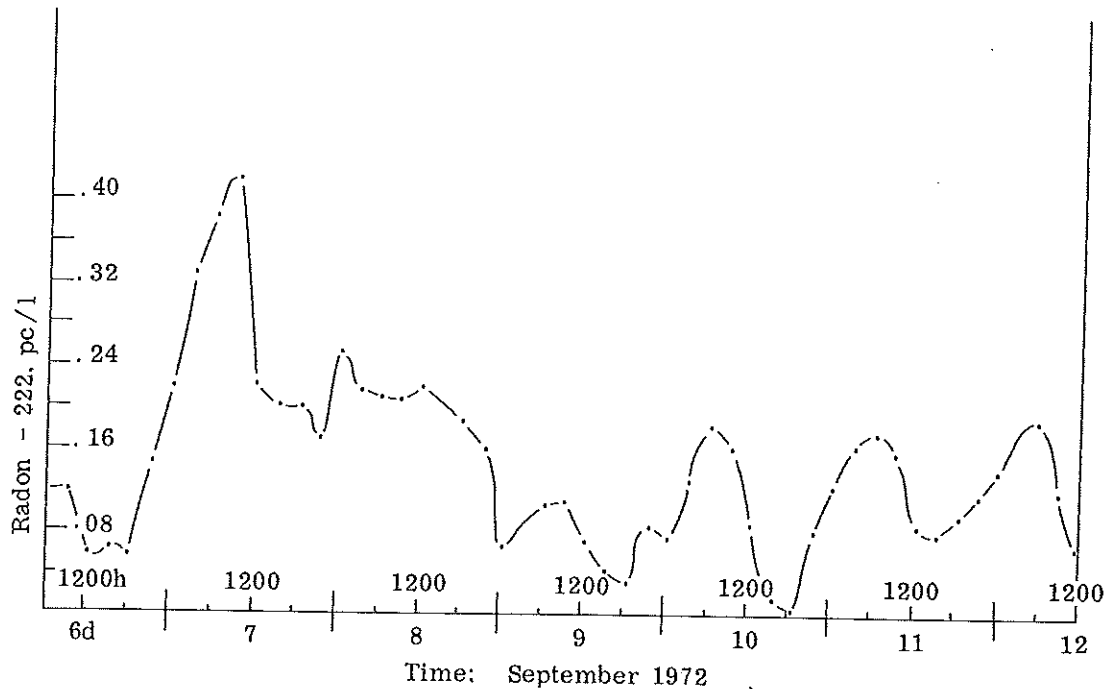


Figure 2. Variation of atmospheric radon over Ottawa.

air in a region, the ionization chamber should be useful for background corrections in high sensitivity gamma-ray spectrometer surveys.

Several tests in the Gatineau Hills showed that on windy days the air from a 30-foot height at Pinks Lake contained roughly twice as much thoron as radon and at Fortune Lake twice as much radon as thoron. These ratios are similar to those observed in soil gas and appear to reflect the relative thorium and uranium content of the soil and rock in the areas.

By placing the chamber in a boat on a lake and passing through it compressed air, which had been used to agitate the water, a reading proportional to the radon content of the water was obtained.

The tests carried out to date with the ionization chamber show that suitably modified and perfected it could become a useful tool in the search for uranium.

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21. CANADA - NEWFOUNDLAND
MINERAL DEVELOPMENT PROGRAM, PROJECT 6;
GEOCHEMICAL - GLACIAL GEOLOGICAL SURVEY (Geochemical Phase)

Project 720036

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Resource Geophysics and Geochemistry Division, Ottawa

The objective was to outline areas in Newfoundland with rich potential in metallic mineral resources, in order to facilitate discovery by exploration companies and thus contribute to the economic and social development.

This summer's pilot studies developed and tested geochemical exploration methods. The program was carried out for, and in cooperation with, the Newfoundland Department of Mines, Agriculture and Resources, Mineral Resources Division. J. M. Fleming and P. Davenport of the division were active in aspects of the survey.

Regional and detailed geochemical exploration studies were carried out in two areas of Newfoundland in the field time available. They are: A - New Bay Pond area of Notre Dame Bay, for sulphide mineralization in the volcanic and sedimentary rocks of the Wild Bight Group; and B - Daniel's Harbour area of the Northern Peninsula, for zinc mineralization associated with the St. George - Table Head disconformity. In both areas the following sample materials were collected and analyzed for Cu, Zn, Pb, Ag, Co, Ni, Mn and Hg: -80 mesh stream sediment; stream water; -80 mesh centre lake bottom sediment; lake water; -250 mesh till and -50 + 250 mesh heavy mineral separate till samples which were collected from the till-bedrock interface primarily; -80 mesh B & C horizon soils; and -80 mesh till at the peat-till interface and the occasional peat. Selected samples will be analyzed for other elements.

Conclusions at the time of writing are based on a preliminary examination of most, but not all, of the analytical data.

Conclusions are:

Area A - Lake and stream water and upper till interface sample data are, at present, inconclusive. Stream sediment data are useful providing that appropriate computer processing of the data by regression analysis is carried out to resolve the influence of manganese. Regional lake bottom sediment sampling is a successful technique when used in conjunction with geological and other applicable regional information. Overburden drilling using equipment described by Gleeson and Cormier¹ is a very useful and successful technique in suitable till conditions. In this area, till conditions were not optimum. However, till sampling data can be used to detect and indicate the probable source of till anomalies and as a discriminatory technique for evaluating conductors of geophysical anomalies.

Area B - Soil, stream sediment and lake bottom sediment sampling techniques are effective for geochemical exploration in focal and regional surveys respectively. Overburden drilling programs in shallow till provide data to detect and delineate the source of till anomalies.

¹Gleeson, C. F. and Cormier, R.: Evaluation by geochemistry of geophysical anomalies and geological targets using overburden sampling at depth; Can. Inst. Mining Met. Special Vol. No. 11., p. 159-165, 1971.

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22. DISPERSION OF FLUORINE IN THE VICINITY OF FLUORITE DEPOSITS

Project 720092

Jean-Pierre Lalonde

Resource Geophysics and Geochemistry Division, Ottawa

Three weeks of field work were carried out early in the summer of 1972 in an area containing known fluorite deposits near Madoc, Ontario. These deposits occur predominantly in Precambrian marbles and Paleozoic limestone as irregular and discontinuous veins in faults and fractures. Mineralization consists of fluorite, barite, celestite, and calcite with minor sulphides such as pyrite, sphalerite, and galena, and also bituminous material. From 1905 until 1960, one hundred and twenty thousand tons of metallurgical grade fluorspar were produced in the area.

The objectives of this study were:

1. To determine the secondary dispersion of fluorine in surface and groundwaters, stream sediments and soils.
2. To establish the feasibility of locating fluorite and barite veins with geochemical exploration methods in the Madoc area.

Regional secondary dispersions of fluorine were studied by sampling 45 soil profiles along two regional traverses, collecting approximately 60 stream sediments, 80 surface waters, and 200 ground waters. Soils were also examined along seven detailed traverses crossing known fluorite deposits or their extension. The analytical methods chosen include selective ion electrode analysis for fluoride, atomic absorption spectrophotometry for zinc, and X-ray fluorescence for barium and strontium.

The major findings after analysis are:

- a. The average fluoride content of surface waters in the Madoc area is 130 ppb and values above 250 ppb may be considered as anomalous. Fluoride surface water anomalies were found in 3 lakes and 2 streams. The dispersion trains in surface waters are traceable for several miles.
- b. Fluoride in groundwaters clearly delineates areas of known mineralization as well as other areas of possible interest.
- c. A positive correlation exists between fluoride anomalies in groundwaters and fluoride highs in the soils of regional traverses.
- d. The lateral dispersion in soils of fluoride from subcropping fluorite veins is restricted. This is probably due to a combination of three factors: the limited mobility of fluoride ion in the soils of the area, the small size of the fluorite veins, and the lack of topographical relief. Fluoride soil anomalies can be used to pinpoint subcropping fluorite veins.
- e. The best soil horizon to sample in the Madoc area is the organic "A" soil horizon. It accentuates the contrast between background and anomalies.
- f. Barium and zinc in soils are also useful tracers of fluorite veins in the Madoc area.
- g. Geochemical exploration methods have proven useful to re-evaluate the potential of the old fluorspar mining area and may help locate new deposits.

23.

SUB-AQUATIC ORGANIC GELS;
A MEDIUM FOR GEOCHEMICAL PROSPECTING IN
THE SOUTHERN CANADIAN SHIELD

Project 700046

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At present (1972) surficial geochemical methods, for use in both detailed and regional surveys, have been applied or developed with reasonable success to most areas of Canada. British Columbia, the Yukon, the Maritimes and the High Arctic can be adequately prospected by stream sediment and soil geochemistry. In the last few years large areas of the Shield in the Northwest Territories, northern Quebec and extreme north of Saskatchewan and Manitoba have been shown to be amenable to geochemical prospecting when inorganic, silty, lake sediments and frost boils are employed as the sample media. Two large units of Canada remain. These are the Interior Lowlands and the forested, non-permafrost, southern Shield. The former is primarily of economic interest in relation to oil and gas reserves, and may be better suited to various bedrock geochemistry techniques. The latter area consists of a small part of northern Manitoba and Saskatchewan, most of Ontario and southern Quebec and the south of Labrador. It has proved to be the nemesis of geochemistry and has largely contributed to the notion that geochemistry does not work in the Shield and is thereby of dubious use elsewhere. In essence, geochemistry using surficial materials as the sample media began in what is probably the most complex of areas. However, this area of Canada is also that which contains the major part of Canada's known mineral wealth. Because of the past discovery of ore in this area, and also because of the fact that its southern location means that smaller orebodies are economical to develop, this is the area where industry wishes to apply geochemistry. However, it is also becoming increasingly evident over the last few years that several geochemical projects using surficial sample media and carried out by industry in this area of the Shield, have resulted in confusing data. This problem of finding, testing and developing a viable surficial geochemical exploration technique for the southern Shield is one of the outstanding problems in geochemistry in Canada.

After studying materials found as sediments in lakes over most of the Canadian Shield, the authors believe that such media can be broadly divided into three categories:

1. Organic gels
2. Organic sediments
3. Inorganic sediments.

For a simple analogy, one can think of these three as being similar in differences and complexity to the A, B, and C horizons of soils. Within each category there are innumerable variations. However, in each category, the broad chemical, physical and as the case may be mineralogical characteristics, principles and processes are relatively uniform. The end members are 1 and 3. Category 2 is intermediate and incorporates all of the problems and complications, usually in varying degrees of both other categories. Unfortunately, most sediment samples collected from drainage systems particularly lakes,

fall into category 1 or category 2 or such. This, drainage systems southern Shield

1. Organic
in parts of the Shield, gels often extend to the edge of the lake, reducing conductivity, lustreless or, etc.

2. Organic
the Shield, Inorganic areas, they are

3. Inorganic
Shield which is predominately inorganic in areas of diagenesis. By inorganic and clay with organic. The trace elements in the lattices of the minerals are higher in the southern Shield. has been proved in the Shield.

The two types are respectively

Detail of the Canadian Shield recently, same. In order to assess the samples, both types be solved;

1. What is
interpretation of the relationships

2. Where
material from the inhomogeneity of the distribution truly represents

This is the by detailed sampling in detailed analysis of organic chemistry

fall into category 2. Usually the samples are considered to be either from category 1 or 3 and are consequently analyzed and the results interpreted as such. This, in the authors' opinion, has been the predominant reason for some drainage system surveys producing confusing results in both the northern and southern Shield regions.

Short Definitions of Lake Bottom Materials

1. Organic gels: Materials found in organic-rich lakes, that usually occur in parts of the Shield, with a mixed deciduous-coniferous forest cover. These gels often extend for up to 30 feet or more above the inorganic sediment base of the lake. They are almost completely organic in nature, smell strongly of reducing conditions (H_2S) and are thixotropic. They dry into a hard, dark, lustreless organic cake which is difficult to break and does so conchoidally.

2. Organic sediments: Materials thought to occur in lakes in all areas of the Shield. In the north they may be incipient examples of category 1. In all areas, they represent varying mixtures of organic and inorganic sediments.

3. Inorganic sediments: Materials which occur in lakes in areas of the Shield which are sparsely forested above the treeline. The area where they predominate is above the treeline. However, they are also commonly found in areas of discontinuous permafrost in the northern zones of coniferous forest. By inorganic sediments, the authors imply various combinations of sand, silt and clay with inorganic oxides and hydroxides and virtually no organic matter. The trace elements in this material are held on or in the silicate or sulphide lattices of the minerals comprising the sample. Usually concentrations are higher in the finer size fractions, the silt and the clay. As such, this material has been proved successful in prospecting at several scales in the northern Shield.

The two materials predominating in the southern and northern Shield are respectively organic gels and inorganic sediments.

Discussion of Organic Gels as a Sample Media

Detailed studies of organic gels in lakes in the Grenville Province of the Canadian Shield have been conducted over the last three years. More recently, sampling has been extended to two locations in the Superior Province. In order to assess the usefulness of taking organic gels as geochemical survey samples, both for detailed and regional prospecting, two main problems must be solved:

1. What is the origin of the trace elements in organic gels? i.e. the interpretation of the sometimes unusual and confusing elemental contents and relationships which are manifest in these organic gels.

2. Where in the lake should these gels be collected? i.e. the choice of material from a part of the lake that will minimize the chances of sample inhomogeneity and optimize the chances of getting a trace element concentration truly representative of the surrounding bedrock.

This latter question is the easier to solve and can largely be answered by detailed sampling of several representative lakes. The former is a problem in detailed analyses of these gels involving perhaps a considerable use of organic chemical techniques.

The first question relates to the considerable variation in the nature and structure of these gels. Observation has led the authors to believe that even these, at first appearance, homogeneous gels are in fact made up of several materials, derived from widely differing sources. These materials are thought to be:

1. Organic precipitates of colloidal origin, possibly soluble fulvates and humates.
2. Residual organic matter derived from the decay of plants, algae and plankton.
3. Pollen of predominantly local origin.
4. Inorganic minerals of very small particle size, (X-ray analysis indicates that quartz and feldspar are the dominant minerals).

Further investigation may, of course, reveal more materials or hopefully show that some of the above are insignificant in their influence on trace element variations.

Obviously item 4 will be affected by the rock type and soil types in the area, whereas, items 2 and 3 will bear a strong relationship to the local vegetation. Further, this vegetation may be related to the rock type of the area, thereby introducing further complications. Possibly, material 1 is composed of flocculated organic colloids perhaps dominated by fluvates and humates. As such, these scavengers of dissolved metals will not be significantly affected by the trace element concentrations of the original parent vegetation. Extraction and analysis of this material may remove some of the problems.

Already, it is evident that there is a large difference between the inorganic sediments from the northern Shield and the organic gels from the southern Shield. Whereas the former is largely a "lithogeochemical" sample media, the latter is largely a "biogeochemical" sample media. As mentioned, the trace element contents of the total gel may be strongly related to the preferential gathering of selected metals, to different degrees, by various source plants. We have in essence arrived at a very complex media, which may have derived a large part of its trace element content via a multistage process:

ROCK → SOIL → VEGETATION → HUMUS → STREAMS → LAKES → GELS

It may in the end prove more feasible to collect a media closer to the original bedrock. However, two main facts make the gels a good choice for the southern Shield. These are:

1. Because of its derivation and subsequent location in lakes it is obviously one of the few regionally representative sample media to be found in the area. By contrast, rock, soil or vegetation samples are very local in nature.
2. The advantages of collecting a geochemical sample medium associated with lakes in the southern Shield is apparent from a practical and economic standpoint. Sampling of these gels from small fixed wing planes is very easy and rapid. From helicopters it would be even more rapid and simple.

It is because of these facts that this medium should be assessed in considerable detail before it is rejected because of its suspected complexity.

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Clyde Forks, Red Lake and Uchi Lake Sample Areas

In the light of the above discussion, samples have been collected by the authors from three localities in the southern Shield. One is in the predominantly deciduous forest area of the Grenville Province, and the other two in the predominantly coniferous forest areas of Red Lake and Uchi Lake in the Superior Province.

In the Clyde Forks area (31 F/2) approximately 150 samples of co-existing inorganic sediments and organic gels were collected from two lakes, Lavant Long Lake and Perch Lake. In the former, water is about 45 feet deep, and in the latter about 35 feet deep. Sampling was by scuba equipped divers, who also made visual observations concerning the gels. Water samples were collected in the upper 3 feet of water and near the bottom of the lake above the surface of the gels. All the inorganic sediments and gels have been analyzed for organic carbon, carbonate, S, Zn, Cu, Pb, Ni, U, Ag, Hg, As, Sb, Mn and Fe. Waters have been analyzed for Zn, Cu, Pb, Ni, U and Hg. Distribution of metals between the inorganic sediments and organic gels favoured the gels by factors from 1 to 5 depending on the element considered.

The organic gels when dried were quite variable. This variation seemed to be related to the distance from the shoreline at which the samples were collected. The deeper the water, the finer and more gel-like was the sample. In the shallow water, a mull-like chaff was prevalent. Closer to the shore the samples were, by our original definition, organic sediments. Inorganic sediments were unobtainable in the deeper parts of the lakes because of the depth of organic gels.

Preliminary carbon, Fe and Mn analyses indicated that the most homogeneous samples come from the deeper parts of the lakes. The dry samples contain between 25 and 35% by weight organic carbon and from 1 to 2% by weight sulphur.

The trace element concentrations of the gels can be related to the local geology. For example, base metals (Zn, Pb and Hg) are elevated in an arm of Lavant Long Lake which lies in Grenville marbles, whereas Cu and Ni are elevated in areas of the lake in biotite-rich gneissic rocks. This reflection is better reproduced in the gels than in the inorganic silty sediments. The water data correlate best with the organic gels. This observation is probably related to the presence of dispersed and dissolved organic materials in the waters of these organic-rich lakes. Also, this may indicate a more favourable hydrogeochemical solution to prospecting in the southern Shield than in the northern Shield, where this branch of geochemistry, with some exceptions, has been unfruitfully applied.

Sampling at Clyde Forks has been concerned with comparisons of organic gels, water and inorganic sediments to trace element concentrations in bed-rock. Both lakes are in areas of known geology but, so far, unknown mineralization. The other two study areas, at Red Lake and Uchi Lake, are located in the Uchi Volcanic Belt of northwestern Ontario. As such, they are both areas of potential for the discovery of base metal mines. At Red Lake, there are several gold mines, some in operation for many years, and at Uchi Lake there are abandoned gold mines and a newly discovered and developed Cu-Zn mine. Both areas are mineralized and considered to be of high economic potential. Both are typical Archean volcanic-sedimentary belts, dominated by basic to intermediate volcanic rocks with minor amounts of acid volcanics. At both these areas, it was decided to collect only organic gels. In up to

90 per cent of the sample sites, true gels were obtained. For the remaining 10 per cent mostly organic sediments were sampled. Samples were collected using an Ekman-Birge Dredge from the floats of a DHC-2 Beaver aircraft. This procedure was extremely efficient, with samples taken in depths varying from 6 to 150 feet. There was seldom a problem in finding the correct, thixotropic sample medium and in most cases several sample bottles (1000 ml.) were filled at each site. As was mentioned above the physical nature of the gels was different from the gels from Clyde Forks. It was finer grained and less fluffy than the Clyde Forks gels. The area at Uchi Lake produced the most uniform and easily collected samples.

The Red Lake volcanic belt (52 N/4) covers some 200 square miles. In this area, three lakes were sampled in detail, one in basic volcanic, one in acid volcanic, and one in granitic rocks. Up to 30 samples of gels were collected from various parts of each of these three lakes. Several separate samples were collected at each sample site. Also, most samples were divided into sub-samples. A suite of sites was sampled in that part of Red Lake most likely to be influenced by the gold mines near Red Lake, Cochenour and McKenzie Island. Samples were also collected from widely spaced sites (2 to 3 miles apart) from most parts of the Red Lake volcanic belt. These sites were chosen to represent variations in regional geology and metallogeny. Several consecutive samples were collected at each sample site.

The Uchi Lake volcanic belt (52 N/2) covers some 300 square miles. Samples to determine dispersion from known mineralization (or recent sources of trace element pollution) were collected in three places: near South Bay Mines' Cu-Zn mine; near known minor showings on Confederation Lake (Cu-Zn) and near an abandoned gold mine on Casummit Lake (Au, Ag, As). Samples related to the regional variation in geology and mineralization were collected over the volcanic belt at intervals of some 4 to 5 miles. As at Red Lake, at all sample sites several consecutive samples were collected and samples were subdivided.

In total, at both the Red Lake and Uchi Lake areas, samples from 30 regionally scattered locations were collected. Along with the samples from the four dispersion studies and the three detail studies, approximately 200 one litre polyethylene bottles of organic gels were collected for future analysis.

Analyses of Organic Gel Samples

As mentioned previously, the success or failure of these organic gels as exploration media depends primarily on knowing both the physical site, i.e. in pollen, degraded organic matter or in inorganic materials and the chemical bonding of the trace elements in the gels. Once determined this may be related to the original source of the trace elements, i.e. surrounding bedrock, mineralization, algae or shoreline vegetation. Work currently in hand involves extraction and characterization of selected organic gel samples as well as analysis schemes to fractionate some of the samples already collected. Preliminary analyses will be made using simple extractants to help indicate the direction further studies should take. Should any of these preliminary results give trace element concentrations that can be related to known geology and mineralization, the problems of using the gels as a sample media will be greatly reduced. However, to fully understand the parameters involved in the migration and accumulation of specific elements in organic-rich drainage systems of the southern Shield, studies of the basic nature of metal binding in these subaquatic organic gels are underway.

It is expected that preliminary results at least will be available before the season of 1973, so that gels can be used in geochemical prospecting with greater confidence.

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24. THE ANALYSES OF METALS IN GEOLOGICAL MATERIALS BY D.C. ARC DIRECT READING EMISSION SPECTROMETRY

Project 580175

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An analytical method has been developed for the rapid analyses of trace metals using an A. R. L. 29000 PCQ direct reading emission spectrometer interfaced to a dedicated mini computer. The D. C. arc method is intended to produce quantitative analyses of as many metals as possible of geochemical interest in large suites ($n \times 1000$) of samples with reasonably constant matrix composition. An example of such a suite is the 4,100 lake sediments collected for operation Bear-Slave.

Alternative methods currently available using a direct reading emission spectrometer were considered and rejected either because their throughput was too low or because their accuracy at near-background concentrations was too poor. Studies were made of various parameters such as buffer composition, electrode dimensions, sample to buffer ratios, arcing current etc. and resulted in the decision to develop a method based on the controlled selective volatilization of metals into the D. C. arc and partial integration of the analytical lines for each metal. Following further investigations a special arc chamber incorporating a gas jet and a preformed electrode to fit the chamber were designed.

The direct reader-computer system used has already been described¹. This system is very versatile and by suitable programming, each capacitor used to store the voltage produced by light of a particular wavelength striking a phototube can be read at any time during the burning of a sample thus ensuring maximum line to background ratios. "Volatile" metals such as Cu, Zn, Pb, Ag, are measured during the initial stages of the burn while "involatile" metals such as Be and Zr, are measured near the end of the burn. This procedure eliminates one of the causes of the slow throughputs of most published methods, namely the need to use a different buffer and electrode for "volatile" metals than that used for the "involatile" metals.

Further increase in throughput is achieved by using preformed electrodes for the sample which are self-positioning with respect to the instrument optics, no electrode adjustment during the burn, automatic control of the gas flow, and computer control of spectrometer functions.

Pd and In are used as internal standards with the computer selecting the appropriate one for each metal. In the ranges of concentrations for which the method is used, the working curves are essentially linear and consequently only one standard need be used to establish working curve gradients. This standard should be a natural material of physical and chemical composition as close as possible to the samples' composition. For example, for the analysis of a suite of lake sediments the standard should be a composite lake sediment. The metal concentrations in the standards are originally determined by a combination of methods, usually atomic absorption, colorimetry, optical spectrography and X-ray fluorescence. A unique and useful characteristic of the one standard/linear working curve method is that, firstly, by including control standards during routine sample analysis, sample concentrations can be adjusted for inaccurate calibration and instrumental drift and secondly, the sample concentrations may be adjusted if more accurate analyses of the standard become available.

The instrumental details of the method used to correct for the background contribution to each analytical line are essentially the same as previously published^{2,3} in which one or more phototubes are used to measure the background at various points on the spectrum. The technique described by these authors uses ratios determined from synthetic standards containing 0 ppm of the analyte metals to calculate the background contributions to the analyte lines in the natural samples. This technique was investigated and found to give inaccurate results for some metals due to the different burning characteristics of synthetic compared to natural samples. A new technique was devised based on movement of the primary entrance slit. This enables background corrections for most metals to be derived from the standard sample, and results in more accurate estimations of background contributions.

The computer program to control operation of the spectrometer and to carry out calculations was written in assembler language. The essential functions of this program are as follows:

1. The metals to be analyzed are selected.
2. The background ratios are calculated from the burning of 1-10 standard samples.
3. The gradients of the working curves are determined from the burning of 1-10 standard samples. Standard concentrations are read in prior to each burn.
4. The sample number is typed in.
5. The sample is burned.
6. The concentrations in parts per million and per cent are typed out and punched onto paper tape.
7. Operation continues from 4.

Sample throughput depends on two criteria: sample preparation time and analysis time. With the present system calibration of the instrument is required once every three or four hours. Calibration takes one hour and samples can be analyzed at the rate of 20 per hour. For a six hour day an approximate throughput of 80 samples can be expected. To achieve this throughput three persons are required for sample preparation.

The system described above has now analyzed over 2,000 sediments in routine operation and is producing satisfactory results for the following elements: Ag, Ba, Be, Ca, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Ni, Pb, Sr, Ti, V, Y, Zn, Zr. More comprehensive details of the method will be published at a later date.

- ¹ Jones, F.W. and Horton, R.E.: A data acquisition system with computer control for an optical emission spectrometer; *Can. Spectroscopy*, v. 16, p. 1-4 (1971).
- ² Tennant, W.C. and Sewell, J.R.: Direct reading spectrochemical determination of trace elements in silicates incorporating automatic background and matrix corrections; *Geochimica Cosmochimica Acta*, v. 33, p. 640-645 (1969).
- ³ Thompson, G. and Bankston, D.C.: A technique for trace element analysis of powdered materials using the D.C. arc and photoelectric spectrometry; *Spectrochimica Acta*, v. 24B, p. 335-350 (1969).

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