NATIONAL ADVISORY COMMITTEE ON RESEARCH IN THE GEOLOGICAL SCIENCES

PROCEEDINGS, SYMPOSIUM ON GEOCHEMICAL PROSPECTING, OTTAWA, APRIL, 1966

Edited by E.M. Cameron

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FOREWORD

The Symposium on Geochemical Prospecting, sponsored by the National Advisory Committee on Research in the Geological Sciences and hosted by the Geological Survey of Canada, attracted more than two hundred and fifty scientists to Ottawa for a meeting whose vigour reflected the interest in this field. The contributions to the Symposium, which was held from April 20 - 22, 1966, were virtually entirely concerned with the application of geochemical methods to exploration for metallic mineral deposits. This volume contains the papers of those authors who desired publication and submitted manuscripts prior to September 1, 1966. Abstracts are given for all other papers presented at the Symposium.

For those present at the sessions it was not difficult to detect that geochemical prospecting is moving from its infancy into a period of greater sophistication and broader and more successful application. This approaching maturity manifested itself in the unusually wide range of topics, both factual and introspective, that were introduced. A frequently voiced feeling was that geochemical methods have too often been applied as a rather simple, direct way of finding ore. Unusual concentrations of elements have been sought in surficial materials in the expectation that such concentrations invariably overlie ore bodies. In many cases, of course, this does happen. But in many others, unusual concentrations of elements at the surface are unrelated to geochemical features in the underlying bedrock. The presence of ore bodies is often expressed by only subtle changes, if any, in the composition of the overlying surficial materials.

There is a very apparent need for the applied geochemist to receive more support from basic geochemical studies, in order that he can more efficiently plan his work and more successfully interpret his data. Knowledge of the behaviour of elements in the soils, sediments, waters, and plants that form our immediate landscape are in many respects less well known than the behaviour of these same elements deep within the crust. But it is equally apparent that the knowledge of the Pleistocene geologist, the hydrologist, pedologist and others has not been fully used by the applied geochemist.

The trend towards automation which all science is undergoing is a particular boon to geochemical prospecting. The value of the greater productivity of the newer analytical methods is, of course, obvious. However, automation will be equally significant in allowing the applied geochemist to spend a much greater proportion of his time on interpretation of data and on the proper integration of his methods with other exploration techniques. Few are those in any branch of geochemistry who have not, in the past, spent much of their time on analytical concerns or plotting data onto maps or charts. The direct flow of analytical information from automated instruments to the computer for basic statistical interpretation and plotting is already being done; in a few years it could be almost universal.

One very practical problem facing the applied geochemist lies in learning of the successes and failures of others. Only relatively few of the applications of geochemical prospecting become known to a wide audience. This seeming paucity of publications is more apparent than real, for geochemical case histories are scattered throughout the literature but are not easily accessible. Geophysicists have been more successful in bringing case histories together into volumes where they can be more readily consulted.

The success of this symposium was achieved only through the active support of a large number of persons, most particularly those who presented papers and chaired the various sessions. We are much indebted to those who came from other countries to share their knowledge with us. The meeting was first suggested by Dr. P. E. Grenier of the National Advisory Committee. Dr. R.W. Boyle served as Chairman of the Program Committee, Mrs. A.V. Leech as General Secretary and Dr. D.F. Sangster as Chairman of the Exhibits Committee.

E.M. Cameron,
Editor and Chairman, Organising
Committee.

Ottawa, September, 1966.

THE DISCOVERY OF THE KEYSTONE GOLD MINE, CLEARY HILL AREA, FAIRBANKS DISTRICT, ALASKA - A Geochemical Prospecting Case History

L.M. Anthony*

GEOGRAPHY AND GEOLOGY

The Cleary Hill area is located in the Yukon-Tanana Upland about twenty miles north of Fairbanks, Alaska. Rock types underlying the area belong to the Yukon group of Precambrian or early Paleozoic age and younger intrusives. Quartz-mica schist and micaceous quartzite comprise the greater part of the local sequence. The principal peak in the area (Pedro Dome, 2600 feet) is a quartz-diorite pluton of Cretaceous age. Free-milling gold quartz veins are the most important ore deposits and they are genetically related to quartz-porphyry stocks and porphyritic dikes of late Cretaceous or Early Tertiary age.

Two cycles of deformation are in evidence. The older produced overturned to recumbent northwest trending folds with overturning to the northeast. The younger cycle formed isoclinal folds trending northeast with overturning to the northwest.

The principal structural feature is the Cleary Hill Anticline. A major fault more than eight miles long and one hundred feet wide follows the crest of this anticline and strikes north seventy degrees east.

The lode gold deposits at Cleary Hill occur in steeply dipping discordant fissure veins localized near the crest of the Cleary Anticline. The veins contain stibnite, galena, and jamesonite in variable amounts from one to five percent, and trace quantities of zinc and copper.

The topography is mature with well-rounded ridgetops and narrow valley floors. Hillside erosion is dominated by frost action and downslope creep. This results in the mixing and multilayering of stone stripes, soil, and other materials.

Overlying the area of lode mineralization is a layer of residual sub-arctic brown forest soil. The vegetation cover is typical sub-arctic boreal forest of the type found close to tree line. Less than one percent of the area bedrock is exposed.

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* Associate Professor of Mining Extension, University of Alaska, College, Alaska

MINING HISTORY AND PAST EXPLORATIONS

Placer gold deposits are widely distributed in the stream valleys of the Cleary Hill area and mining activity dates from 1902. Lode mining commenced in 1910. The district is one of the most prospected in Alaska. The geologic anomaly in this area was known in the early 1900's and it was reported in the literature of the United States Geological Survey as early as 1912.

Very little geophysical exploration has been attempted in the area. This is principally due to the narrow and erratic nature of the veins and the presence of graphitic schist.

GEOCHEMICAL EXPLORATION AND DISCOVERY

The Keystone gold vein was discovered as the result of geochemical soil exploration by three Fairbanks prospectors. The men used a general geochemical exploration technique for copper, lead, and zinc developed at the University of Alaska. They learned the method by attending a two-week course in geochemical prospecting fundamentals.

The area selected by the prospectors for soil sampling was between two formerly productive but presently inactive gold properties. (Cleary Hill and Hi Yu Mines). Samples were taken with a small diameter soil auger from the "C" soil horizon just above the upper-most stone stripe layer. Sampling depth was variable but averaged thirty-three inches. The horizon had an average pH of 5.9. The other soil horizons were as follows: A_0 and A_{00}, three inches thick, pH 4.6; A, five inches thick, pH 4.8; and B, twelve inches thick, pH 5.2 A twenty-five foot sample interval was used but line spacing varied from fifty to several hundred feet.

Analysis was done on the spot by University of Alaska Method One, Modified. This procedure consists of hand sorting one-quarter of a gram of fine wet soil and placing it in a twenty-five milliliter graduated test tube. Pure sodium chloride and metal-free water are added and the total soluble copper, lead, and zinc is extracted by shaking with measured amounts of dithizone solution. In this method, a saturated solution of dithizone dissolved in unleaded white gasoline is prepared. The white gasoline used consists of pentane and hexane and it is refined to the specifications as set forth by the American Society of Testing Materials Distillation Standard Number Eighty-Six. The product is marketed as high quality pressure appliance fuel and is readily available in Alaska. However, only those brands which are additive-free should be used. The method is described in detail at the end of this paper.

The three prospectors detected a promising geochemical soil anomaly, as a result of their work. The anomalous readings ranged from twice to more than sixty times background. The length of the anomaly exceeded two thousand feet; however, the maximum width was only two hundred feet and at one place it was only twenty-five feet wide.

One line of soil samples was taken in an old bulldozer trench and this showed an anomalous reading. Subsequent trenching of the anomaly revealed a high-grade gold quartz vein averaging two feet in width and more than two thousand feet in length. The vein was located one foot below the bottom of the abandoned bulldozer trench.

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THE UNIVERSITY OF ALASKA'S GEOCHEMICAL PROSPECTING METHOD #1

As Modified
For Hand-Sorted Wet Soil Samples
by Leo Mark Anthony

SUPPLIES

1	16-oz squirt type resin demineralizer (for metal-free water)
2	test tubes, pyrex brand glass stoppered with polyethylene, 25 ml. capacity, graduated in 0.2 ml. or 0.5 ml. (for testing samples).
1	32 or 16-oz bottle, polyethylene with polyethylene cap (for preparation of saturated dye solution).
1	16 or 8-oz polyethylene washing or dropping bottle (for dye solution).
1	8 or 4-oz bottle, polyethylene with polyethylene insert dropper and screw cap (for sodium chloride).
2	2-oz bottles, polyethylene with polyethylene insert droppers and screw caps (for basic and acidic pH adjusters).
1	porcelain spatula, Coors No. 1 with ¼ gram scoop.
1	pHydrion paper, pH 1-11 (for checking pH)
1	small package facial tissues (for cleaning spatula).

1 lb.	sodium chloride, A.R., fine crystal.
½ oz	ammonium hydroxide, A.R.
½ oz	hydrochloric acid, A.R.
5 gm.	dithizone.
1 gal.	Blazo or white gasoline in unopened container.

PREPARATION OF TESTING MATERIALS

Dye Solution

1. Use the Coors #1 spoon to place one spoonful of dithizone in 32 or 16-oz polyethylene bottle.

2. Fill bottle ½ full of Blazo or white gasoline.

3. Cap bottle and shake it vigorously for 15 minutes either continuously or intermittently. Solution should turn emerald green.

4. Allow one or two minutes for excess dye crystals to settle to bottom of mixing bottle. If this does not happen, add another spoonful of dithizone and shake the solution another 15 minutes. When excess dye crystals settle out of the solution, it can be considered saturated.

5. Decant the dye solution into a 16 or 8-oz washing bottle, carefully retaining the undissolved dye crystals. The decanted solution is then ready to use.

6. Additional dye solution can be prepared by adding more dithizone and gasoline to the maxing bottle. If additional solution is not needed immediately, the mixing bottle should be washed with small amounts (10-20 ml.) of unleaded gasoline to remove excess dye crystals from the bottle. This prevents oxidation of the dye crystals.

Metal-Free Water

1. Collect fresh clear stream or spring water of low heavy metal content in the demineralizer bottle and insert the resin demineralizer cap.

2. Invert bottle and squeeze it to force out metal free water as needed.

Basic pH Adjuster

1. Wash a 2-oz polyethylene dropping bottle 3 times with metal-free water.

2. Pour about 1½ oz of metal-free water into bottle and add about ½ oz of ammonium hydroxide, A.R. Shake well and label.

Acidic pH Adjuster

1. Wash a 2-oz. polyethylene dropping bottle 3 times with metal-free water.

2. Pour about 1½ oz of metal-free water into the bottle and add about ½ oz of hydrochloric acid, A.R. Shake well and label.

Sodium Chloride

1. Remove cap and insert dropper from 8 or 4 oz. polyethylene bottle and shave the dropper opening to make it about 1/8 in. in diameter.

2. Shake the sodium chloride to break up any lumps.

3. Fill the polyethylene bottle with sodium chloride and replace insert dropper and cap.

CHECK-OUT PROCEDURE

1. Wash a 25-ml test tube three times with metal-free water.

2. Take a 10 ml metal-free water sample.

3. Add about ¼ gram of sodium chloride.

4. Carefully add 1 ml of extracting dye solution.

5. Stopper test tube and shake it vigorously for one minute.

6. Observe the color of the dye solution. If the layer is unchanged or a light green, heavy metals are absent or present in low concentration. The geochemical kit is ready for field use.

   If the dye solution turns brown, yellow, violet, blue, pink, or any of the in-between shades, the kit is either contaminated or the dye solution has oxidized.

7. Wash the test tube thoroughly with detergent and water, using a nylon brush. Then repeat check-out procedure.

IF THE DITHIZONE SOLUTION IS SUSPECTED TO BE OXIDIZED, TEST IT BY:

1. Wash a 25 ml. test tube three times with metal-free water.
2. Place about 5 ml. of dithizone solution in test tube.
3. Add about 5 ml. of metal-free water.
4. Add two to three drops of basic pH adjuster.
5. Stopper the test tube and shake it vigorously for 15 seconds. (70 strokes).
6. Allow the contents of the cylinder to separate. If the solvent layer is green, repeat steps 4 and 5.
7. If the solvent layer is colorless, the solution is free of oxidation and suitable for testing. If the solvent layer is yellow to brown, oxidation has taken place and the solution should be discarded. A pink-colored solvent layer indicates contamination from either water or test-tube.
8. Any bottle which has held an oxidized dithizone solution should be washed with unleaded gasoline to remove the products of oxidation. Then a new dithizone solution should be prepared for testing.
9. To avoid oxidation of dithizone solution, it is recommended that fresh solutions be prepared daily. Unused solutions should be discarded and the bottles thoroughly washed with unleaded gasoline.

TESTING PROCEDURE

1. Take a handful of soil from the sampling tool, sort out and discard vegetation, grains of sand and coarse lumps of material. Select only fine clay-like soil for sampling.
2. Place one scoop (¼ gm.) of fine soil in a clean 25 ml test tube. Clean scoop with facial tissue before reuse.
3. Pour about ¼ gm. of sodium chloride into the test tube. (If necessary, the ¼ gm. spoon may be used to measure the sodium chloride.)
4. Wash down the soil and the sodium chloride from the inside wall to the bottom of the test tube with metal-free water, filling the test tube to the 5 ml mark.

TESTING PROCEDURE (Cont'd)

5. Cap the test tube and shake it vigorously a few times. Then moisten a strip of pHydrion paper with the solution and check the pH against the scale on the pHydrion dispenser. For normal work the pH should be between 5-6. If the pH is too low, add one drop of basic adjuster. If too high, add one drop of acidic adjuster. Repeat if necessary.

   (In a sub-arctic brown forest soil environment, common to most of Alaska, the pH of the "C" layer is usually in the 5-6 range and corrections, when needed, are usually slight.)

   It is only necessary to check two or three samples for pH when samples are tested in new areas.

6. Carefully add 1 ml of dithizone solution, stopper the test tube and shake it vigorously for 15 seconds (70 strokes).

7. Allow the layers to separate and observe the color of the solvent layer. If the color is faint to strong green, little or no heavy metal or metals are present. For any other color, repeat step 6.

8. The total ml of dithizone solution added to reach the first detectable green (end point) serves as an index value of the heavy metals present in the sample.

Identification of Heavy Metals

First Indicated Color	Metal
Violet	Zinc or other
Pink	Lead or other
Yellow-green to brown	Oxidation
Olive-green to brown	Copper

When an olive-green color is obtained, to avoid confusing it with the green end point, add ½ ml of the dithizone solution to the test tube and shake it gently, holding the test tube to strong light. The olive-green color will change slowly to violet as the fresh solution mixes with the old. This indicates a high copper content. The color may then turn back to olive-green; but as the sample is diluted it will go through a violet or pink color phase.

Specific copper work may be done in the pH range of 2-3.

In the general pH range (5-6) high copper, lead or zinc readings are sometimes identified by distinctively colored pigments produced during dilution. These pigments settle at the interface between the aqueous and the solvent layers.

Pigment Color	Metal
Red or pink	Lead
Brown	Copper
Black or violet	Zinc

Other Tests

It is recommended that several metal rich soil samples be collected for testing with metal ion test papers. These rapid spot tests will identify the specific trace metals present in the samples.

RECOVERY AND PURIFICATION OF SOLVENTS

In remote areas it may be necessary to purify and recover used solvents. The method described here will work for any organic solvent, but they must not be mixed.

Supplies

2	32 oz polyethylene bottles with screw caps.
1	polyethylene funnel.
1 pkg.	filter paper, Whatman #20 or similar.
4 oz	decolorizing charcoal.

Recovery Procedure

1. Place about 16 oz of used gasoline solvent, oxidized solvent and/or contaminated solvent in a 32 oz polyethylene bottle. Carefully separate the gasoline from any water or soil by decanting it into the other 32 oz bottle. Some soil may remain with the gasoline. If so, add 50-100 ml of clear water and shake it vigorously for about a minute. Allow the layers to separate and carefully decant the gasoline.

2. Add about one heaping tablespoon (two or three pocket-knife blades full) of decolorizing charcoal to the collecting bottle.

3. Secure bottle cap and shake the bottle vigorously for about ten minutes.

4. Allow charcoal to settle and observe whether the gasoline appears colorless. If is is colored, add about one more heaping tablespoon of charcoal and repeat step 3. Repeat until the gasoline is colorless.

   To conserve charcoal, allow mixture to stand for several hours or overnight. This allows the charcoal to absorb more of the metal impurities.

5. Fold a piece of filter paper into a cone-shaped filter, place it in the funnel and place the funnel in a 32 oz polyethylene bottle or other suitable container. Filter the charcoal out of the gasoline by slowly pouring the mixture into the funnel.

6. The colorless gasoline must be absolutely free of charcoal. If necessary, use a new filter paper and repeat the process of filtering.

7. Remove most of the used charcoal from the collecting bottle by washing it out with small amounts of gasoline.

   If fresh charcoal is added to the collecting bottle as the used solvent is added, most of the impurities will be removed. This saves time in recovering spent solvents.

A METHOD OF DETERMINING TRACES OF MERCURY IN GEOLOGIC MATERIALS

L.M. Azzaria*

INTRODUCTION

The mercury halo method of mineral exploration is presently receiving a great deal of attention. Interest in this method is due to the fact that it has been demonstrated that soils and rocks in the vicinity of many base and precious metal deposits contain anomalous quantities of mercury (Ozerova, 1959; Ozerova, 1962; Hawkes and Williston, 1962; James and Webb, 1964; Williston, 1964; Bercé, 1965; Sutherland Brown, 1966). Another reason for the increasing interest in this method of prospecting is the development of reliable techniques for the determination of the nanogram (1 nanogram=10^{-9} grams) quantities of mercury present in geologic materials.

There are several methods used for determining low mercury content of geologic materials. The more sensitive methods depend on the absorption by mercury vapour of ultraviolet light in the 2537 Angstrom range. There are several instruments of this type. First are the well known instruments that operate on a single beam system. In these instruments the gaseous sample is passed between an ultraviolet lamp and a device that is sensitive to this radiation. These instruments, however, suffer from interference by organic matter, water, and sulphides in geologic samples. However, they have been successfully used in geochemical prospecting by selecting samples that are reasonably free from interfering substances (Sutherland Brown, 1966). Second are the more recently developed sophisticated instruments that are based on double beam systems (Hawkes and Williston, 1962; Williston, 1964; James and Webb, 1964; Vaughn and McCarthy, 1964; Clews and Walker, 1964; Williston and Morris, 1965; Williston, 1965). In the present work an instrument developed by Williston and Morris (1965) was used. In this mercury vapour meter the sample is heated to vaporize the mercury. The resulting gases are then split into two equal portions and the mercury removed from one of them. Then the difference in absorption of ultraviolet radiation by the two portions is measured. In this arrangement, the effect of the interfering gases cancels due to its presence in equal amounts in the two portions. In the method of Vaughn and McCarthy (1964) the mercury of a gaseous sample is collected on gold foil while the interfering gases are exhausted. Next the gold is heated to volatilize the mercury which is drawn into another double beam instrument. In the present work the method of Vaughn and McCarthy for collecting mercury on gold was used. The work was begun in 1964 and was carried out independently of the investigation of Vaughn and McCarthy.

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* Department of Geological Sciences, McGill University, Montreal, Canada.

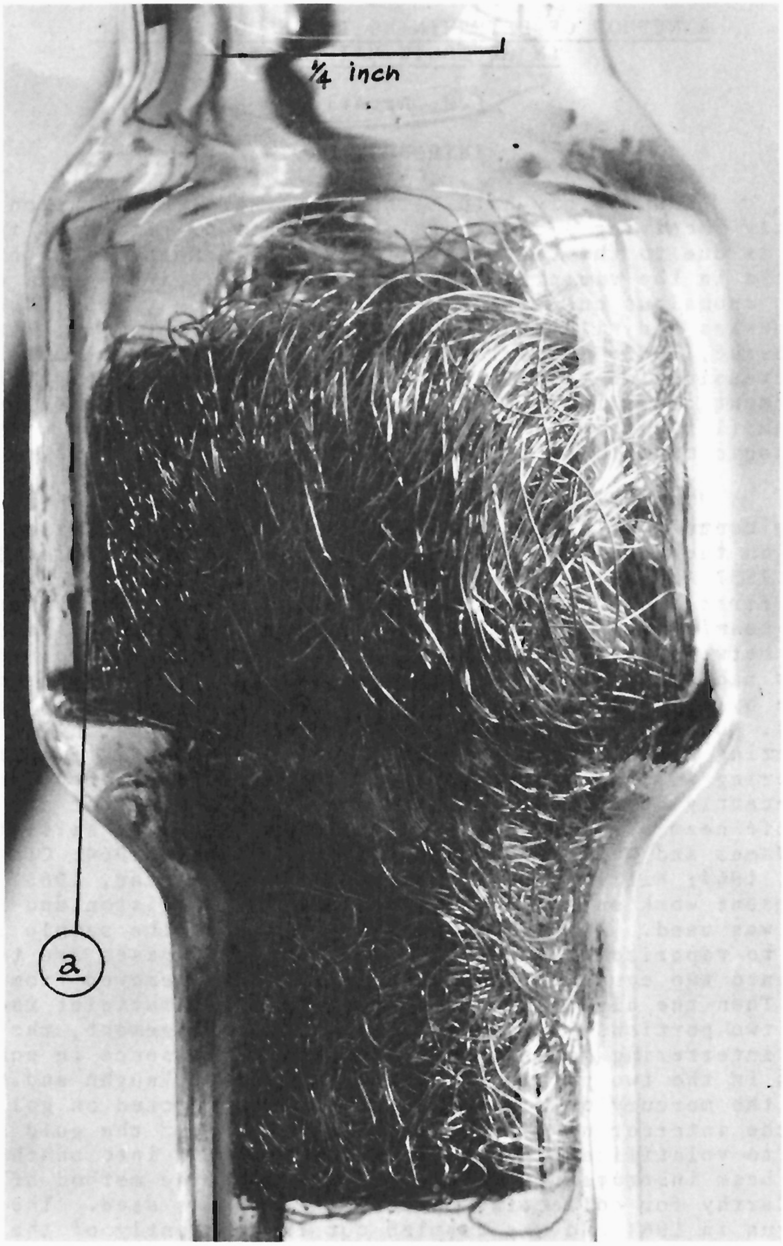

Figure 1. The gold wool collector and emitter of traces of mercury. a: The space produced all around the bulb due to the packing of the gold wool.

The present work deals with (1) the properties of gold wool as a collector and emitter of traces of mercury, and (2) the application of these properties to the determination of traces of mercury in geologic materials containing interfering substances. These substances not only interfere with instruments using single beam systems but, in some cases, interfere with instruments using double beam systems. In the present work the sample is heated to vaporize all the mercury which is collected on gold wool while the interfering substances are exhausted. Next the gold is heated to volatilize the mercury which is measured with a mercury vapour meter (Williston and Morris, 1965).

ACKNOWLEDGMENTS

This work was carried out in the Department of Mineral Technology, University of California, Berkeley, under the sponsorship and with the active interest of Professor H. E. Hawkes. Mr. S. H. Williston and Mr. M. H. Morris of the Cordero Mining Company, Palo Alto, California, generously made available their recently developed mercury vapour meter. Mr. Williston suggested the type of gold and the design of the gold bulb that played such an important role in the present investigation. Mr. J. M. Bryan of Technical Research Center, Cominco Limited, Trail, British Columbia, critically discussed the results and offered valuable suggestions regarding their significance. Mr. Ernest Kendall made most of the optical pyrometer measurements. Professor G. R. Webber of the Department of Geological Sciences, McGill University, reviewed the manuscript.

THE COLLECTOR AND EMITTER OF TRACES OF MERCURY

Traces of mercury vapour were collected on gold wool which was usually held at room temperature. The mercury vapour was charged on the gold wool by releasing the mercury into a stream of air that was passed through the wool. When the charging was completed, the gold was heated rapidly to a temperature ranging from 800 to 850°C. to release the collected mercury. Then the released mercury was passed through the mercury vapour meter which expresses the mercury content in volts. The gold was next allowed to cool to room temperature and thus was ready for a new cycle of collection and emission of mercury.

The gold wool was placed in a quartz bulb (Figure 1). The wool was made from gold wire whose composition was 99.99% Au, and whose diameter was 0.003 inches. Three hundred feet of wire were usually used in a given collector. This has a theoretical surface of 34 square inches. The gold wire was first shaped in the form of wool and then was packed in position in the bulb by means of glass rods.

The gold was charged with mercury while air was being passed through it at the rate of 2 liters/minute. The bulb was placed in an upright position during charging. By connecting

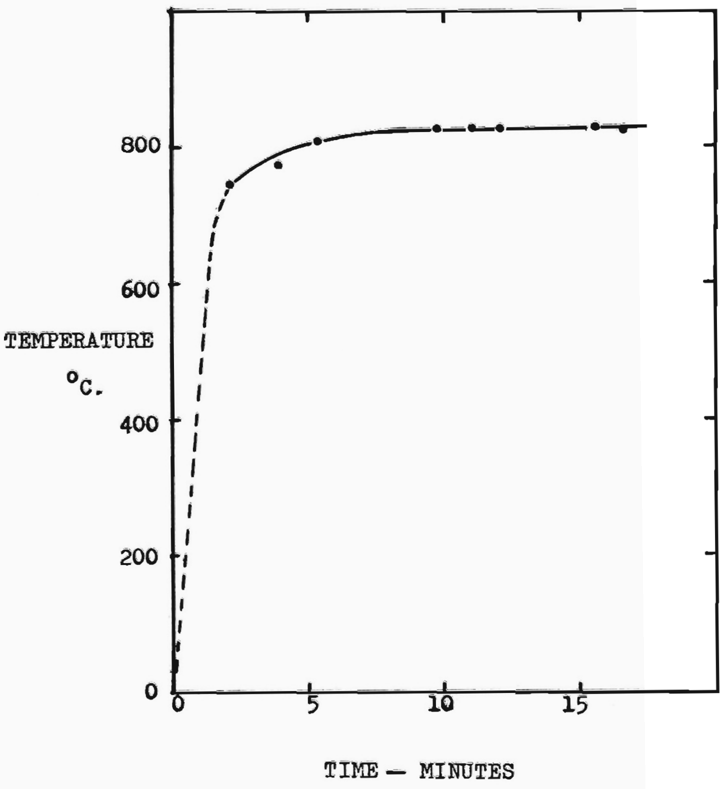

Figure 2. The temperature of a gold collector heated in the induction furnace.

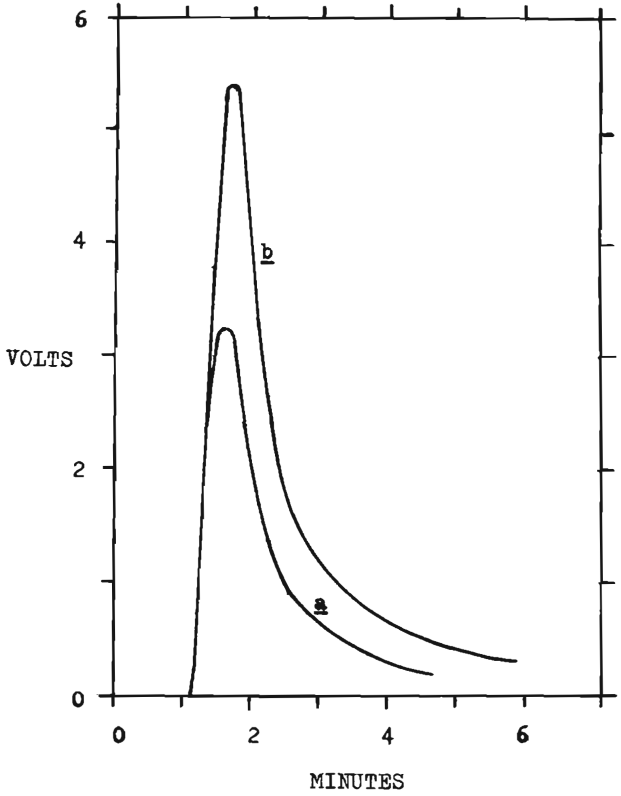

Figure 3. The release of mercury as a gold wool collector is heated in the induction furnace beginning at time 0 minutes. Curve a is due to a charge of 165 nanograms and curve b is due to a charge of 260 nanograms of mercury.

the bulb directly to the mercury vapour meter during charging, it was demonstrated that there was complete collection of mercury vapour when flow rates ranging from 2 to 8 liters/minute were used. Any mercury that escaped collection on the gold would give a voltage reading on the instrument.

The charged gold wool was heated with an induction furnace (Leco, model 521-500) to release the mercury. An example of the temperature of one of the gold wool collectors as it was heated in the furnace is shown in Figure 2. The temperature was measured with an optical pyrometer (Leeds and Northrup No.8622). The induction furnace was set so that a gold collector would always be heated at the same desired rate.

After a number of collection and emission cycles, the gold wool packed inside the bulb and produced a gold-free space between the wool and the inside surface of the bulb (Figure 1, a). However, at the same time the wool slid down on the inner shoulder of the bulb and produced an effective seal preventing the escape of mercury vapour before it had amalgamated with the gold. Using the shape of bulb shown in Figure 1, sealing of space a would not take place if the bulb were not in an upright position.

The sensitivity of the mercury vapour meter used in the present work is in the order of 1 nanogram. However, another model developed by Williston (1964) has a sensitivity of 0.001 nanogram.

Untreated room air was used to carry the mercury vapour through the gold wool and the mercury vapour meter. This air contained a measurable quantity of mercury. Table 1 shows the mercury content of the laboratory air during certain intervals of time of the work.

TABLE I

MERCURY CONTENT OF LABORATORY AIR (Room 432A, Hearst Mining Building) PUMPED THROUGH A GOLD WOOL COLLECTOR.

Date	Pumping Rate (liters/Minute)	Volume Pumped (liters)	Mercury Content (nanograms/100 liters)
April 4,65	2	200	8
April 9,65	2	180	10
April 19,65	6	420	9
May 3,65	6	570	8
May 4,65	6	450	3
May 10,65	6	396	8
May 10- May 11,65	2	1160	6
May 12,65	2	110	12
May 13- May 14,65	2	1200	6

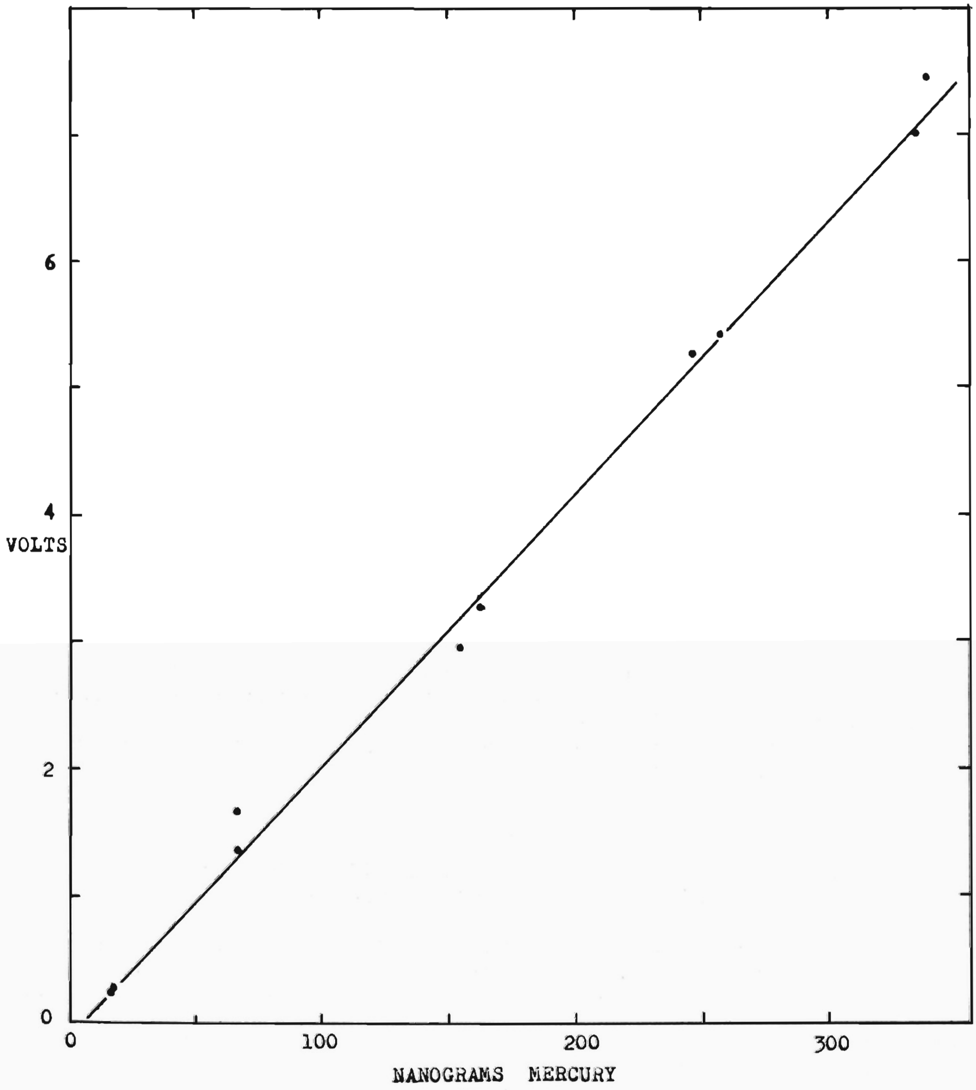

Figure 4. The change in the height of the voltage peaks with mercury content.

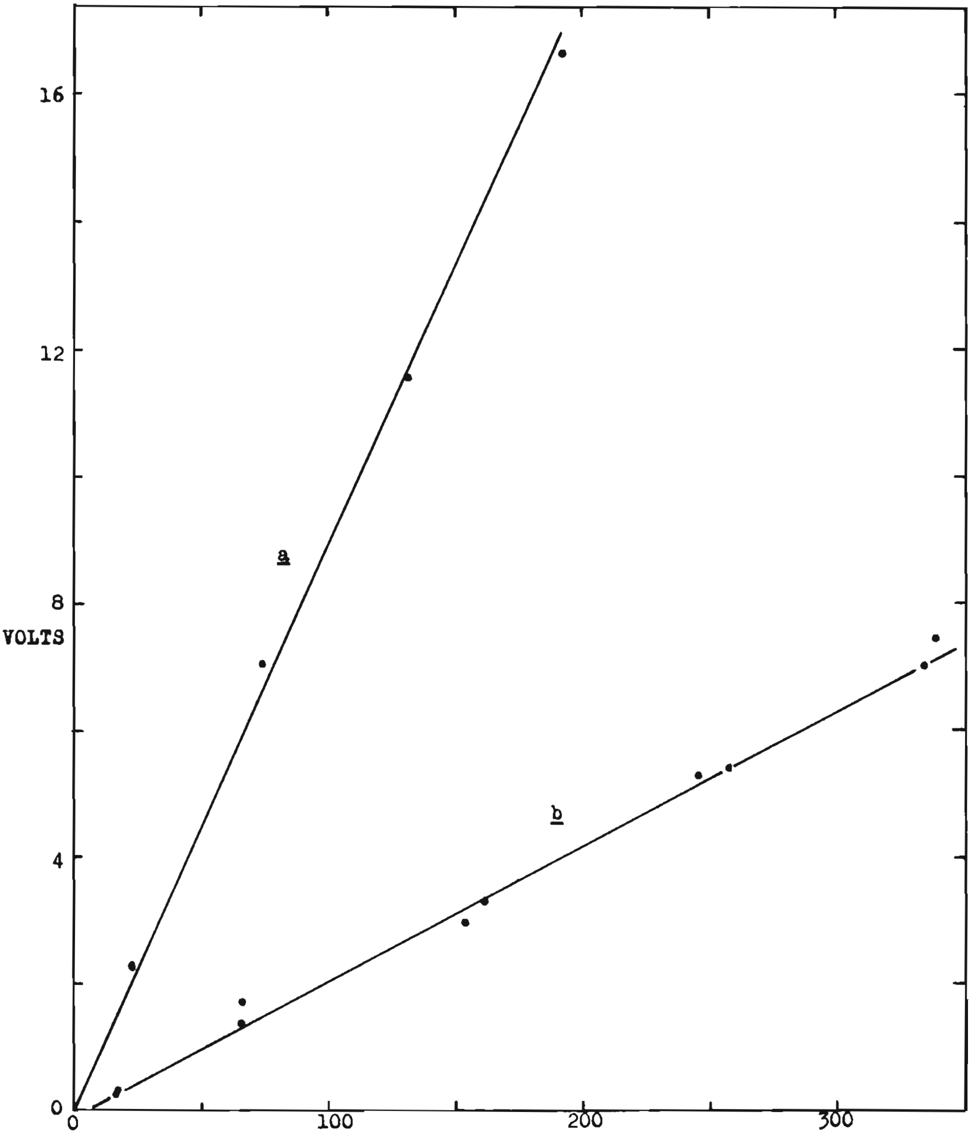

Figure 5. Comparison between the height of the voltage peaks of two calibration curves.

b: The mercury is charged and emitted from gold wool.

a: The mercury is injected directly into the mercury vapour meter.

COLLECTION AND EMISSION OF TRACES OF MERCURY

A gold wool collector was held at room temperature and charged with a standard mercury vapour sample. Next, the gold was heated in the usual way to volatilize the mercury. This procedure was repeated with another standard sample. The results of the two runs are shown in Figure 3. Here the vapour was flowing through the absorption cells of the mercury vapour meter at the rate of 1 liter/minute. It took 14 seconds to obtain a meter signal from mercury released in the induction furnace. Therefore, Figure 3 shows that it took 53-54 seconds to begin to release the mercury from the gold, and it took another 34-37 seconds to reach a voltage peak.

The standard mercury vapour samples were obtained by taking known volumes of air saturated with mercury at known temperatures. The mercury content of a sample was then calculated from the perfect gas law. Figure 4 shows a plot of voltage peaks with mercury content of the runs of Figure 3, as well as of additional runs using the same flow rate. The points of Figure 4 fall close to a straight line and this was used as the calibration curve.

Figure 5 compares the calibration curve shown in Figure 4 and a curve produced by injecting mercury vapour directly into the mercury vapour meter (Figure 5, a). The same absorption cell flow rate was used in both series of runs. Curve a shows higher peaks than curve b due to the presence of more mercury vapour in the absorption cell of the meter at a given time. Thus it seems possible to make the method that uses gold for collection and emission more sensitive. This may be done by releasing the mercury from the gold at a faster rate, and by passing the mercury through the absorption cell at a slower rate.

Gold wool was held at different temperatures ranging from 24°C. to 325°C. and was studied in terms of collection and emission of mercury vapour. The gold collector was brought to a given temperature and was charged with a known quantity of mercury vapour ranging from 70 - 210 nanograms. The collector was held at that temperature for 5 minutes after it was charged. Next, it was heated in the induction furnace and its mercury content measured. At the same time, the same quantity of room air that was passed through the collector being charged, was also passed through a second collector. This was done in order to find the quantity of mercury contributed by room air. This was measured and applied as a blank correction which, however, was usually negligible. The results of these experiments are shown in Table 2.

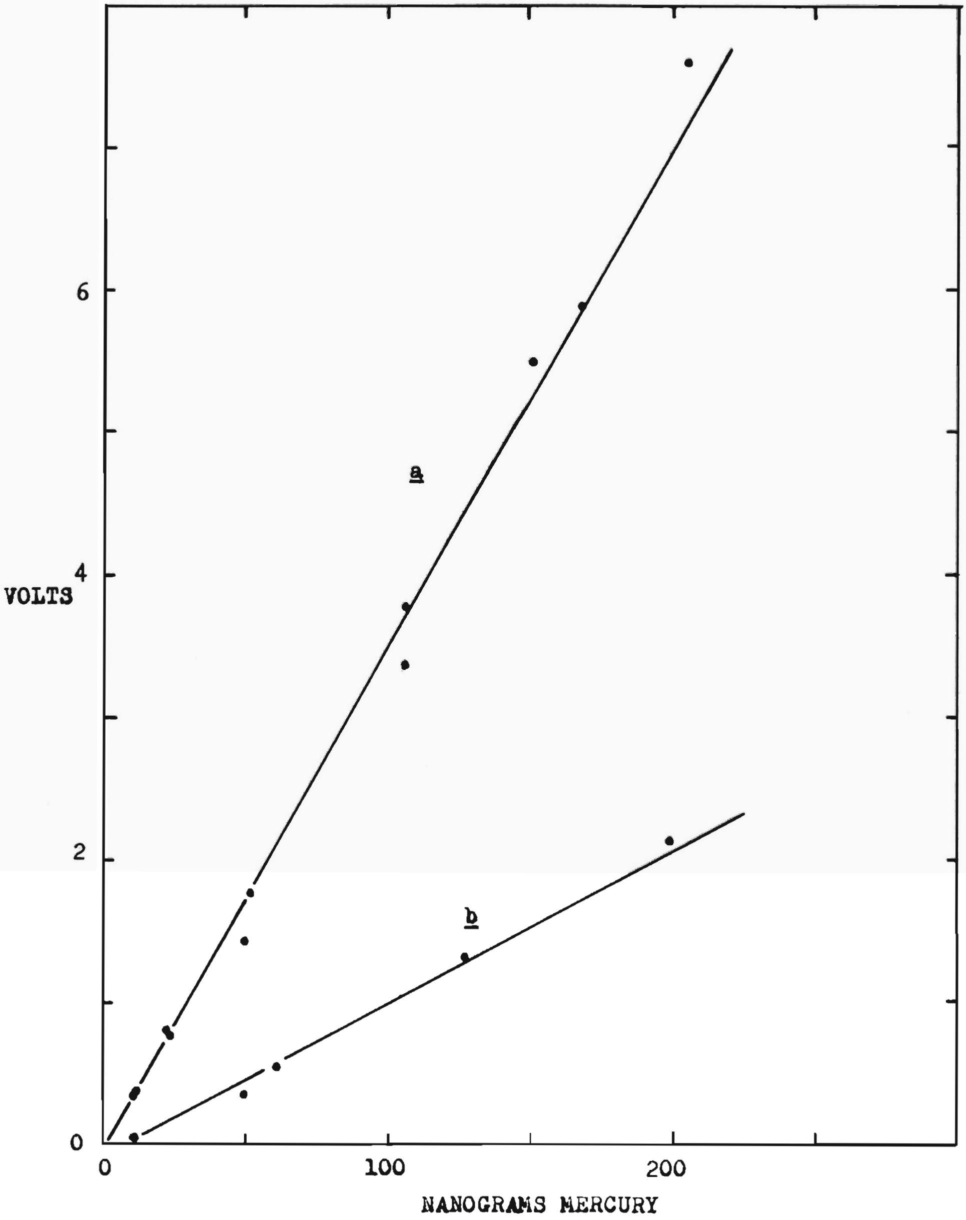

Figure 6. Two calibration curves using the same gold wool collector. Curve a obtained while the collector was less used than in the case of curve b.

TABLE 2

COLLECTION OF MERCURY ON GOLD WOOL AT DIFFERENT TEMPERATURES

Temperature °C.	$\frac{\text{Hg Recovered}}{\text{Hg Charged}} \times 100$
24	96
99 - 107	109
198 - 201	104
213 - 219	107
249 - 258	113
312 - 325	8

It was observed that the slope of the calibration curves, using gold, changed gradually as a result of the continuous use of the gold for collection and emission of mercury. Figure 6 compares two peak voltage curves produced by a collector - emitter in two states of use. Curve b consists of voltage peaks for the same collector - emitter as in curve a but many collection and emission cycles later. It was also observed that, under the conditions of the present work, mercury begins to vaporize from a used collector several seconds later, compared to a new one. It was further observed that the time from the beginning of volatilization until a voltage peak is reached is several seconds longer in the case of a used collector compared to a new one.

The decrease in slope of the calibration curve is directly proportional to the number of collection and emission cycles as well as to the amount charged in a given cycle. The greater the amount charged in a given cycle, the greater the decrease in slope. It took close to 50 cycles to produce any noticeable change in slope of the calibration curve of a new collector if charges of less than 500 nanograms were used. Therefore, the slope of the curve was checked regularly with standard samples.

It was observed that not all the mercury charged on a collector, held at room temperature during charging, is volatilized on heating the first time. This is also indicated in Figure 3 by the way in which the voltage drops to near zero after reaching a peak. Three to six per cent of the mercury was released as a result of a second heating cycle. However, mercury volatilized by a second heating cycle, from a collector held at temperatures ranging from 215-255°C. during charging, was found to be less than 2% of the total mercury charged. This small percentage of mercury was usually neglected in routing runs, but when it represented a large quantity of mercury the collector was cleaned by reheating before it was recharged.

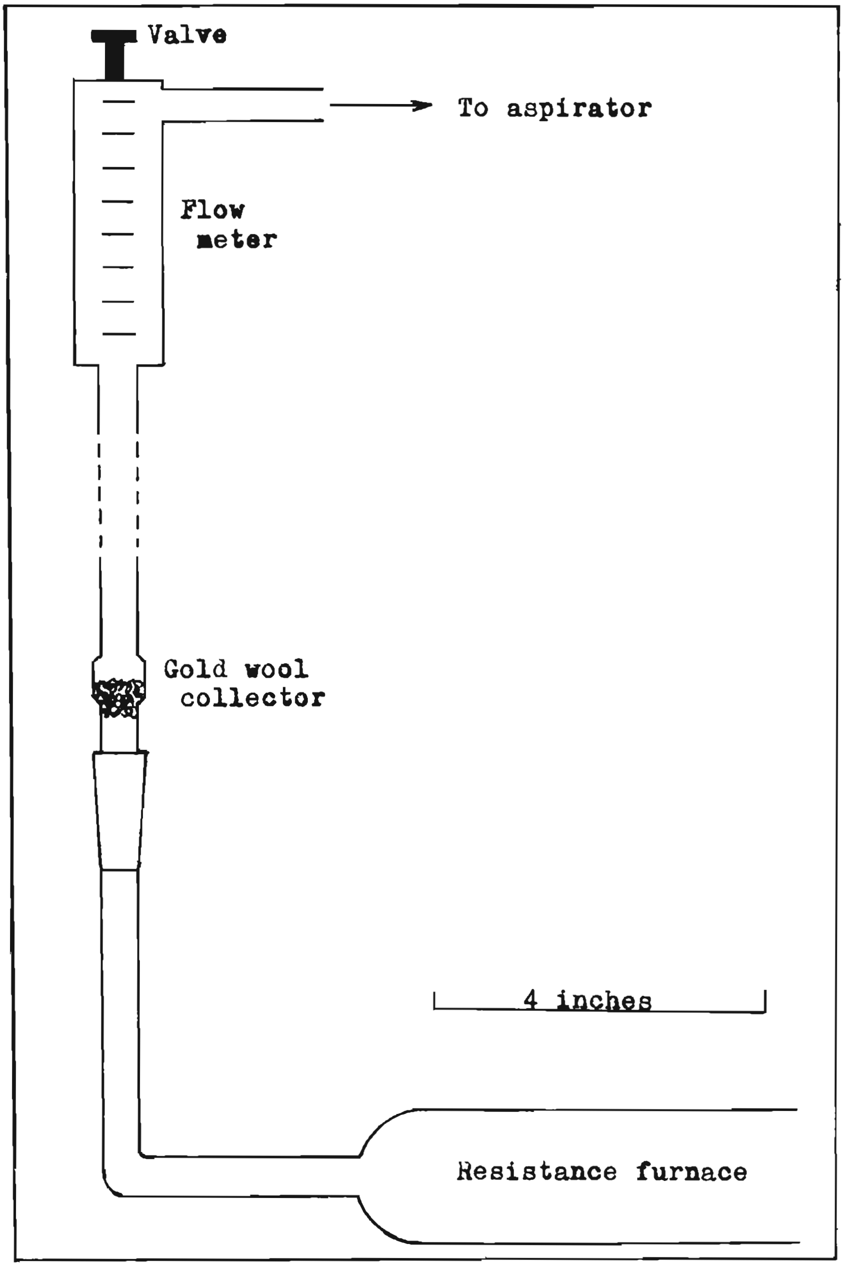

Figure 7. Simplified diagram of apparatus for collecting mercury from sulphides.

Gold collectors were placed in air saturated with mercury at room temperature for periods up to 15 hours. They were placed in sealed containers containing excess liquid mercury. The concentration of mercury in the containers ranged from 17 to 23 nanograms/c.c. The surface of the collectors varied from 40 to 45 square inches. Preliminary tests suggested that the gold was amalgamating with mercury at the rate of 1000 nanograms/hour in the beginning, and gradually decreasing to 150 nanograms/hour after 15 hours.

DETERMINING MERCURY IN SULPHIDES

It seems that the accumulation of more data on the mercury content of sulphides, and on the mode of occurence of mercury in sulphides, would help in interpreting mercury halos related to sulphide deposits. Therefore an attempt was made to determine the mercury content of sulphide minerals.

The first attempt was made by heating the samples to approximately 800°C. in the induction furnace, and determining the mercury with the mercury vapour meter (Williston and Morris, 1965). The results were unreliable. Next, sulphide samples, weighing 0.01-0.10 grams, were covered with 1.3 grams of 40 mesh iron filings, and were heated to approximately 800°C. in the induction furnace, and the mercury determined with the same meter. The results were also unreliable. Finer iron filings were not used due to their high mercury content. In further attempts, the samples were covered with larger quantities of iron filings, up to 6.5 grams, but still no reproducible results were obtained.

MnO_2, 12-20 mesh in size, was also used in an attempt to trap the interfering substances that were released when the sulphides were heated. The attempt failed because the MnO_2 trapped the mercury vapour.

Next, the arrangement shown in Figure 7 was attempted. This makes use of a gold wool collector (Figure 1). The sample, weighing 0.1-0.5 grams, was transferred to a porcelain boat and placed in the resistance furnace for 2-5 minutes. The furnace was held at 900°C. and the temperature was measured with a chromel alumel thermocouple. While the sample was being heated, room air was aspirated through the system at the rate of 1-2 liters/minute. Thus, the mercury of the sample was collected on the gold wool while the sulphur oxides were exhausted. In the case of samples of galena and sphalerite, minor lead and zinc oxides deposited along the tube joining the furnace to the collector. When the sample heating was completed, the gold collector was heated in the induction furnace and the mercury content determined with the mercury vapour meter. The mercury content was then expressed per billion (p.p.b.). The results of determining the mercury content of some sulphide specimens is shown in Table 3. It took 4-7 minutes to determine the mercury content of a weighed sulphide sample.

TABLE 3

MERCURY CONTENT OF SULPHIDE SPECIMENS

Mineral	Mercury Content (p.p.b.)	Average of % Dev. from Arith. Mean
Galena 1	29, 24, 32, 37, 25	14
Galena 2	90, 85, 75, 75, 115	14
Galena 3	135, 150, 120	7
Galena 4	420, 470, 485	6
Sphalerite, light brown	5250, 10100, 9900, 4000, 4300	39
Sphalerite, dark brown	100, 95, 25, 40 25, 65	48
Chalcopyrite 1	280, 470, 230, 190	30
Chalcopyrite 2	80, 75, 65	8
Bornite	2850, 2920, 3150	4

DETERMINING MERCURY IN OTHER GEOLOGIC MATERIALS

The properties of gold wood as a collector and emitter of mercury were outlined above. The properties offer definite possibilities for determining traces of mercury in various materials, such as vegetation, organic soils, water and gases, that contain interfering substances.

To use this technique, the sample must be heated in such a way that elemental mercury vapour is produced. This can then be collected on the gold wool and the interfering substances exhausted. There are cases where it is suspected that some interfering substances, such as tars, condense on the gold and thus lessen its effect as an amalgam by allowing some mercury to escape detection (Vaughn and McCarthy, 1964, p. 126). In such cases, as well as in cases where water vapour may condense on the gold, the gold may be kept at a suitable temperature between 25 and 250°C. during the collection of mercury. This would eliminate or minimize the condensation.

After the mercury has been collected on the gold, it may be volatilized and measured in a low cost portable single beam mercury vapour meter. This offers the possibility of modifying such low cost instruments for field use where samples containing interfering substances are encountered.

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THE EDUCATION OF THE APPLIED GEOCHEMIST: WILL THE UNIVERSITY MEET HIS NEED?

Harold Bloom*

This meeting marks a very special occasion for Geochemical Prospecting in North America. I believe it is one of the first symposia that has not been a small part of another, much larger, meeting. Indeed, this could be a time of appraising the status of Geochemical Prospecting as it is today, and for assessing its growth potential. We could ask, "How healthy is it now?" and "How will it fare in the years to come?"

It is quite apparent that since its launching in the United States some 18 years ago, the momentum has picked up until in recent years we see Applied Geochemistry on a new threshold. Like the fast growing adolescent suddenly faced with planning a sound career for his future, we too, need to take stock of where we are going.

Let us first look at some of the problems that beset us today, simply to see where we stand: (1) We see an increasing demand for competent, trained geochemists which we are not able to supply. (2) We are aware of the large numbers of geochemical prospecting projects being carried out, the results of many of which have been described as less than satisfactory. (3) We are being faced with increasingly difficult research problems that need to be solved to insure our sound growth and, (4) finally, due to the world-wide impact of the need for development of the mineral resources of new nations, we are receiving from United Nations, A.I.D. and mining companies, a continual flow of people for training purposes.

This state of affairs is certainly one to take stock of. We need to clean up some of these present day problems, but where do we start?

STATUS OF EDUCATIONAL PRACTICES

A large part of the development in applied geochemistry has come about in spite of a hands-off attitude on the part of North American colleges. A very worthwhile starting point to relieve the shortages, I believe, is to see what can be done on the college level to attract and train graduate students.

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We have been guilty in the past of overselling geochemistry by referring to its utter simplicity. We have proclaimed that students with a high school education can run field tests and that almost anyone can conduct the field programs. Why therefore, should we have expected more than just a casual reference to the role of education?

In the United States, we have seen the educational role first handled by the Geological Survey who, for many years, trained groups of people on a two-week program. Because it is a research organization, it no longer engages in this role except on special occasion. The Colorado School of Mines took over the two-week program, and with the assistance of one or two members of the U.S.G.S., has given the course annually for the past 5 years. Over 60 people, comprised of geologists, mining engineers and college instructors have taken the course. Other colleges around the country, Utah, Penn State, to name a few, offer one or two semester courses in applied geochemistry. The University of California, Berkeley, and others, have instructed Peace Corps personnel in geochemical techniques. Prospector's courses at the University of Alaska have been held for many years.

The Geological Survey of Canada has played the key role of educator in Canada, along with Provincial Surveys. Numerous colleges have been offering one and two semester courses as part of a broader program in pure geochemistry, or exploration geology. All of these efforts must be considered as stop-gap attempts, improvised to cope with a continual shortage, but none are planned degree programs.

It would be interesting for us to review the devious educational routes most of us have taken to now find ourselves in geochemical exploration. Should this remain the pattern of the future recruitment program too?

The problems of education should be left to the colleges and the opportunity should be given there to train a student in some depth in applied geochemical theory and practice. This cannot, however, be on the basis of a one or two semester course in techniques. It is the speaker's experience that courses extending over at least one year and preferably longer are necessary to develop a firm interest in an individual. A smrong background in geology is a requisite for this type of training. He must not only satisfy the standards of any geology department regarding his ability in the field, but must be given the opportunity to develop a geochemical thesis on a sound geological base.

I know of no effort in any of these countries that approaches the program carried out at the Royal School of Mines, London, under Professor J. S. Webb. Here, for many years, a program leading to a Ph. D. in Applied Geochemistry has been given. Many of their graduates are present in this audience, today, and are participating as speakers on this program. Their contributions to both research and practice of geochemical exploration in Canada and elsewhere are a fine example of what such a program can do.

While it is quite impossible to duplicate the setup of the R.S.M., we here can strive for greater cooperation among the colleges, geological surveys and the mining industry. The latter could exert a powerful influence in this regard. By extending financial aid in the form of fellowships and scholarships earmarked for applied geochemical studies, they could help the overall program and most of all, themselves.

To summarize, I would submit that a planned educational program in applied geochemistry, principally on the graduate level, will do much toward alleviating some of the problems set forth here today. Increased numbers of properly trained geochemists can be of service in many areas - teaching, research, field practice - and in so doing provide a basis for a sound and continued advancement in the years ahead. The chairman of this Symposium, Dr. R. W. Boyle, in a recent article that appeared in Economic Geology regarding a geochemical research problem stated, "With respect to later formations it may be true that mineralized zones are not reflected through thick sequences of later rocks such as Tertiary flows or sediments or through thick glacial tills or clays, although I have reason to believe that it will be only a matter of time and research before such areas are also amenable to geochemical exploration techniques". This statement carries my best wishes for success, but I would personally feel better if the universities could become a part of this research effort.

GEOCHEMICAL PROSPECTING - RETROSPECT AND PROSPECT

R. W. Boyle*

RETROSPECT

Geochemistry is literally speaking the chemistry of the earth. More specifically, it is the science that deals with the migration, concentration, and dispersion of the elements and their isotopes in the lithosphere, pedosphere, hydrosphere, atmosphere, and biosphere of the earth. As in all sciences, there is a pure or fundamental aspect and an applied aspect. The latter is entirely dependent upon the former, a feature that is often neglected. Among the applied aspects of geochemistry the most important is probably geochemical pospecting, but there are others that are assuming ever increasing importance. Included in these are the mounting problems of pollution of the various spheres of the earth as the population of the globe increases and industrialization proceeds; the elucidation of the role of nutrient and trace elements in the health of the human species; and the problems of radioactive contamination. In this paper only geochemical prospecting will be considered.

It is difficult to pinpoint the actual beginning of geochemical prospecting methods since these have grown with advances in the chemical and geological knowledge of the earth. Both chemistry and geology have long histories that stretch far back into actiquity, and as might be expected, suggestions as to how chemistry can be applied in the search for concentrations of the elements have been advanced since early times. One can see in Agricola's writings, particularly in his "De Ortu et Causis Subterraneorum" and "De Re Metallica", frequent references to the importance of the use of springs and natural waters in prospecting for veins.

In "De Re Metallica" Agricola says, "Now I will discuss that kind of minerals for which it is not necessary to dig, because the force of the water carries them out of the veins. Of these there are two kinds, minerals - and their fragments - and juices. When there are springs at the outcrop of the veins from which, as I have already said, the above-mentioned products are emitted, the miner should consider these first, to see whether there are metals or gems mixed with the sand, or whether the waters discharged are filled with juices. In case metals or gems have settled in the pool of the spring, not only should the sand from it be washed, but also that from the streams which flow from these springs, and even the river itself into which they again discharge. If the springs discharge water containing some juice, this also should be collected; the further such a stream has

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flowed from the source, the more it receives plain water and the more diluted does it become, and so much the more deficient in strength. If the stream receives no water of any kind, or scarcely any, not only the rivers, but likewise the lakes which receive these waters, are of the same nature as the springs, and serve the same uses." And further, "The waters of springs taste according to the juice they contain, and they differ greatly in this respect. There are six kinds of these tastes which the worker especially observes and examines; there is the salty kind, which shows that salt may be obtained by evaporation; the nitrous, which indicates soda; the aluminous kind, which indicates alum; the vitrioline, which indicates vitriol; the sulphurous kind, which indicates sulphur; and as for the bituminous juice, out of which bitumen is melted down, the colour itself proclaims it to the worker who is evaporating it" (in Hoover and Hoover, 1912).

These are remarkable statements about hydrogeochemical methods written as far back as the middle of the 16th century. Other excerpts from Agricola's "De Re Metallica" are no less startling when we moderns think we are discussing new methods based on thermal effects due to oxidation of ore deposits and others based on biogeochemical principles. For instance Agricola says, "Further, we search for the veins by observing the hoarfrosts, which whiten all herbage except that growing over the veins, because the veins emit a warm and dry exhalation which hinders the freezing of the moisture, for which reason such plants appear rather wet than whitened by the frost. ...... Therefore in places where the grass has a dampness that is not congealed into frost, there is a vein beneath; also if the exhalation be excessively hot, the soil will produce only small and pale-coloured plants. Lastly there are trees whose foliage in springtime has a bluish or leaden tint, the upper branches more especially being tinged with black or with any other unnatural colour, the trunks cleft in two, and the branches black or discoloured." And finally, "Likewise along a course where a vein extends, there grows a certain herb or fungus which is absent from the adjacent space, or sometimes even from the neighbourhood of the veins. By these signs of Nature a vein can be discovered."

Certainly these statements are a clear exposition of the role of indicator plants and what we moderns call chlorotic or toxic effects due to an excess of trace elements in soils overlying mineralized zones.

Botanical associations with ores have been noticed for a very long time, at least as early as the 8th or 9th century A.D. The early Chinese, according to Professor Needham (1959), observed that certain species of plants occur near silver, gold, copper, and tin deposits, and that a correlation existed between the appearance of plants and underlying ores. The early Chinese were also aware that plants contained the metals and in some cases extracted mercury from certain species.

The first successful "geochemical prospector" appears to have been Giovanni de Castro, a Genoese gentleman who lived in the middle of the 15th century. He went to Syria and for some time was engaged in manufacturing alum from the alunite mines near Edessa in that country. While there he observed a particular type of holly plant that characteristically grew near the veins. On returning to Italy he found similar plants growing in the hills at Tolfa, near Rome. While prospecting around he soon found alunite float and later the veins from which it came. This led to an important alum industry at Tolfa, and for his efforts Pius II granted Castro a generous annuity and erected a statue in his honour.

These then are some of the early attempts to use chemical and biochemical methods in prospecting for ores. Numerous other examples could be mentioned from the writings of the geologists and chemists of the 17th, 18th, and 19th centuries, but lack of space prohibits pursuing further details of the early efforts here.

Turning to the 20th century and the development of modern geochemical prospecting we note that most of the research and the application of the various methods began in the thirties, mainly in the U.S.S.R. and Scandinavian countries. A.E. Fersman, the great Russian geochemist, and N.I. Sofronov were the first to stress the importance of primary and secondary dispersion haloes associated with ore deposits, and they were followed in the late thirties and early forties by E.A. Sergeev, V.I. Nikolaev, S.D. Miller, A.P. Solovov, I.I. Ginzburg, and numerous other Soviet geochemists who worked out the details of the various geochemical prospecting methods utilizing trace elements and heavy minerals. By 1950 geochemical mapping on detailed and reconnaissance scales was in full swing in various parts of the U.S.S.R. Biogeochemical research and biogeochemical prospecting, utilizing plant analyses and indicator plants, began with V.I. Vernadsky and A.P. Vinogradov as early as 1936 in the Soviet Union, and these subjects have been pursued assiduously ever since in the U.S.S.R. by Soviet geochemists, particularly D.P. Maliuga.

In Scandinavian countries the fundamental geochemical researches of V.M. Goldschmidt stimulated efforts to apply the results to geochemical prospecting. In 1936 experiments by S. Palmqvist and N. Brundin of the Swedish Prospecting Company on trace elements (Sn, W, Pb, Zn) in plant ash were conducted in the vicinity of mineral deposits in Cornwall and Wales with positive results. For several years thereafter the Swedish Prospecting Company carried out numerous surveys utilizing plant analyses in conjunction with geophysical work for mining companies. Most of this work was of a confidential nature and has not been published.

Geochemical prospecting methods were not considered in the United States, England, France, Canada and other countries until after 1945. H. Hawkes and B. Lakin of the Ulited States

Geological Survey began experimental work utilizing pedogeochemical methods in 1947 and this has been followed by research in hydrogeochemical, stream sediment, and lithogeochemical prospecting methods by many other geochemists of the Survey. Biogeochemical methods have also been the subject of much research, especially by Helen Cannon and her colleagues. In the United Kingdom the establishment in 1953 of the Geochemical Prospecting Research Center at the Imperial College of Science and Technology, London, under the able direction of Professor J.S. Webb, led to an increase in research in geochemical prospecting methods in the United Kingdom and various parts of the British Commonwealth, particularly in Africa and the Far East. In France an active group of geochemists have been engaged in research and development of geochemical prospecting methods at the Bureau de Recherches Géologiques et Minières (B.R.G.M.) and at the Commissariat à L'Energie Atomique since 1955. Numerous other research institutes throughout the world such as the Geological Survey of Finland; the Geological Survey of Sweden; the Geological Survey of India; the Geological Survey of Norway, Trondheim; and the Bureau of Mineral Resources, Canberra, Australia are now actively engaged in developing geochemical methods suitable for the particular terrains and climates in which they are resident.

In Canada research in geochemical prospecting, particularly biogeochemical prospecting, began at the University of British Columbia in 1945 under the able leadership of Professor H.V. Warren and R.E. Delavault. Later Professor J. Riddell began a series of geochemical prospecting investigations at McGill University. A large scale geochemical survey using stream sediments was carried out in northern New Brunswick in 1954 for a private company by H.E. Hawkes, H. Bloom, J.E. Riddell, and J.S. Webb. This survey has been followed by numerous others by private companies throughout the length and breadth of Canada.

The Geological Survey of Canada began research in the geochemistry of primary haloes around gold deposits in the Yellowknife area in 1949, and this was followed in 1954 and 1955 by geochemical surveys of stream and spring waters and soils in the Keno Hill area, Yukon. Reconnaissance surveys of stream water and sediment were begun in Nova Scotia in 1956, and these were continued in 1957 and subsequent years in both Nova Scotia and New Brunswick. In recent years geochemical prospecting research and surveys have been pursued along many lines and in many parts of Canada. A reconnaissance bedrock survey has been carried out in Northwestern Ontario, surveys of reef-bearing limestones and dolomites have been done in Western Canada, an investigation of uranium prospecting by water analyses in the southern part of the Canadian Shield has been pursued, methods using gas chromatography for outlining oil pools and gas fields have been tried, detailed and reconnaissance biogeochemical surveys have been done, and stream sediment and water surveys over broad areas in which as many as 15 elements have been determined in each sample have been carried out by helicopter and conventional methods in the Yukon and New Brunswick. During these surveys a laboratory quantograph, field spectrographs, and field preparation and field colorimetric laboratories have been extensively employed.

Looking back at the phenomenal advances made in geochemical prospecting the following significant landmarks in chemical and geological knowledge seem to this writer to be the most important.

1. Recognition of primary and secondary dispersion haloes and trains that are associated with all mineral deposits. Haloes and trains have been known for a very long time. Their importance, however, in a geochemical prospecting sense was first emphasized by Fersman in the early 1930's.

2. Development of accurate and rapid analytical methods utilizing the spectrograph and the various specific sensitive colorimetric reagents, especially dithizone. Kirchhoff and Bunsen founded the science of optical spectroscopic analysis in 1859, and Assar Hadding first employed x-ray spectrography in chemical analysis in 1922. Both methods have given immeasurable service in geochemical prospecting. Dithizone was first prepared in 1878 by Emil Fischer who noted that its reactions with heavy metals gave brilliantly coloured products. No analytical use, however, was made of it until 1925 when Hellmut Fischer demonstrated its particular use in estimating the amounts of various trace metals in substances. Since then dithizone and many other similar organic compounds have been widely used in geochemistry and geochemical prospecting. Actually, dithizone methods approach the limits obtainable by spectrography and in some cases surpass them.

3. Development of polyethylene laboratory ware of all types. This permitted greater freedom in field analysis and reduced the incidence of contamination. The introduction of resins for the production of metal free water for use in trace analysis requires no comment.

4. Development of gas chromatography. This is probably the most significant development with regard to rapid analysis of traces of hydrocarbons in petroleum prospecting using soils and waters.

PROSPECT

Having looked at the past and its accomplishments we now look at the future and especially at some of the problems that demand solution in order that we can better outline ore deposits in extent and depth.

To this writer there are seven fundamental problems on which we must focus. These can be conveniently tabulated as follows:

1. Definition of geochemical provinces and their relation to mineral deposits.

2. Development of methods for discovering large low grade deposits.

3. Development of methods for discovering deeply buried deposits.

4. Further development of methods to outline primary haloes.

5. Elucidation and formulation of techniques to relate the size and trace element intensity of haloes and dispersion trains to grade of deposits.

6. Development and refinement of biogeochemical methods, expecially those based on indicator plants, chlorotic or toxic effects, and microbiological techniques.

7. Delineation of the nature and extent of geochemical and biogeochemical haloes associated with oil and gas fields.

1. Geochemical provinces:

All geologists are familiar with the fact that most types of mineral deposits are clustered in certain areas of the earth's crust. Some of these are in highly folded terranes, others are in relatively undisturbed rocks. We tend to call these clusters "metallogenic provinces", which in my opinion is a misnomer. For instance we often hear of a gold province, as in certain greenstone belts of the Canadian Shield. In reality these deposits are great concentrations of silica in the form of quartz, or of calcium, iron, magnesium, and carbon dioxide in the form of carbonates. Gold is only an incidental metal, present generally in a concentration of less than 15 ppm (0.5 oz/ton). Or again we may take another example from the lead, zinc, copper, and nickel provinces. These are in reality sulphur provinces in most cases. The point is that these provinces are not metallogenic provinces but rather geochemical provinces in which a variety of non-metals and metals are concentrated. Surely the concentration of silica in the case of the gold deposits and sulphur in the case of the sulphide deposits is as important geochemically as the metals since all of these so called "dross or gangue elements" generally occur in much greater abundance than the valuable metals and non-metals. If we are to understand these so called provinces we must state the facts clearly, and the facts are that the clusters of deposits represent a chemical concentration, generally of a number of metals and non-metals, far in excess of that normally found in ordinary rocks and other earth materials. The reason for stressing the terminology "geochemical provinces" is I think self evident since many of the gangue elements are excellent indicators of the more valuable metallic elements. I need only mention here that arsenic provinces are often gold provinces, boron and fluorine provinces often mark tin provinces, and manganese may indicate barium and silver provinces.

We could spend a lot of time arguing the various points why there are tin belts, centres of nickel concentrations, lead-zinc belts, copper belts, etc., but this would avail us nothing from the practical viewpoint of geochemical prospecting. What we want to know is - by applying geochemical techniques to waters, stream sediments, soils, biological materials, and rocks, can we outline geochemical provinces in which we may expect to find deposits of a certain type? At the present state of our knowledge we can I think answer in the affirmative for waters and stream sediments in certain geological terranes. For soils and biological materials the answer is less definite, and for rocks uncertain.

Work in a number of countries on the chemical constitution of surface and underground waters suggests that these reflect geochemical provinces, particularly those in which zinc and uranium deposits occur. Few other elements have been utilized in water analyses over broad areas, and hence our knowledge is considerably restricted. Further research is, therefore, desirable to ascertain the usefulness of water analyses in outlining geochemical provinces for the other elements of the periodic table. In this work the new method of atomic absorption spectroscopy will undoubtedly play a large part because of its great sensitivity.

Analysis of stream sediments has proved most effective in outlining geochemical provinces rich in copper, lead, and zinc deposits. This I think is recognized by many, but here again most surveys are concerned only with the three elements. It would seem that surveys in which the other elements of the periodic table are determined would also be effective in outlining their geochemical provinces. Certainly this seems to be true for silver, arsenic, antimony, and manganese judging from the surveys done by the Geological Survey in eastern and western Canada.

Soils and biological materials are useful in geochemical surveys on a local basis, but their effectiveness in outlining geochemical provinces is as yet indefinite. Until research on these materials is done over broad areas, and the results treated statistically, an unequivocal answer cannot be given.

The effectiveness of rock analyses in outlining geochemical provinces is even more indefinite. In a gross way certain clusters of granitic intrusives exceed the norm in their contents of tin or molybdenum, and these have associated tin or molybdenum deposits. Likewise, certain basic intrusives with higher than average contents of nickel and platinum metals may have associated nickel-platinum deposits. These relationships also extend to certain shales enriched in copper such as the Kupferschiefer, the copper shales of Zambia, and those in Michigan at White Pine. Certain carbonate rocks with abnormal amounts of lead and zinc may also contain within them deposits of these two metals. For a variety of other metals and non-metals, mainly those occurring in veins and massive sulphide deposits, such as silver, gold, uranium, lead, zinc, and copper, the relationships between the contents of metals in the deposits and those in their enclosing country rocks is obscure to say the least. From my own research on the geochemistry of gold, silver, lead, and zinc I have to say that the contents of these metals in the normal country rocks do not seem to reflect the presence of deposits of these metals in the belts where I have studied them. There are neither above normal amounts of the metals in the rocks such as should occur if the metals were introduced from outside, nor below normal depletions of the metals such as might obtain if the metal were secreted from the rocks. This is an enigma which only further geochemical research will solve. Perhaps the metal contents of rocks containing deposits differ only by infinitisimally smaller or larger amounts from those that are barren, and these differences may appear only after sophisticated statistical treatment of the analytical results.

2. Development of methods for discovering large low-grade deposits:

As the demand for metals and non-metals increases and as the rich high-grade deposits are exhausted, it will be necessary to turn to sources that are only slightly enriched in the elements we wish to extract. These sources include the black shales and schists that are great reservoirs of sulphur, the base metals, uranium, and other elements; large granitic masses slightly enriched in copper, molybdenum, uranium, thorium, tin, lithium, and other elements commonly found in acidic rocks; basic masses of rock enriched in nickel, chromium, and platinum; carbonate rocks containing disseminations of lead and zinc minerals; the laterites and other products of weathering; the sediments of the sea; underground waters; and in certain cases the sea. The economics of winning elements from these sources depends not only on technological progress in mining and processing the materials but also on their grade. It is a matter of simple economics to understand that a black schist belt containing 200 ppm copper can be more economically exploited than one containing only 100 ppm of the metal.

Fortunately, all of the geochemical prospecting methods are particularly well adapted to the discovery of large low grade sources since the targets are broad. Most of the methods are direct and, with proper sampling intervals, should give estimates of the grade after statistical treatment of the analytical results.

Little research has been done on methods of outlining large low grade deposits although some work has been done on uranium and beryllium-bearing granites and on manganese-bearing oceanic sediments. Thought should be given now to integrated geological, geochemical, and geophysical methods for defining metal-rich zones in black schists, in gabbroic and granitic masses, in weathered products, and to the discovery of underground waters slightly enriched in metals like lithium, rubidium, cesium, rare earths, uranium, etc.

3. Development of methods for discovering deeply buried deposits:

Most of the successes in discovering deposits by geochemical and geophysical methods have been in geological situations where the mineral concentrations either intersect the surface or lie at depths of only a hundred feet or so. Since it seems probable that as many deposits lie deeply buried as have now been revealed, it is imperative to develop methods that have a deep penetration. As far as geochemical methods are concerned the problem can be resolved into two general categories.

1. Development of methods for the discovery of deposits beneath deep surficial deposits such as glacial materials, residual outwash, and Tertiary and Recent sediments or volcanic rocks.

2. Development of methods for the discovery of deposits that lie at depth in the rocks.

With respect to the first, three geochemical prospecting methods - analysis of overlying materials, hydrogeochemistry, and biogeochemistry - would seem to offer the best hope of success.

Analysis of the near surface horizons of thick sequences of clays, tills, overlying sediments, etc. may not be effective in most areas since these materials may have little if any physical or chemical contact with underlying mineral deposits and in many cases may be entirely foreign to the deposits or their dispersion haloes. In these cases deep drilling to obtain samples of the overburden near the bedrock is the only feasible method. This is of course costly, but if the drilling is guided by good geological and geophysical work, the costs can be considerably reduced. The preliminary stages of such a program should include the projection of known favourable structures into heavily overburdened terrain, geomorphological studies to determine the topographic expression of shear zones, faults, fractures and folds, and geophysical studies. In the initial stages, deep sampling should be restricted to projected structures and geophysical anomalies. Imagination and optimism in the work are vitally important.

Groundwater percolates through the deep overburden of many terrains and appears as springs in low areas or wells up in deep draws or at the bottoms of lakes. Sampling of the waters at these effluent points, followed by plotting on a detailed map may indicate the mineralized zones. In some cases it may be necessary to drill deep holes on a grid or along projected structures to sample the groundwaters. Knowing the metal content of the groundwater and the direction of flow, which can be obtained in some cases by injecting a radiotracer or a dye, it should be possible to trace metal anomalies in the groundwater system to their source.

The roots of trees and certain plants often penetrate deeply and may actually sample deep layers of overburden in contact with deposits. In other cases the roots may sample the groundwater in contact with deposits covered by thick layers of overburden. Sampling of plants and trees under such conditions may be useful in outlining mineralized zones. Some research along these lines has been done, but much more is required to assess adequately the effectiveness of the method.

Deep seated deposits that do not reach the surface will always be difficult to detect, but in certain cases geochemical methods may be effective if properly integrated with geological and geophysical work. Research on two methods would seem to offer the most promise - lithogeochemical surveys (analysis of rock and drill core samples) to outline primary dispersion or leakage haloes associated with buried deposits, and hydrogeochemical surveys of the groundwater system.

When carrying out lithogeochemical surveys using either rock samples or drill cores, the following points should be kept in mind. In addition to analyzing the rock and core samples of the massive rocks, all shear zones, fractures, contorted zones, and altered zones should, likewise, be sampled and analyzed for their metal content or for indicator elements such as mercury, arsenic, and antimony. A detailed map showing all of these geological features, as well as any small veins, no matter what size, should be plotted and the metal or indicator element contents of the samples entered at the appropriate sites. When drilling is done, sections with all of this detail should also be prepared. Only in this way is it possible to observe patterns in the primary metal or indicator element dispersion in the rocks, and from these patterns to predict the locus of large deposits. It should be constantly borne in mind that most large deposits have a halo of smaller satellites developed in subsidiary or parallel fractures, faults, folds, and other structures. Trace element work on small shear zones, fractures, and faults increases our ability to differentiate smaller and smaller satellites. It may well be that the data, when plotted and contoured, will show an increase in the metal or indicator element content in a certain direction, or that the number of metal-bearing fractures, crenulations, and other discontinuities in the rocks increases toward some favourable geologic structure or zone containing the sought-after deposit.

Groundwaters, circulating along faults or through porous zones, frequently come into contact with deposits, pick up traces of the elements in the deposits, and hence are ideal for sampling and tracing the elements to their source. The sampling part of the technique is a simple matter, especially where springs are present, where a grid of drill holes is available, or where the waters flow from faults or fractures into underground workings. The difficult part is in tracing the dispersion train in the groundwater system. To solve this problem a knowledge of the hydrologic gradient is imperative, and this can be obtained only after a thorough study of the topography and geologic structure. Certain geophysical methods may be useful in some cases, and radiotracers and dyes may assist where a sufficient number of drill holes are available. All of these techniques are relatively undeveloped and require considerable research before they can be placed on a practical basis.

4. Development of methods to outline primary haloes:

The form and intensity of secondary dispersion haloes in glacial overburden soils, waters, stream sediments, and vegetation has received much attention, and our knowledge of these is increasing rapidly. The same cannot be said for primary haloes probably because the phenomena involved are much more complex.

It is evident that each type of mineral deposit has its own characteristic primary halo, a feature that depends on a number of geological and chemical factors, including primarily the type of host rock, the degree of fracturing of the host rocks, and the porosity and permability of the host rocks. As can be seen the parameters are multiple, and a knowledge of the primary haloes in one geological setting may not apply without modification to another.

To establish a basis for practical prospecting utilizing primary haloes the following research is desirable:

1. Determine in as many geological situations as possible the shape and extent of the characteristic primary trace element haloes associated with specific types of mineral deposits, viz. lead-zinc deposits in carbonate rocks; massive sulphide deposits in volcanic terranes; layered deposits in sedimentary rocks; gold deposits in sedimentary and in volcanic rocks; pegmatites; etc.

2. Determine the lateral and vertical extent of leakage haloes or trains of the primary elemental constituents of deposits along faults, fractures, or porous zones. Particularly important in this research is the determination of the distances through which the more volatile constituents such as traces of mercury, arsenic, and antimony have migrated laterally and vertically from the main focus of mineralization.

5. Elucidation and formulation of techniques to relate the size and trace element intensity of haloes and dispersion trains to grade of deposits:

Everyone who finds a geochemical anomaly either of a primary or secondary nature asks himself the questions - Is the anomaly related to a deposit of ore grade, is it caused by disseminated minerals not of ore grade, or is it the result of an enriching chemical process entirely unrelated to primary mineralization processes?

These three questions can only be answered by detailed studies of case histories over the years. In this work a knowledge of the overall grade and constitution of the deposits, the types of enclosing rocks, the depth of overburden, weathering characteristics, the chemistry of the overlying soils and other types of overburden, the chemistry of the groundwaters and stream sediments, and the chemistry of the uptake of the constituent elements in the deposits by vegetation are imperative. Since so many interacting variables are involved it is obvious that statistical studies and computer programs will have to be employed before precise relationships appear.

6. Development and refinement of biogeochemical methods:

Geochemical methods utilizing the analysis of plant ash have been extant for a number of years and have proven successful in a number of cases. It is now imperative to expand research in biogeochemical methods and experiment with indicator plants as well as investigate the toxic and dwarfing effects that metals and non-metals have on plants in the vicinity of ore deposits. In this work the services of trained botanists, especially plant physiologists, will be required, since the work is highly specialized. The results to be obtained from detailed studies of the distribution and population of indicator plants and growth stimulating, toxic, and dwarfing effects promises to be very fruitful indeed for geochemical prospecting, judging from the small amount of research that has been done up to the present in this field. Another interesting approach is that of utilizing microbiological techniques. Work of this type, particularly on bacteria that flourish in the soils and rocks in the vicinity of oil fields, has been done in U.S.S.R. Little, if any, research of this type has been carried out on soils and rocks in the vicinity of sulphide deposits, yet we know from some published studies that sulphur and other types of bacteria and algae frequent such an environment. Studies based on population counts of such bacteria in the soils and rocks in the vicinity of sulphide and other types of deposits could be rewarding.

7. Delineation of the nature and extent of geochemical and biogeochemical haloes associated with oil and gas fields:

Despite its obvious importance, geochemical prospecting for accumulations of petroleum and natural gas has not been extensively employed. This situation has been further complicated by a number of controversies that have arisen through the years with respect to the effectiveness of the methods. The only way to resolve these differences is by further research.

It is evident from our present knowledge that many oil and gas fields are marked by macro-seeps along faults or through porous zones. It is logical to suppose from this data that there are also micro-seeps which should be detectable by the modern methods of hydrocarbon analyses, especially gas chromatography.

The distribution of micro-seeps in the rocks and overburden constitutes the dispersion haloes of the natural hydrocarbons from oil or gas accumulations. Unfortunately our knowledge of these haloes, especially their areal and spatial distribution and their intensity with respect to distance from oil and gas accumulations is not well known and requires very careful detailed study as a basis for geochemical prospecting. A few well defined oil and gas fields should be selected and the distribution of the hydrocarbons in the rocks, waters, and overburden studied in the minutest detail to determine their primary and secondary dispersion characteristics. Work already done along this line in a number of countries suggests that the haloes are quite distinct and have a high contrast in some cases, and that the dispersion of the gaseous hydrocarbons is detectable many thousands of feet above large gas and oil fields. Certain trace elements may also be enriched in these haloes, although relatively little is known about their precise distribution. These findings should spur on petroleum geochemists to seek further knowledge about the gaseous and trace element haloes and their effective use in prospecting.

Another interesting approach in petroleum prospecting is based on population counts of micro-flora and fauna which oxidize hydrocarbons, particularly propane, during their metabolic processes. Where soils, rocks, and groundwaters are enriched in hydrocarbons, certain strains of bacteria and perhaps other forms of lowly life flourish, and their density of population is apparently proportional to the content of hydrocarbons present. By utilizing specialized bacterial counting techniques it is possible, as a number of geochemists in U.S.S.R. have shown, to plot contour maps showing the distribution of the bacteria and, hence, hydrocarbons. Some of these contour maps show peaks and haloes that mark accumulations of oil and gas at depth. This promising biogeochemical exploration method is worthy of considerable research in conjunction with gas analysis, water analysis, and trace element studies.

CONCLUSIONS

Prospecting methods using chemical and biological techniques have been applied since early times, and today are assuming an ever increasing importance in the search for mineral deposits. Their effectiveness has been proven in many geological terranes and under a variety of climatic conditions. In the past few years they have directly or indirectly led to the discovery of a variety of mineral deposits in a number of countries.

To improve the effectiveness of the methods further detailed research on the nature and morphology of primary and secondary haloes is imperative. The methods now available should be sharpened for detection of large low grade deposits and for deposits buried by considerable thicknesses of overburden or lying deep in the rocks. Finally, more detailed research in geochemical prospecting methods for detecting accumulations of oil and natural gas is warranted.

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GEOCHEMICAL PROSPECTING BY THE GEOLOGICAL SURVEY OF SWEDEN

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For many years the Geological Survey of Sweden (SGU) has been active in prospecting for ore deposits in the northernmost parts of the country (cf. Lindbergson, 1963). This activity embraces all phases of prospecting and ranges from regional geological surveys and airborne geophysics to detailed geological and geophysical investigations and it also includes the final drilling. Since 1963 geochemical work has been a regular part of this activity. Before this, considerable experimental work on soils and plant material near known mineralization was carried out by B. Dahlman, K. Fredriksson (1966), S. Landergren (1957) and P.H. Lundegårdh (1956), but the following report confines itself to the main aspects of the present work.

The present work may perhaps be best indicated by quoting some figures. Last year (June 1965 - June 1966) approximately 15,000 sediment samples and 3,000 soil samples were collected. In addition about 1,000 rock samples from drill-cores were analyzed for trace elements in a study of primary dispersions. A few hundred samples of plant material were also collected for experimental studies. In the present (1966) field season the number of stream sediments will be about the same, whereas the soil samples will increase to about 8,000. The number of rock-samples will also increase, the final figure depending on the capacity of the analytical lab. Our biosampling has not yet passed the experimental stage and will therefore remain limited.

The geochemical staff of the Survey is composed of three geochemists and two technicians. Their work comprises the lay-out of geochemical prospecting projects, supervision of field work and the recording and interpretation of the results, mainly in support of mineralogical and Pleistocene geology work. During the field season about 25 men are temporarily hired for the sampling operations; most of these are high school students or inexperienced geology students from the universities.

The analytical work, as well as the sample preparation, is done by the laboratory staff of the Survey. Routine analysis is made by a quantometer using the tape method. For this technique the different types of samples require different pretreatment: soils are sieved to minus 100 microns, stream sediments are finely ground in a swing mill after initial sieving to minus 2 mm, rocks require a similar grinding and special buffering. When extra sensitivity is needed, chemical pretreatment (sulfide-isoformation) may be employed.

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In studies of primary dispersions rocks are generally analyzed for 20-25 elements, but in routine work with soils and stream sediments only the following elements are recorded: Cu, Zn, Pb, Ni, Co, Mo, W, Sn, Bi, As, Ca, Ti and Fe. Of these Ca, Ti and Fe are required for background corrections but they also indicate the general nature of the analyzed sample. For Mo, W, Sn, Bi and As the sensitivity obtained restricts the usefulness to strongly anomalous samples.

Before these procedures had been developed and adequately tested (Brotzen and Danielsson, 1963), field analysis was made at the camp-site, using semiquantitative spot-tests for Cu, Ni and Zn on solutions obtained after 20 hours cold leaching in strong nitric acid. With the present analytical facilities this work appears superfluous. To maintain reasonable control of the soil-sampling projects the current production (100 samples/day) of the laboratory matches approximately the rate of soil-sampling, so that the sampling teams receive the analytical data two weeks after collecting the samples. Analysis of the stream sediments, on the other hand, is postponed till after the field season, since analytical control is not essential in such sampling programs. The follow-up of anomalous stream-sections is done most conveniently in a following year, when a complete picture of all the stream work permits a better selection of promising targets and therefore a better planning of the work.

Regarding the general planning and lay-out of geochemical prospecting work, procedures vary according to the nature of the projects. Most stream sediment surveys cover areas where traces of mineralization, especially glacially transported ore-boulders, are known to occur, or where the geological conditions are, in a general way, thought to be favourable for mineralization. These areas are also selected to fit into the plans of geological work going on in the district, which makes possible close contact with the geologist in charge. Quite generally stream surveys are employed as a means of regional reconnaissance at moderate cost and with an accepted incomplete coverage.

The detailed procedures of stream surveys follow a few simple rules. Samples are taken of the active sediments, at intervals of 200-300 m, and all streams in the area are sampled and followed into their smallest branches. Notes are taken regarding the width and flow-rate of the stream, and the nature of the sediment. No geological notes are taken. Though silty, inorganic samples are preferred, no restrictions are imposed in this respect. It is thought better to have a sample of low quality, rich in organic mud, from the swampy stream, or a very coarse grained sample from a mountain rapid, than no sample at all.

The given sampling interval results in a mean density of about 7 samples per square kilometer, but this figure varies greatly with the topography. Stream anomalies often persist for about 1 kilometer, which means that more than two consecutive samples are anomalous, which minimizes the need for resampling to eliminate spurious results.

Projects of soil sampling, on the other hand, require detailed planning in close collaboration with the geologist in charge of the area. Due to the higher costs soil surveys usually cover an area of a few square kilometers, which occasionally may increase to the order of ten. They often mark a stage in prospecting when the detailed geological and geophysical investigations have been completed and they are then used to select drilling objects. Such surveys are often made on the request of the geologist in charge of a project, or alternatively they represent follow-up work related to a stream anomaly. Relatively open grid surveys are also employed as a method for local reconnaissance in areas where the bedrock geology remains incompletely known due to extensive overburden and where the geophysical indications are weak or difficult to interpret.

The detailed planning of soil surveys is preceded by a rapid assessment of the Pleistocene geology of the area. This is based on an inspection of air photographs and (or) brief field trips. Special attention is given to evidence of the direction of glacial transport and whether this was simple or complex. Other important observations concern the presence and thickness of moraine, the details of the soil profile and the extent of late- or postglacial sands or clays, which do not, generally, justify geochemical soil sampling of the present type. In complex areas special Pleistocene research has to be carried out concurrently with the soil sampling.

The usual sampling pattern is a rectangular grid with fixed intervals of the order of 50 m, although this may vary by a factor of two according to conditions. In special cases, however, traverse lines may be separated by as much as 500 m, but application of this type of reconnaissance work is often limited by the conditions of Pleistocene geology. An example of such limitations is given below. Regarding, finally, the depth of sampling, this is determined by the soil profile. Quite generally podsol profiles prevail, and sample of the B- and C-horizons are accepted for analysis, whereas samples from the A-horizon are rejected. This implies a normal sampling depth of 50-70 cm. In swampy areas samples are taken from the top mineral soils below the peat. In routine work, sampling of swamps to a depth of 2.5 m is easily accomplished. It is fortunate that peat bogs do not exceed this depth very often in the northern prospecting areas.

Our experience of biogeochemistry and the sampling of drill-cores for primary dispersions is too limited to allow adoption of standardized sampling patterns. In investigations of drill cores from known ore-deposits, which are being undertaken as a preliminary step in the application of such work to actual prospecting, three different sampling intervals are now being used.

Ten samples on each side of the ore-body are taken at intervals of 3.0 m; beyond this follow ten samples at intervals of 10 m, and at still greater distance from the ore, intervals are increased to 30 m. Each sample is a composite of three or five 10 cm long sections of the split core taken at regular intervals of 1.0, 2.0 and 6.0 m respectively. If mineralization occurs at more than one depth in the hole, the pattern has to be changed accordingly. Likewise, when strong changes occur in the lithology of the core it is necessary that each composite sample represents only a single rock-unit. The illustrations of primary dispersion patterns shown below represent a much closer sampling, and it is experience from this work which forms the basis for the present sampling procedure. It is hoped that similar procedures can eventually be applied to actual prospecting in the drilling for blind ore-bodies and lead to a better utilization of already available drill-cores. It is a time-honoured and established practice of Swedish prospecting parties to file all drill-cores, which is done at an insignificant fraction of the money required for the actual drilling. It seems reasonable to expect that modern geochemical techniques may prove some of the abandoned, subeconomic mineralization encountered in earlier drilling operations do develop into commercial ore-bodies in depth or laterally.

The information given above clearly shows that the bulk of the geochemical prospecting at the SGU represents standard operations which contain very little research and do not merit further comment before a more complete regional picture has evolved. In working out the routine procedures, and also when facing special problems of interpretation, or when local conditions are met which can lead to a better understanding of fundamental aspects, orientation surveys and special investigations are made, which may be of greater interest. Three examples of such work will therefore be given. They relate to the study of stream sediments, to the metal distribution in till and to the metal distributions in the wall-rocks around two pyritic ore-bodies.

A survey of stream sediments has been made in an area around the sulfide deposits of Stekenjokk in the Caledonian mountains of Sweden. Three major anomalies were found, two of which were clearly related to the known deposits, whereas the third represents an unknown source.

The Stekenjokk area, at 65°N, 14°30E, and an elevation of 700-1100 m, lies above the local tree-limit, and has tundra-like vegetation and a sub-arctic climate. No permafrost occurs and the field-season lasts about two months of the year. Landforms are open and rounded, slopes are moderate. Podsol profiles prevail except in swamps. Glacial transport has been extremely complex, see Svensson (1959). The bedrock is predominantly made up of pelites of the greenschist facies, with intercalated graphitic beds and basic and keratophyric flows and tuffites. Metagabbro and limestone occur locally. All rocks were strongly deformed during the Caledonian orogeny. Mineralization comprises two major pyritic ore-bodies, with chalcopyrite, sphalerite and traces of galena, and a great number of minor sulfide occurences.

The streams in the area are numerous but small, and only two of them reach 20 m in width. They are generally shallow, swift-flowing clear waters. Stream sediments are mostly gravelly sands, showing only weak discoloration. The frequency distribution of metal contents, as determined colorimetrically after leaching 30 min. in 1:1 HCl at 100°C, on fractions minus 300 micron, is shown in Fig. 1 and 2. The metal anomalies in the area are of two genetically different types. At one extreme, a clastic origin can be clearly established by the occurrence of sulfide grains as seen in the microscope. At the other extreme, no ore-grains can be observed and the anomaly must be formed by a chemical dissolution-precipitation process. The first type represents a case where the (sub)outcrop of the ore is near the stream whose course more or less coincides with the predominant direction of glacial transport. The other type again signifies a greater distance to the source and a building up of the anomaly through seepage processes.

In an earlier study (Brotzen, 1966) the relationship between the heavy metals and iron and manganese was investigated, and the same close correlation found then between zinc, in particular, and iron, could be established in the present samples (Fig. 4). The present investigation also showed that this correlation is greater for total (extractable) iron than for the content of either ferric or ferrous iron alone.

The role of pH, grain size, volume weight and content of organic matter were further investigated in the present study.. The variation of Zn and Cu with pH in samples of two different iron contents is illustrated in Fig. 5. The pH was determined electrically on suspensions of the samples in distilled water. Cu is seen to be essentially insensitive to variations in pH within the observed range, whereas 2n shown a certain tendency to be higher in samples with a higher pH. It should be noted, however, that the higher samples also show a higher Fe-content, and this rather than a direct effect of the pH, may be the deciding factor in the fixation of zinc. At least it may be suggested that consideration of the Zn:Fe ratio in stream sediments of this type largely eliminates the need for separate determinations of pH. This ratio appears to be a better parameter for prospecting than the zinc content alone. In fact many zinc anomalies have, in our work, proved to be false, and related not to mineralization but to locally strong iron precipitation in the stream sediments. In this connection it may also be pointed out that actual determination of the forms in which the metals occur in the sediments is necessary before geochemically valid Eh and pH diagrams can be constructed.

Some of the other results are summarized in Fig. 6. Here the bottom row gives the numbering of the samples. The next row shows the weight percentage of four size-fractions, namely 0.6-0.3; 0.3-0.15; 0.15-0.06 and minus 0.06 mm, with the coarse fraction to the left. It is seen that the sediments are of different types, some being dominantly coarse-grained (e.g. 564, 585), while in others the fine fractions are predominant (e.g. 522 and 584). The next row shows the volume-weight (dry) of the individual fractions, expressed in grams per cubic cm. A tendency for lower volume-weights in the fine fractions is obvious. The following row shows the content of organic matter determined spectrophotometrically as the extinction at 5000 A in the acid extract from the individual size fractions. At this wave-length the contribution from $FeCl_3$ to the extinction of the solutions is negligible (Fig. 7). Comparison with the lower rows shows that a high content of organic matter tends to lower the volume-weight of the sample, and that organic matter is generally concentrated in the finer fractions. The following four rows show the contents of Fe, Pb, Cu and Zn on a weight to volume basis. Together with the lower rows they demonstrate that the metal contents in these samples are rather insensitive to variations in grain size, volume-weight and the content of organic matter. The first of these observations indicates that it is not necessary to select some very fine fraction, such as minus 80 mesh, for analysis, which would require tedious sieving and large samples of coarse-grained sediments. It is also of some theoretical interest, because it shows that the fixation of the metals is not strictly a surface effect, or that the influence of the far greater surface of the finer fractions is almost exactly counteracted by some other factor. This factor may be the resting-time of the individual particles. Obviously the coarser particles on the average will stay longer in the metal-bearing environment, and thus be able to collect more of the dissolved metals than the smaller ones, which are sooner swept along with the stream. This again is an inverse function of the total surface of the individual particle (Stoke's law).

The relative constancy of the metal contents in the different size fractions of one and the same sample, if expressed on a weight-to-volume basis, shows that this is a better form than the normal weight-to-weight basis, considering the lower density of the finer fractions. This actually speaks in favour of scooping the samples for analysis, rather than weighing them. The insensitivity of the metal contents to variations of organic matter in the samples from our area strongly differs from the findings of Govett (1960) for tropical streams.

The samples represented in Fig. 6 are taken out of a total crop of about 600 samples. To illustrate the down-stream variation in a single anomaly, related to the main Stekenjokk ore, Figs. 8 and 9 are given. They show the variation in Cu-content and the Zn:Fe ratio in the same size-fractions as before, and again indicate that nothing is gained by selecting the finer fractions for analysis. It is also seen that the Cu-contents decrease faster in the down-stream direction than does the Zn:Fe ratio.

So far this represents early colorimetric data collected by the geochemist. Fig. 10 represents some quantometer data from the same anomaly, although these samples were collected two years later, and the curves now represent total metal contents. This time the size-fractions, from left to right are 20-6 mm, 6-2 mm; 2-0.5 mm; 0.5-0.2 mm; 0.2-0.06 mm and minus 0.06 mm. (In some samples the coarsest of these fractions was missing.) It may be noted that the metal contents thus determined are comparable to those found earlier in spite of the difference in the time of collecting, and also that the general shape of the anomaly remains the same. The similarity in the variations with grain-size of Fe and Zn in some of the samples likewise is striking, whereas Ca, which is one of the controls of pH, shows a variation of its own. These data also show that even the grain-sizes above 0.5 mm and up to 2 mm may be taken for analysis.

Whereas the anomaly described is partly of the clastic type, Fig. 11 shows the corresponding data for a strictly chemical anomaly. It is seen that the chemical features are essentially the same in the two anomalies. Here, as in many other cases, microscopic evidence proves to be of great diagnostic value.

The special investigation of the distribution of ore metals in till over a known ore body was undertaken because a fairly extensive geochemical orientation survey had largely failed to reflect even the known occurences of ore in a central part of the foremost sulfide-mining district of Sweden. Furthermore, this corresponds to earlier negative experience in the same district by a private mining company (Brotzen, loc. cit.). It therefore appeared desirable to find the cause of this failure, especially after it was known that stream sediment surveys worked quite well in the same area.

The geology and ores of the area in question, the Malånäs district, have been described in considerable detail by Gavelin (1939). Also the Pleistocene deposits have received close attention, and boulder-trains of sulfide ores played a significant role in early discoveries of a number of ore deposits. Multiple moraines, with clear-cut contacts have been described repeatedly, as by Högbom (1937), Granlund (1943) and Lundqvist (1943). The salient Pleistocene features are two marked directions of glacial transport, namely one from WNW (older) and one from NW (younger). Most of the area was above the postglacial sea-level, and late- and postglacial sediments are restricted to the recent lakes and stream-channels, and their immediate surroundings. Other topographic depressions are occupied by large peat bogs. The country is dominated by extensive forests of fir, pine and birch on typical podsolic soils.

The test-site covers a small, newly discovered sulfide-deposit, Norra Norrliden, with about 1.5% Cu and 5-10% Zn. Its situation and extent are well known from drillholes, which also give a fairly good picture of the sub-surface configuration of the bedrock. Topographically the site is on the northern slope of a WNW-trending valley, and the surface of the bedrock slopes in the same SSW-direction as does the side of the recent valley (Fig. 12).

For a closer investigation of the overburden four testpits were sunk to a depth of 3.0-3.5 m. They revealed practically homogenous moraine, but in one of the pits there appeared, near the bottom, a change into a more clayey and pebble-rich moraine with a slightly pressed appearance. Samples were taken representing continuous 0.5 m sections in all the pits, except where this particular change was noted, where a closer sampling was made at the critical part of the section. All the samples were then submitted for geochemical and grain size analysis, and the petrographic composition of the gravel fraction was further investigated.

Some of the results have been summarized in Fig. 12, which shows a section through the till at Norra Norrliden with a tenfold vertical exaggeration. The true situation of the ore and the test-pits are indicated on this scale, and so are the sampled sections of the pits. The testpits, with 5-fold exaggeration, are again represented as cumulative diagrams of the size distribution in the samples, and on their left sides the relative proportions of three critical size-fractions, namely 20-2 mm, 0.2-0.02 mm and minus 0.006 mm are indicated. On the right side the relative proportions of three critical rock types, namely granites, porphyrites and metavolcanics are indicated in the same fashion. The Cu and Zn contents of the samples are also given in the diagrams.

A number of features seen in this diagram, and corroborated by a statistical evaluation of the complete data, appear significant. Two types of till are present in the section. The upper one is characterized by a high proportion of granitic rocks, and a convex (upward) curve in the cumulative diagrams. This corresponds to a large proportion of the grain sizes between 0.2-0.002 mm and a small proportion of the gravel size fraction (20-2mm). A low content of Cu and Zn may also be noted. The lower till, on the other hand, has a low proportion of granite and a high proportion of metavolcanics. The curve of the cumulative diagram is concave, which corresponds to higher proportions of the gravel- and clay-sized fractions. The metal contents in the lower till are often two to four times as high as those of the upper one.

These features are easily understood in the light of regional geology and what is known about the glacial transport. The local bedrock is made up of metavolcanics, present in the lower till. The granites of the upper till, in contrast, occur at a distance of more than 10 kilometers in the direction of the later glacial transport (NW). Therefore the upper till contains far-transported material, the gravel-sized fractions having been largely milled to fine sizes. The clay-fraction is nevertheless small, reflecting the mineralogical composition of the granitic source-material. This also explains the low metal-content of the upper till, and its inability to reflect mineralization in the local bedrock.

It is interesting to note, however, that there is no clear-cut contact between the two types of till, and also that there is no perfect correlation between the different distinctive features. This may be demonstrated by the fact that all transitions occur between till which is predominantly granitic, and till made up of metavolcanic material. Another example is seen in the third sample (from the top) of the second pit (from the left). Here the size-distribution of the material is typical of the upper till, whereas the petrographic composition of the gravel fraction is more characteristic of the lower till. Even more striking are the conditions in the lower part of the fourth pit. Here the deepest sample clearly represents the upper type, as can be seen from the convex cumulative curve, the high proportion of granitic rocks and the low metal-contents. Nevertheless it is overlain by a section of the "lower" till, as is evident from the concave curve, the lower proportion of granites and the higher contents of Cu and Zn in the next sample. In this case the complete array of our criteria obviously contradict the actual stratigraphic situation. Furthermore, the next sample (third from the bottom) shows some influence from the local bedrock in its higher Zn content.

All these apparent irregularities show that there has been no normal superposition of a younger till carrying far-transported material upon a bed of older till of local derivation, as has been observed in many places elsewhere in the district. The conditions instead indicate an irregular mixing of the two deposits and even an injection of wedges or lenses of the lower bed of till into the upper one (in the fourth pit). This appears to be related to the topographic situation of the test-site, which occupies a lee-side position in relation to the latest direction of glacial transport.

From the standpoint of geochemical prospecting, this study leads to the following conclusions:

1) Close attention must be given to Pleistocene deposits before launching large soil-sampling projects in areas with glacial soils. This pertains especially to areas where more than one direction of glacial transport has prevailed.

2) Topography plays an important and special role in the formation of secondary dispersions in glacial soils, and in certain respects differs from that in residual soils.

3) The fixing of a general threshold value, such as two- or three times the normal background, as an aid to distinguishing local geochemical anomalies may be misleading. In the present case the known ore-body would certainly have escaped discovery. Likewise, the application of regional continuous trend-surfaces appears inadvisable, because local domains with their own background values are not easily treated in this way. A promising technique involves the comparison of two rolling averages, one representing a small number (5-10) and the other a larger number (30-100) of sample-points.

4) An effective and inexpensive technique for the deep sampling of till is greatly needed.

5) The wider application of biogeochemistry should be further investigated, in the hope that the plants have done the deep sampling for us. Bio-samples were also collected in this study.

The last example of geochemical prospecting by the SGU deals with a study of the primary dispersion of trace elements in the wallrocks around two known ore-bodies. Some of the background for this special work was indicated above. Here it may be added that this work, which was considered earlier at the planning stage of the present geochemical group, has received considerable encouragement from positive reports by geochemists in the USSR (Yanishevsky, 1965).

These reports demonstrate that the ore-elements arrange themselves in a fairly regular pattern around the ores, and this has, in a number of cases, led to the discovery of blind ore-bodies at considerable depths (up to 300 m). Examples given refer mainly to steeply dipping deposits. The two cases described here instead represent flat-lying deposits of solid pyritic ore with chalco-pyrite and sphalerite. One is the main Stekenjokk ore, which is a pencil-shaped body of more than 2 kilometers length occupying a complex structural position in strongly deformed Caledonian rocks, and itself also showing clear evidence of deformation. The other is the Rudtjebäcken ore in the Adak district (Gavelin, 1948), which represents a concordant flat-lying body in a cupola-shaped Precambrian rock sequence. Geological criteria regarding the age-relations show that mineralization in the Adak area, where also cross-cutting vein deposits occur, is definitely epigenetic, and probably post-dates the major folding. In the present study it was found that marked differences exist in the distribution of trace-elements around these two ores.

A longitudal section, with a two-fold vertical exaggeration, through the ore-body at Stekenjokk is seen in Fig. 13, and illustrates the rock types and the variation of some of the elements genetically related to the ore. Co is, however, a lithogene element shown for reference. The introduction of ore-elements into the wallrocks does not reach far from the ore-body at shallow depths, and it is interesting to note that the dispersion extends further in the black, apparently impermeable, shale in hole 59002, than in the meta-keratophyre of hole 60002. In the deeper hole, however, the dispersion of ore-elements reaches about 80 m above the ore, which corresponds very closely to the visible hydrothermal alteration of these rocks. The direct prospecting value of trace element studies, therefore, in this case appears to be limited. It may be noted, however, that the As-halo found near the ore is absent around a subeconomic Cu mineralization, which occurs well above the ore, and which otherwise shows a similar picture of the trace elements. This difference, if consistent in the area, may be helpful in the evaluation of exploratory drilling. The As-halo at Stekenjokk furthermore is noteworthy because the As content of the ore itself is rather low and only around 0.1 %.

A more hopeful picture was obtained at Rudtjebacken. A longitudal section through this deposit, without vertical exaggeration, is seen in Fig. 14. The Rudtjebacken deposit does not actually reach the surface of the bedrock, but its position is clearly marked in the continuation of the ore-bearing strata, as seen in Bh 3. This strata-bound projection of the ore was most certainly very extensive before erosion. Such strata-bound dispersion therefore should reveal similar ore at a considerable distance both horizontally and vertically. Also in the other drillholes a greater dispersion of the ore-metals is found than was the case at Stekenjokk. Most striking is the great vertical extent of the As-halo, which reaches the surface even from the ore at the 250 m level. Here again the ore itself is low in arsenic, but a nearby deposit has portions of solid arsenopyrite. At present it is not known whether the high As content at the surface reflects the localized mineralization of the orebody, or if it is associated with the entire area of mineralization, which is of the stratabound type and includes large portions of subeconomic mineralization. Actually the entire Skellefte district, of which the Adak area may constitute an outlying part, is a markedly As-rich metallogenic province. If therefore the great vertical extension of the As-halo around ore-bodies is repeated elsewhere this might provide a most powerful tool in prospecting for blind ore-bodies.

The present study of primary dispersion is only a beginning, and it shows very clearly that considerable variation occurs in the distribution of trace-elements in the wallrocks of ore-bodies, even if rather similar ores are involved. Much remains to be learned and continued research in this field is obviously necessary before our knowledge will permit any useful application, but interesting aspects already emerge. Above all there is the behaviour of arsenic, which inspires further investigations, primarly in the Adak area. It also calls for special work to improve our analytical methods for this element.

Acknowledgements: We are indebted to Mr. K.A. Lindbergson, Director of the Geological Survey of Sweden, for permission to publish this report, and to Dr. G. Kautsky, head of the Department of Ore Investigation, for his support of this work through all its phases. Special thanks are due to Dr. P. Padget, who kindly corrected the English of the report.

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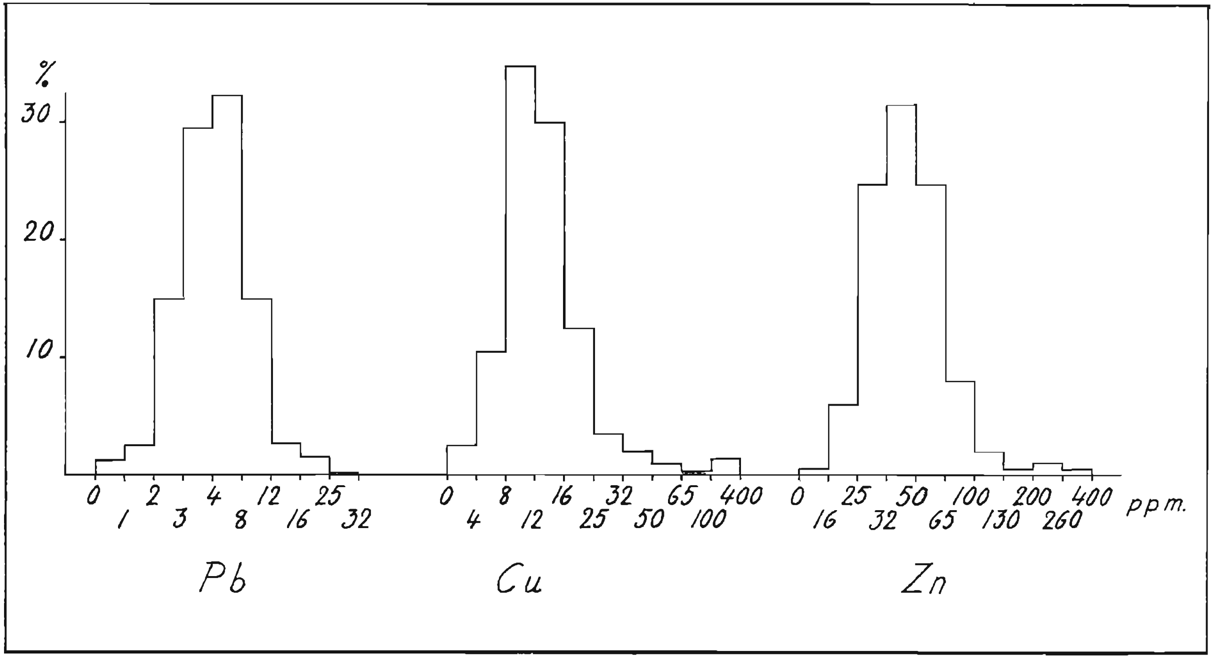


Figure 1. Frequency distributions of metal contents in 530 stream sediments from the Stekenjokk area. Lead values may be systematically low by a factor of 2. Determinations by biquinoline and dithizone upon leaching 30 min. in hot HCl.

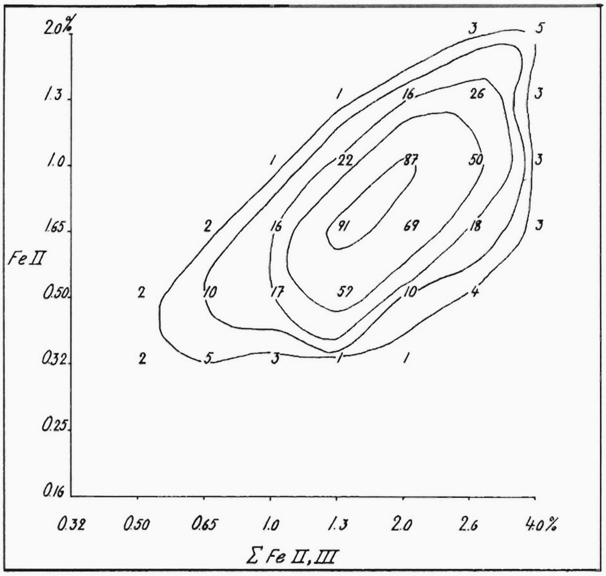


Figure 2.
Frequency distribution of ferrous and total (hot HCl-extractable) iron in 530 stream sediments from the Stekenjokk area. Determinations by orthophenantroline, total iron after reduction with ascorbic acid.

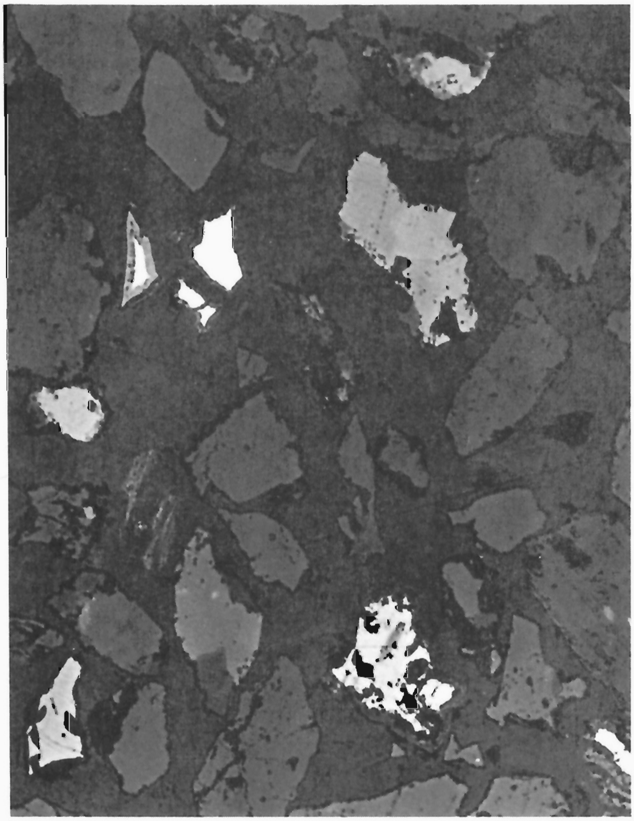


Figure 3.
Sulfide grains, (bright) Fe-Ti oxides (gray) and silicates (dark), in heavy fraction (+ 2.96) of stream sediment from the clastic anomaly caused by the Stekenjokk ore. Polished section of size-fraction 100-200 microns.

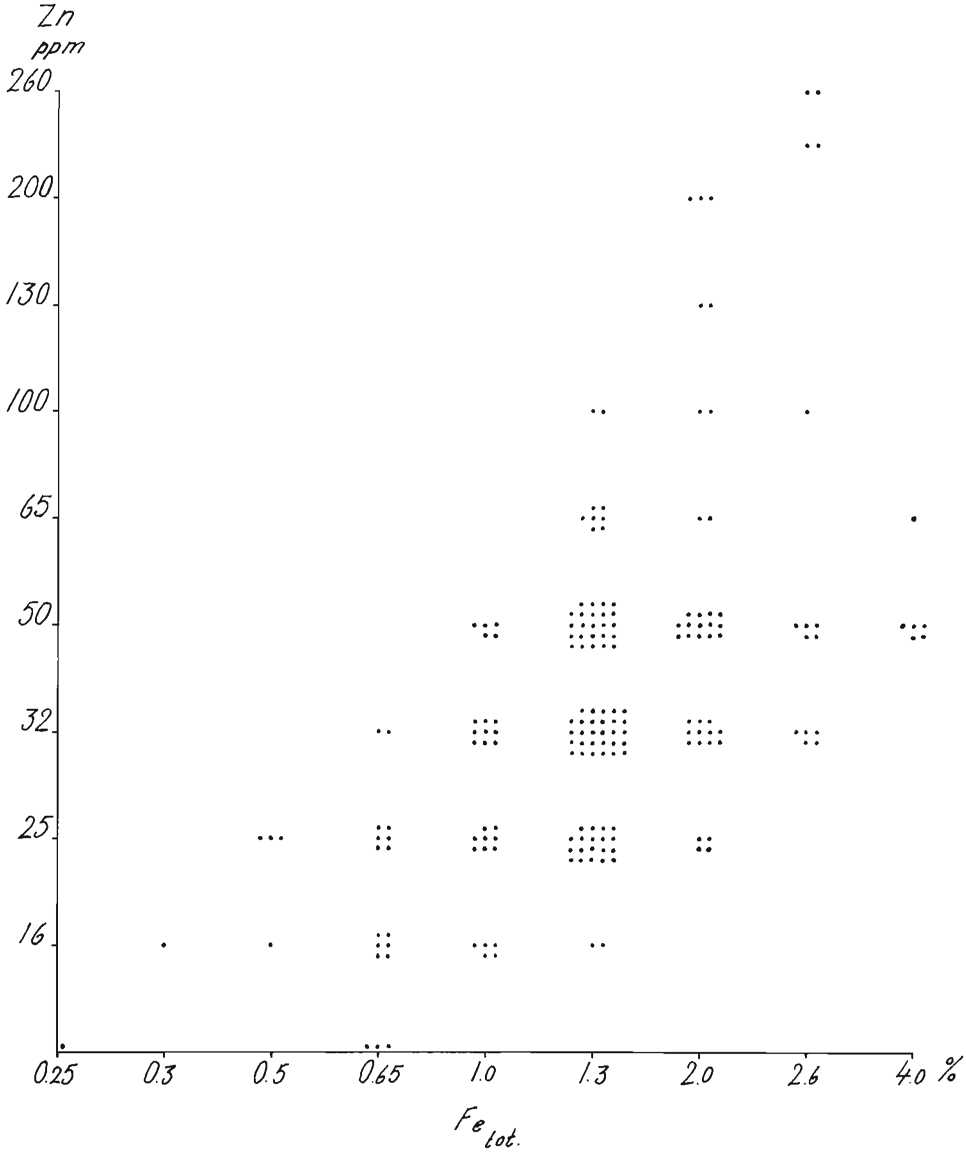


Figure 4. Content of Zn versus Fe in stream sediments from the Stekenjokk area. Colorimetric data.

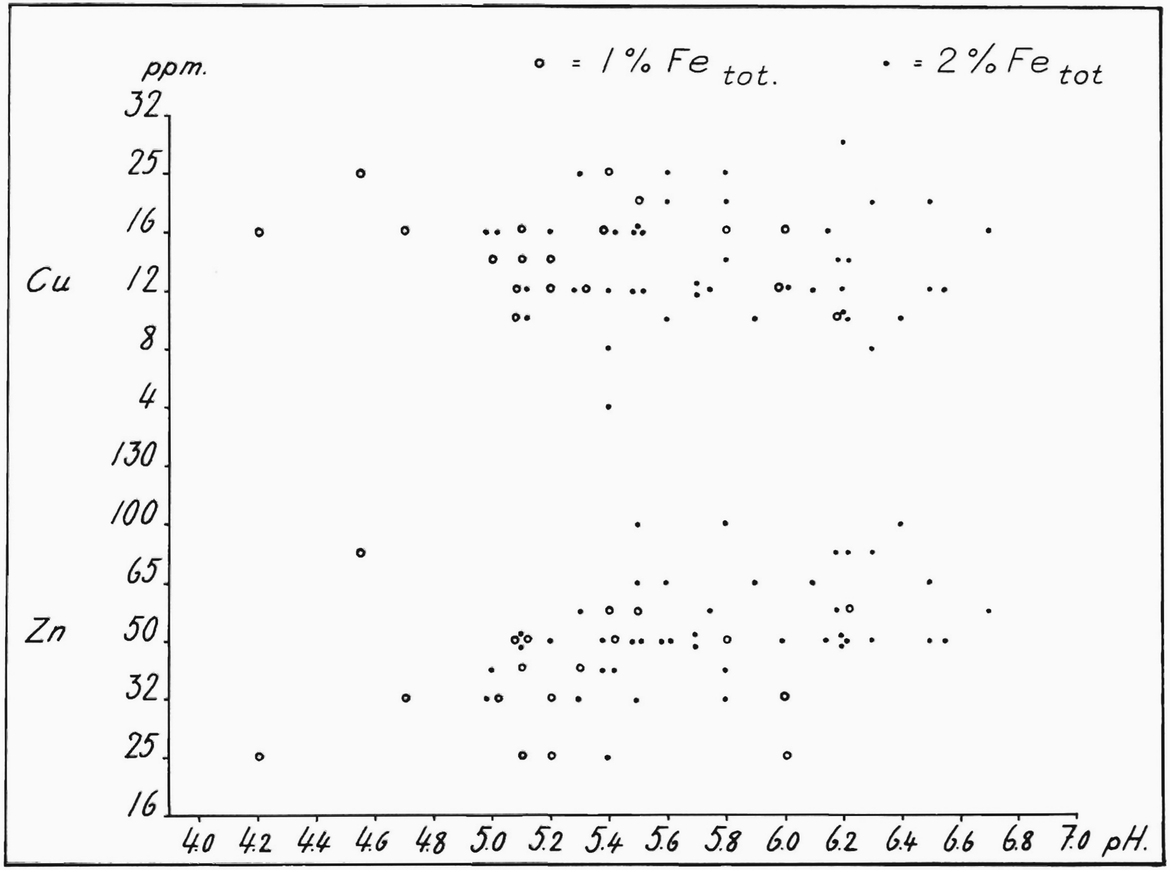


Figure 5. Relationship between Zn, Cu and pH for two different iron contents in stream sediments from the Stekenjokk area.

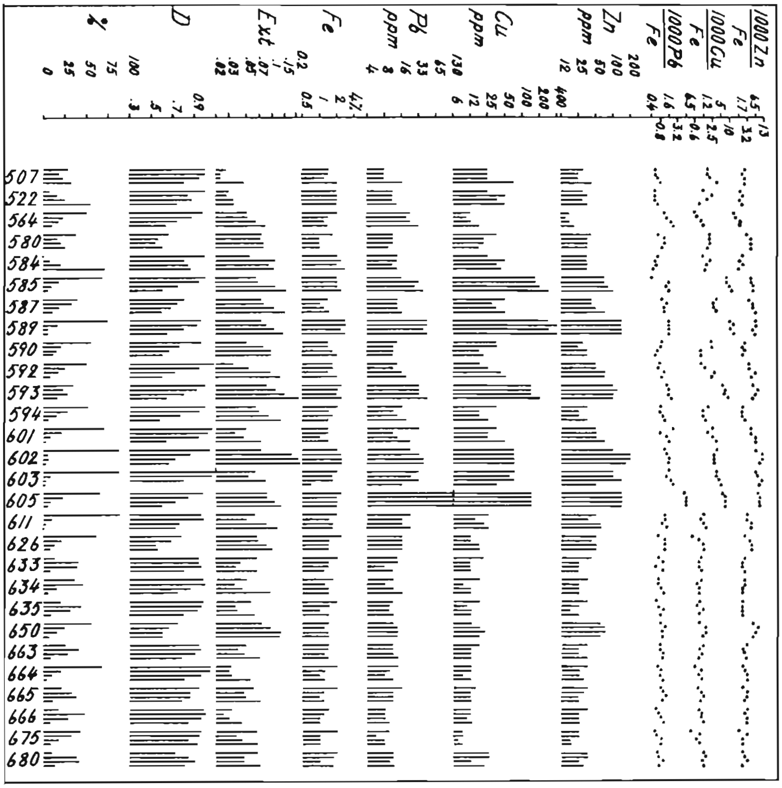


Figure 6. Weight proportion, volume weight (D), content of organic matter (Ext), Fe, Cu, Zn and Pb in the size classes 0.6-0.3; 0.3-0.15; 0.15-0.06 and minus 0.06 mm of some stream sediments from the Stekenjokk area.

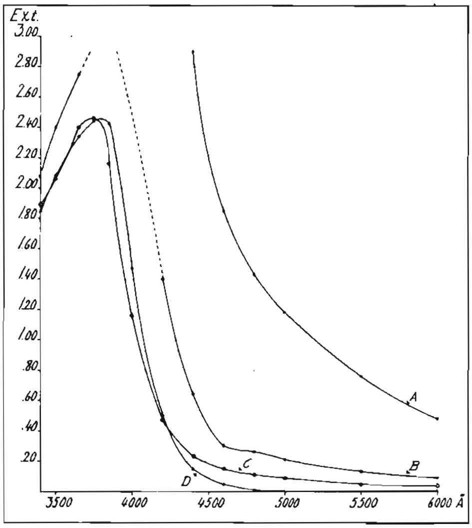


Figure 7. Extinction curves of acid extracts of three stream sediments (A, B, and C) and of a solution of ferric chloride in 1:16 HCl (D) corresponding to a Fe content of 1% in the samples.

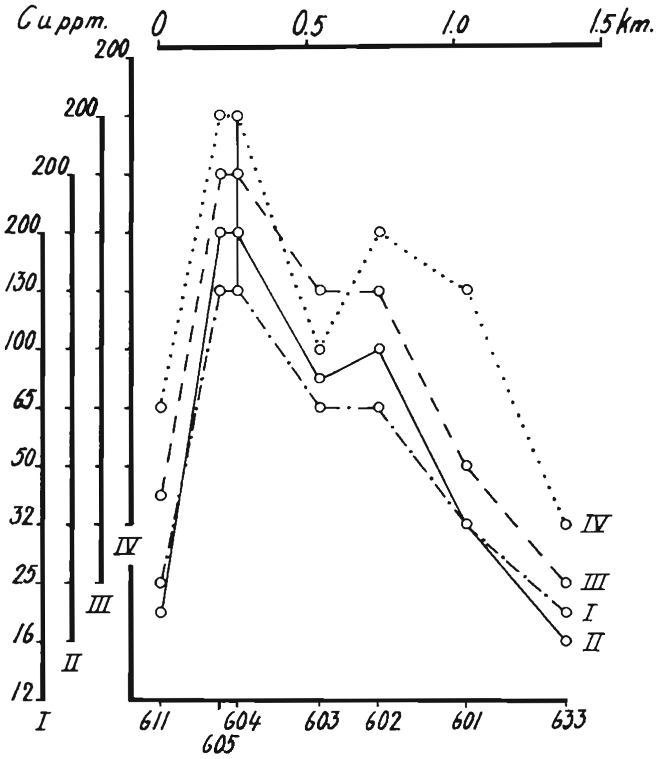


Figure 8.
Cu-contents in the size-classes I: 0.6-0.3; II: 0.3-0.15; III: 0.15-0.06 and IV: minus 0.06 mm in stream sediments constituting the clastic anomaly caused by the Stekenjokk ore. This is situated between sampling stations 611 and 605. Direction of flow is from left to right.

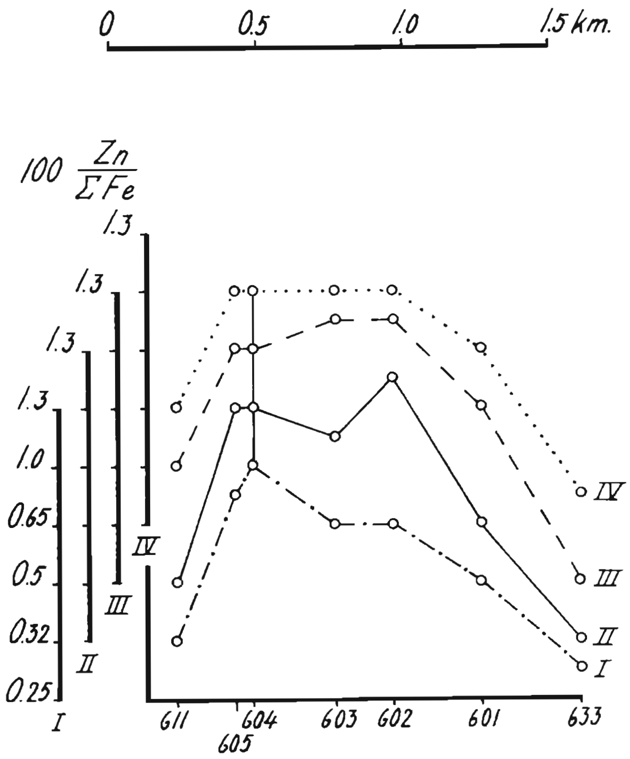


Figure 9.
Zn:fe ratios in the same samples as represented in Figure 8.

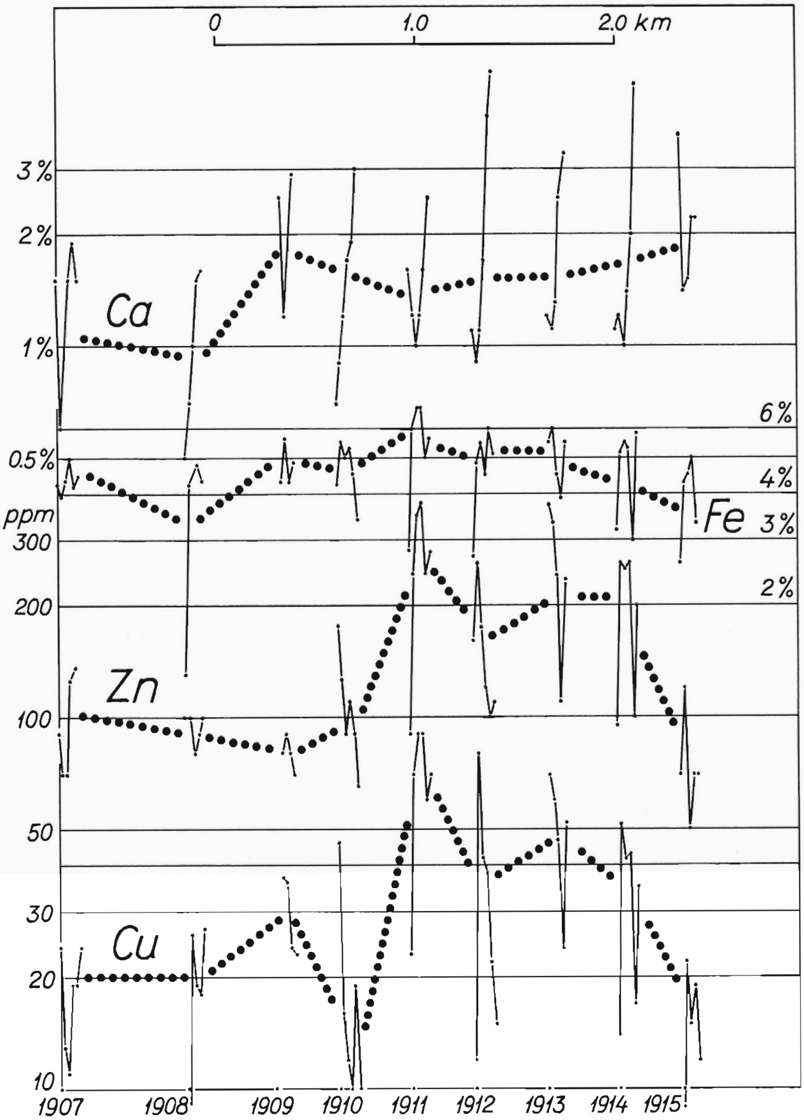


Figure 10. Metal contents in different size classes of stream sediments constituting the clastic anomaly caused by the Stekenjokk ore, cf. Fig. 8. Spectrographic determinations. Size classes for each sampling station are, from the left, 20-6; 6-2; 2-0.5; 0.5-0.2; 0.2-0.06 and minus 0.06 mm. Note the faster downstream (from left to right) decrease in Cu as compared to Zn, and also the general similarity in the variation with grain size of Cu, Zn and Fe at some sampling stations. The orebody is situated upstream between stations 1910 and 1911.

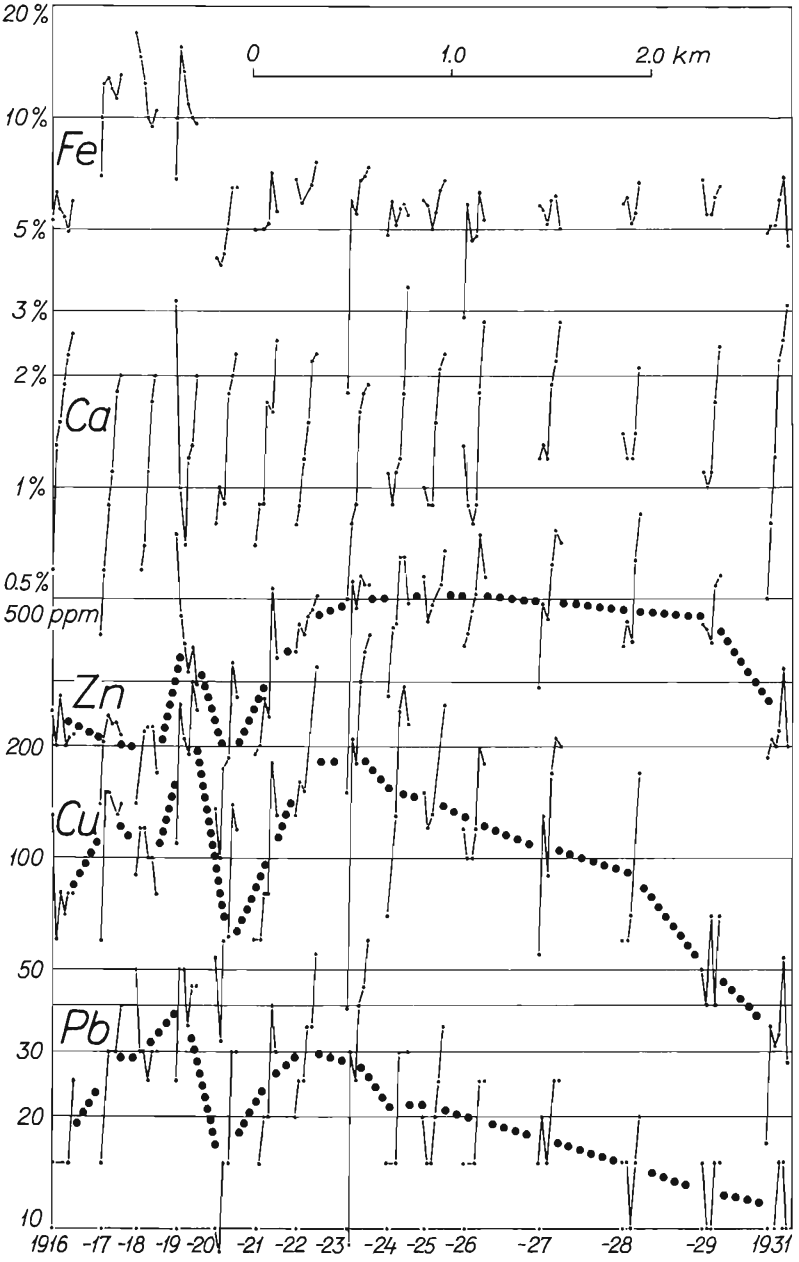


Figure 11. Metal contents in stream sediments constituting a hydromorphic anomaly caused by an unidentified source. Size classes are the same as in Fig. 10.

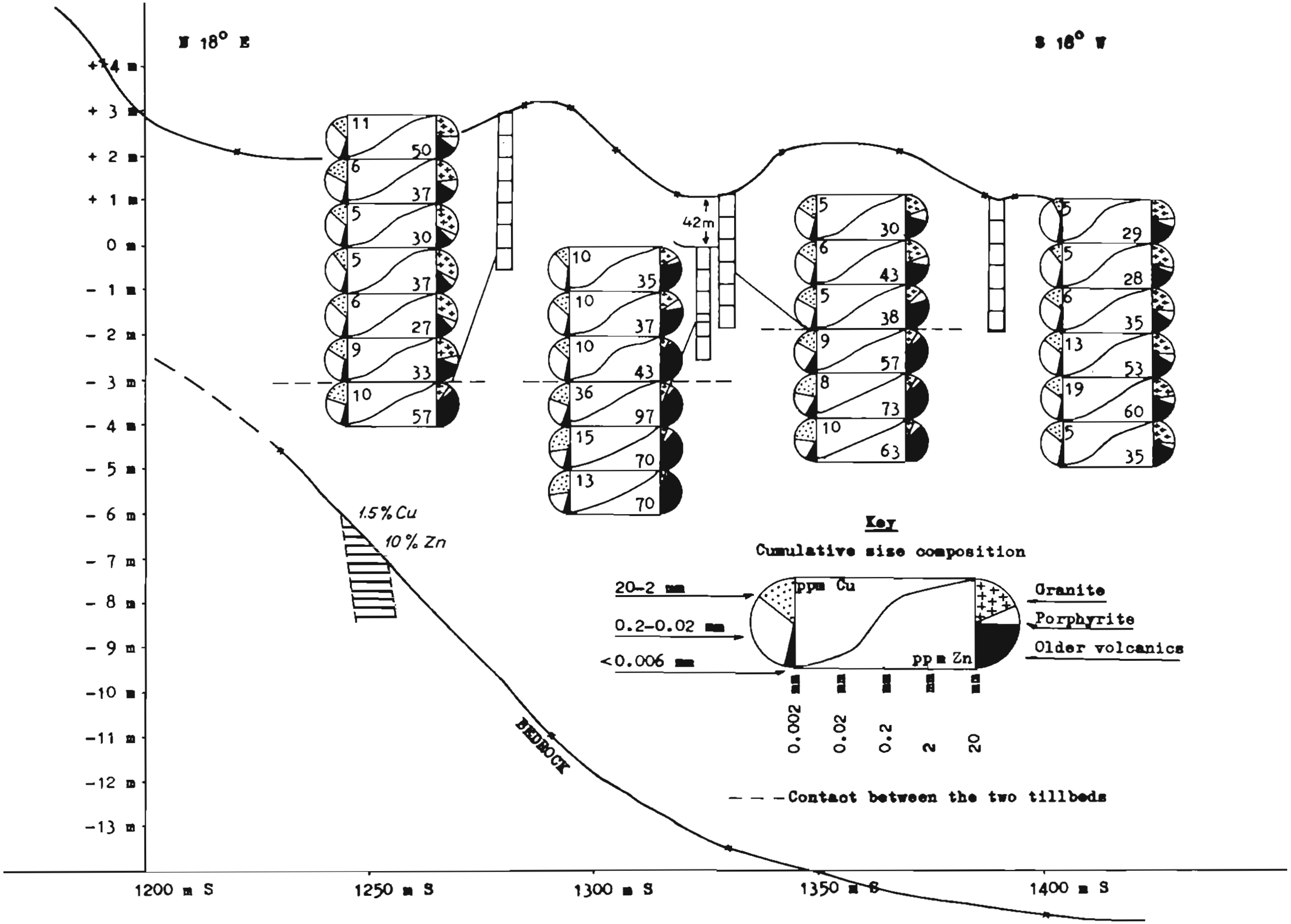


Figure 12. Profiles through the till over the Norra Norrliden ore deposit.

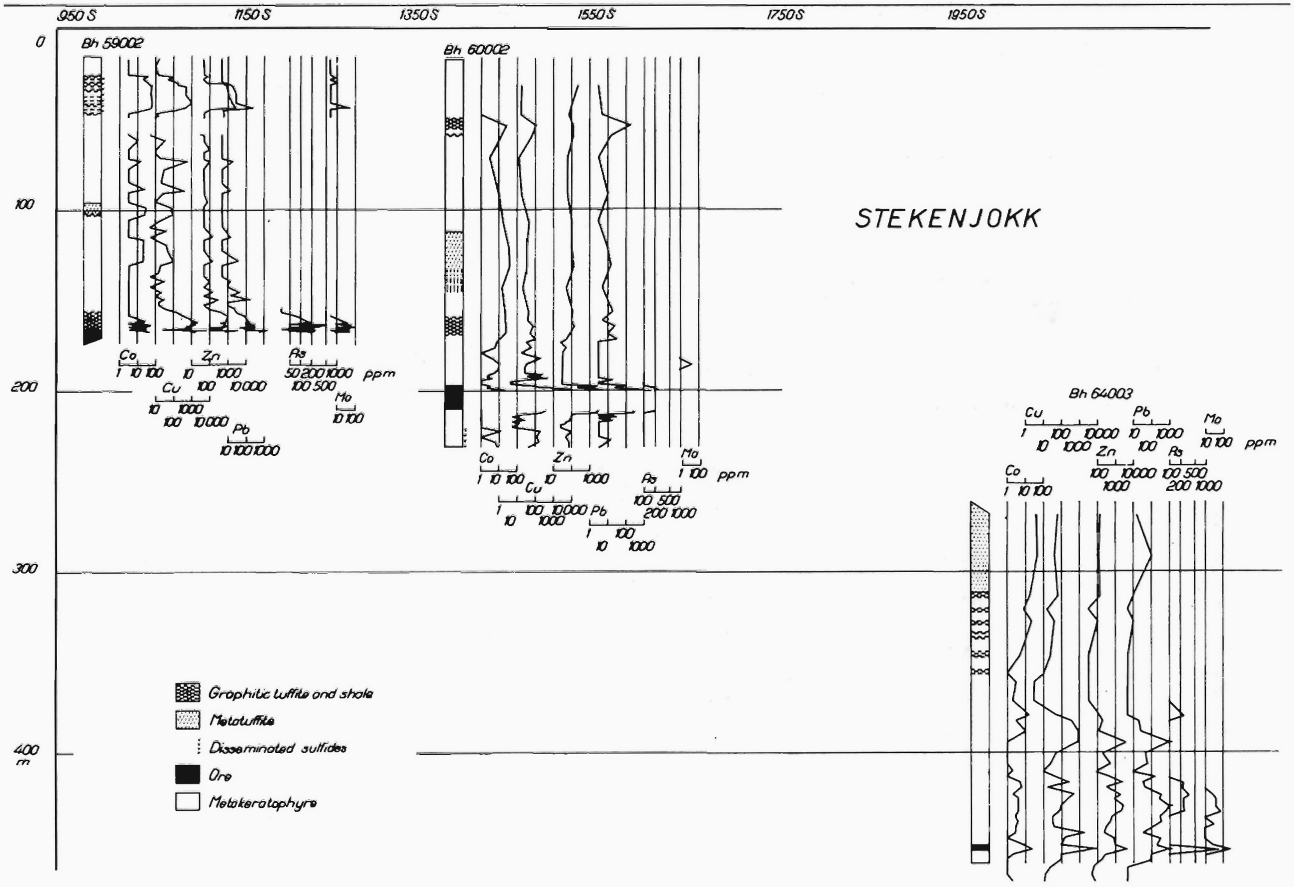


Figure 13. Rock types and distribution of some trace elements in drillholes through the Stekenjokk ore.

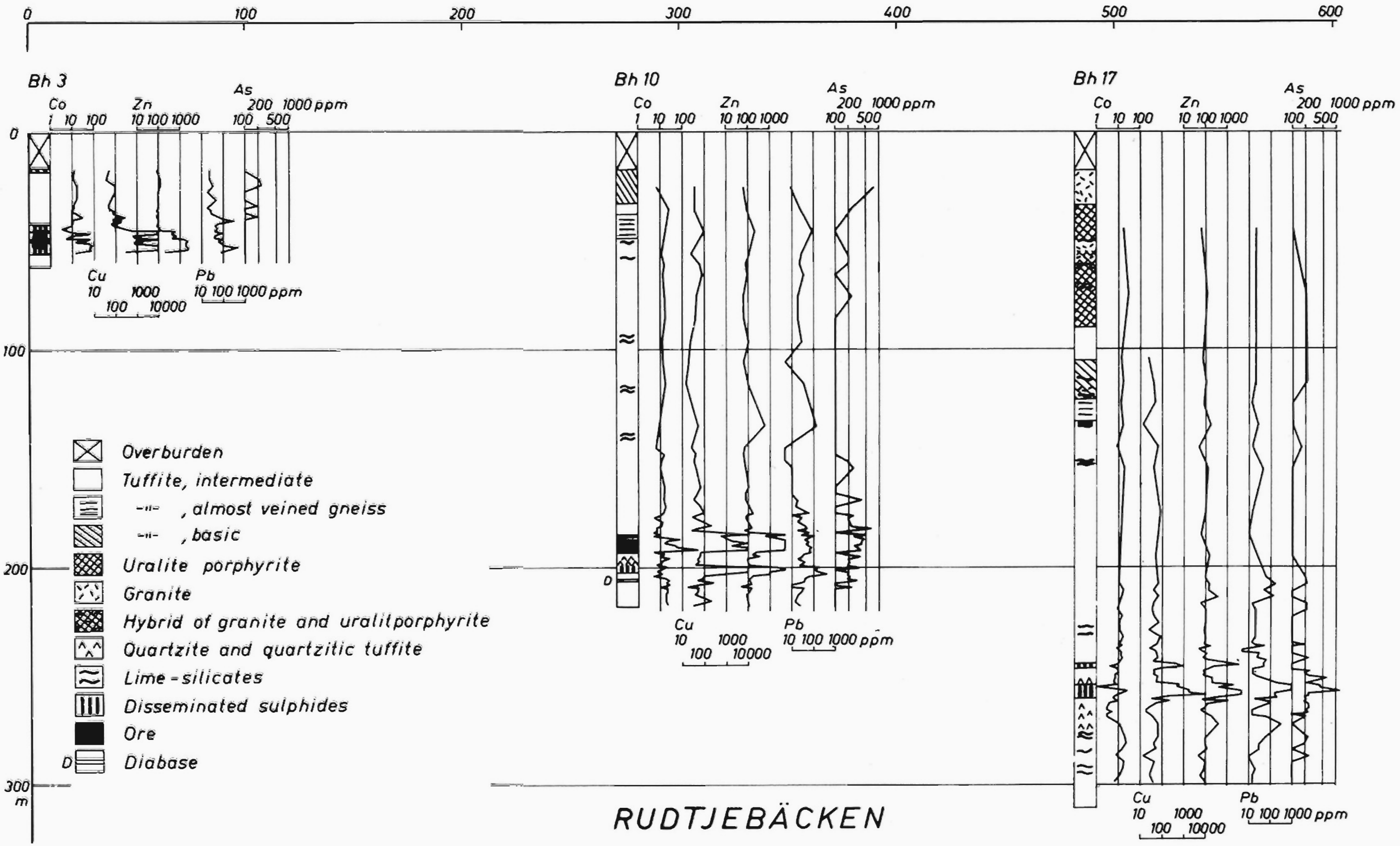


Figure 14. Rock types and distribution of some trace elements in drillholes through the Rudtjebacken ore. (As values for Bh. 17 are too high with correct values of Table 3).

APPENDIX

Hg-dispersions at Norrliden, Stekenjokk and Rudtjebäcken

by O. Brotzen, SGU and John L. Walker, Barringer Research Ltd, Toronto.

The appendix is a direct outcome of contacts established at the Ottawa symposium. Until then the SGU had not been active in Hg-research, but in view of the excellent analytical facilities available in Canada, it was suggested that the samples described in the preceeding text might represent suitable case-material for such work. The data obtained in the ensuing joint study therefore deserve to be put on record.

The analytical results from Norra Norrliden are presented in Table 1, the columns of which correspond directly to the pits represented in Fig. 12 above. The mercury data were obtained on the minus 6 micron fraction, whereas the Zn- and Cu-values, given for comparison, represent averages for all size-fractions, and are the same as given in Fig. 12.

Table 1

Trace Metal Content of Samples from Norra Norrliden

Cu	Zn	Hg	Cu	Zn	Hg	Cu	Zn	Hg	Cu	Zn	Hg
ppm	ppm	ppb	ppm	ppm	ppb	ppm	ppm	ppb	ppm	ppm	ppb
11	50	13									
6	37	9									
5	30	3				5	30	11	5	29	108
5	37	5				6	43	15	5	28	23
6	27	15	10	35	6	5	38	15	6	35	88
9	33	11	10	37	6	9	57	29	13	53	11
10	57	37	10	43	8	8	73	82	19	60	35
			36	97	25	10	63	33	5	35	9
			15	70	31						
			13	70	28						

The following facts may be noted:

1) The mercury-content in the till is low.

2) The mercury data parallel the earlier determinations of Cu and Zn, and thereby corroborate the significance of the geochemical difference between the upper and the lower till in spite of the low contrast.

3) No leakage-halo occurs directly above the ore (i.e. in the first pit from the left).

4) The marked Hg-anomaly in the upper part of the fourth pit (from the left) is not reflected in the other metals, and has no obvious explanation.

For Stekenjokk the core 60002, which is represented in Fig. 13 was analyzed, and the results are given in Table 2.

Table 2

Trace Metal Content of Stekenjokk Drill Core

Depth	Cu	Zn	Hg	Depth	Cu	Zn	Hg
m	ppm	ppm	ppb	m	ppm	ppm	ppb
20	16	220	33	165	59	50	8
36	15	70	16	168	16	<50	9
42	110	130	16	171	210	<50	5
48	63	130	6	174	30	<50	4
60	12	60	6	177	24	<50	4
80	16	60	16	179	27	<50	6
95	43	110	90	180	240	<50	
110	31	110	10	181	37	<50	7
120	32	130	19	182	460	<50	
132	19	50	10	183	20	<50	10
145	43	120	5	184	4	<50	
150	35	100	12	185	4	<50	14
153	71	140	18	186	87	2900	
157	52	90	6	187	260	230	98
160	104	50	16	188	%.	>5000	
162	30	<50	9				

Each analyzed section is a composite of three or more samples. It is seen that the limited dispersion of the ore-elements found around the Stekenjokk deposit at a depth of 188 m also characterizes the behaviour of mercury.

The results for the deepest hole at Rudtjebäcken are given in Table 3. Here the ore is situated at a depth of 259 m.

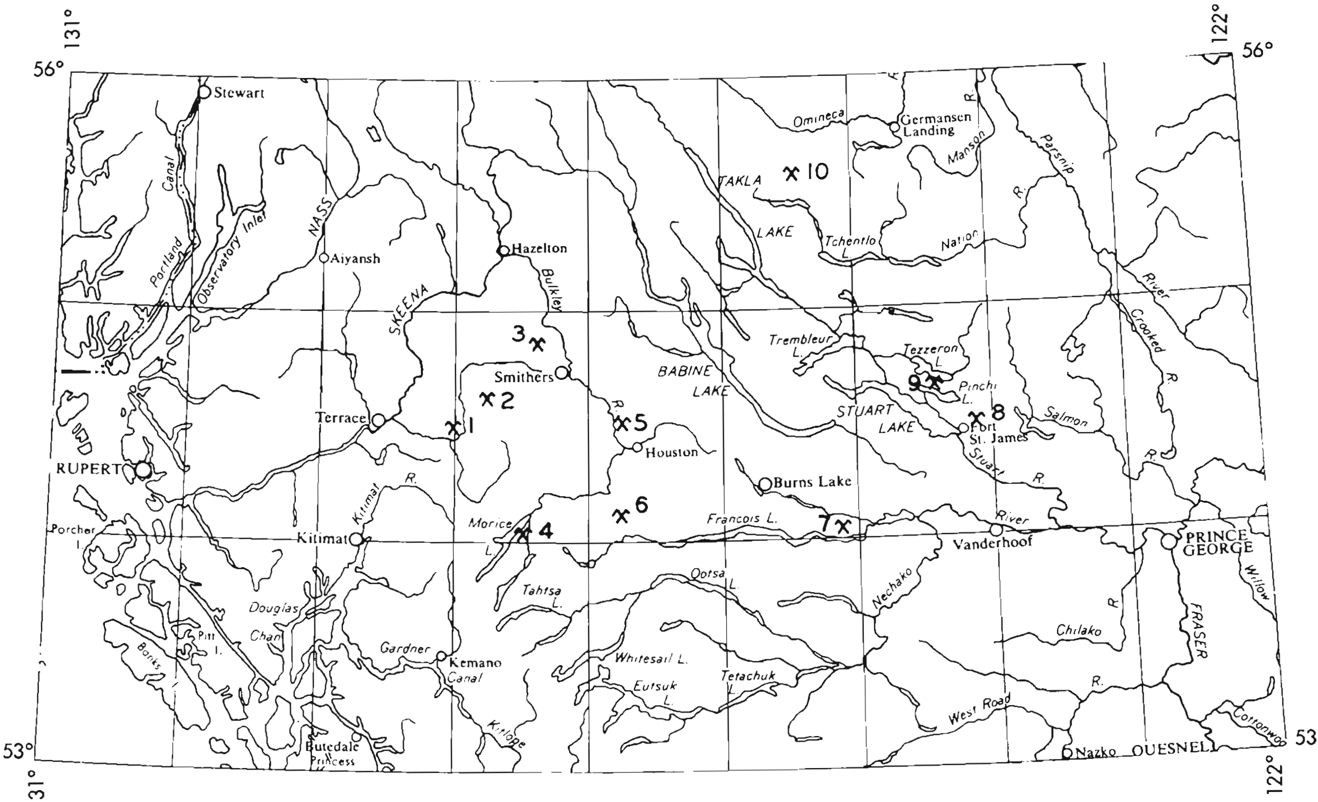
Table 3

Trace Metal Content of Rudtjebäcken Drill Core

Depth	Cu	Zn	As	Hg	Depth	Cu	Zn	As	Hg
m	ppm	ppm	ppm	ppb	m	ppm	ppm	ppm	ppb
45		60	10	44	235	59	90	15	12
75		110	10	31	236	54	160	25	20
104	26	70	30	11	238	27	<50		
115	42	100	10	12	239	53	70	10	10
125	48	80	10	7	242	64	80	20	19
135	14	170	60	4	245	530	3200	10	23
145	63	50	60	6	247	500	200	40	14
155	45	120	10	4	249	52	100	50	19
175	85	100	10	2	252	60	200	210	160
185	65	60	10	2	255	610	1200	280	3400
195	55	150	10	5	257	2000	>5000	350	7280
205	60	100	20	6	259	%	>5000	45	30
208	69	150	10	5	261	140	650	10	12
211	48	140	15	4	263	45	280	10	11
214	70	370		12	266	20	80	10	18
217	43	60	10	11	268	32	170	40	100
220	37	100	60	11	272	62	410	75	8
223	46	100	10	6	278	64	110	10	7
229	28	80	10	6	281	43	100	25	10
232	91	100	10	8					

Also in this deposit the dispersion of Hg is of the same type as that of Cu and Zn.

A fact which perhaps deserves special mention is that both Stekenjokk and Rudjebäcken were drilled long before the start of mining operations. This may be of importance in regard to possible contamination from the use of mercury fulminate in blasting caps, as pointed out by Kurbanayev and Iskov (1964.) The only blasting at these sites that can be suspected might have occurred during the initial penetration of bouldery overburden. These cores therefore represent largely undisturbed conditions, and the same also applies to the till samples from Norra Norrliden.



1. Northwest Group   2. Serb Creek   3. Glacier Gulch   4. Lucky Ship   5. Huber Group
6. Owen Lake   7. Endako   8. Centennial   9. Pinchi   10. Takla Mercury

Figure 1. North-central British Columbia showing properties referred to in text.

INVESTIGATION OF MERCURY DISPERSION HALOES AROUND MINERAL DEPOSITS IN CENTRAL BRITISH COLUMBIA

A. Sutherland Brown*

During routine geological examination of mines and prospects in north-central British Columbia in 1965, the writer collected soil samples and analysed them in the field for mercury. Samples were taken along cut lines or access roads generally from the top of unmodified soil. An attempt was made to extend sample points well beyond the limits of known mineralization. Samples were air-dried, sieved to -40 mesh, and analysed by Lemaire S-1 detector. Care was taken to avoid organic samples and contamination. Samples run in the field were checked in part by more sophisticated instruments and all samples greater than 1 p.p.m. and some less were analysed in Victoria by the Analytical and Assay Branch of the Department of Mines and Petroleum Resources with generally good agreement. The values used in the graphs are those recorded in the field by the writer.

The profiles are chiefly of mercury or molybdenum prospects (Figure 1 shows the geographic locations). These are believed to represent extreme types at which mercury haloes might be expected: the one type being low temperature and mercury-rich; the other high temperature, disseminated, and mercury-poor. In addition, one copper and one silver-lead-zinc prospect were examined. Only summary descriptions of the geology of these deposits are given. Greater details of mercury deposits can be found in Memoir 252 (Armstrong, 1949) and in the Annual Report of the Minister of Mines and Petroleum Resources for 1965.

MERCURY DEPOSITS

The mercury profiles are from localities along the Pinchi fault zone from Fort St. James to Kwanika Creek. A large number of mercury prospects are situated along the course of this major fault zone. The geology may be summarized as follows.

The block west of the fault is formed of Permian limestone and chert (Cache Greek Group) and the block to the east by upper Triassic basic volcanic rocks (Takla Group) intruded by Jura-Cretaceous acidic plutonic rocks in the north and ultramafic bodies in the south. Figures 2A to C show, respectively, profiles across the fault zone in the vicinity of the Pinchi mine, across the fault zone along the road from Fort St. James, and along the fault zone from Kwanika to Kenny Creeks. In general the background varies from 0.02 p.p.m. to about 0.08 p.p.m., rarely to 0.2 p.p.m., and the anomalous peaks range from p.p.m.

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* Department of Mines and Petroleum Resources, Victoria, B.C.

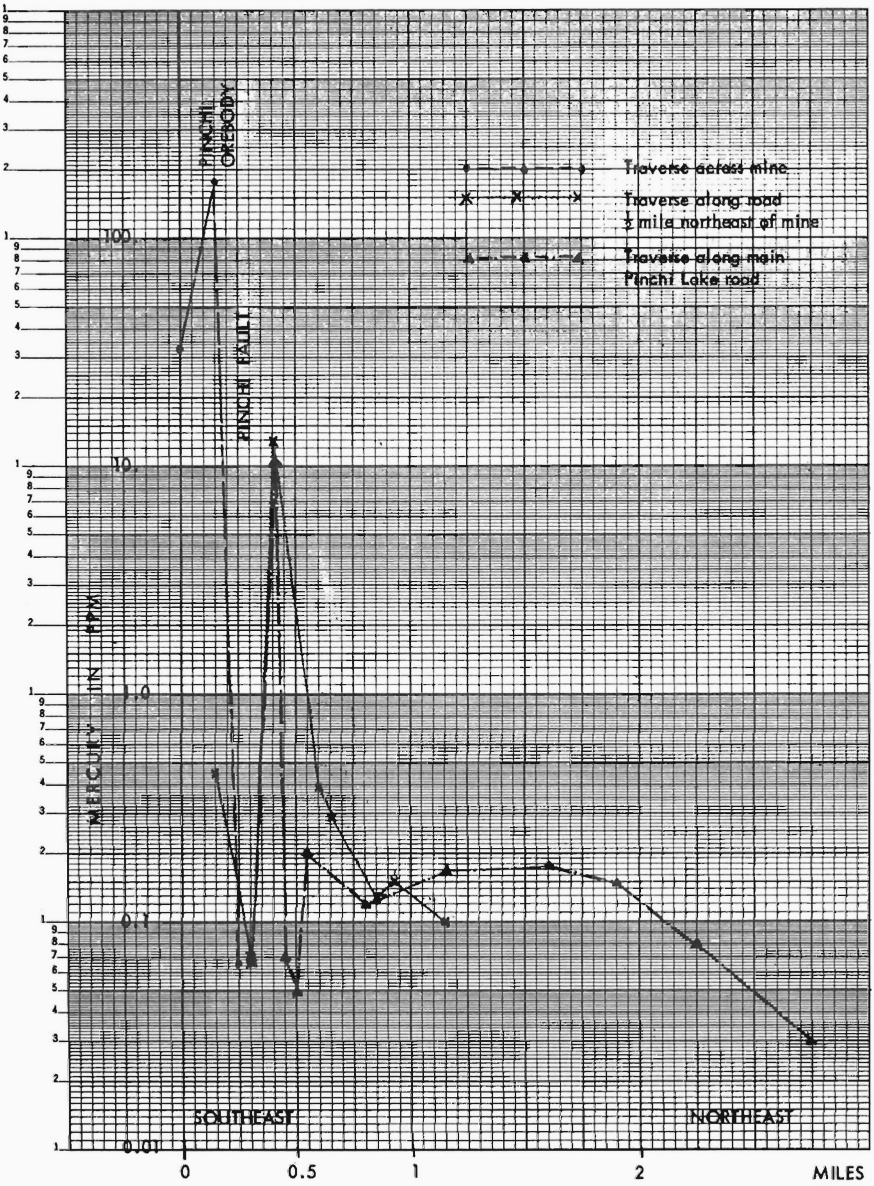


Figure 2A. Mercury content profile, Pinchi Lake; sample locations plotted normal to main Pinchi Fault.

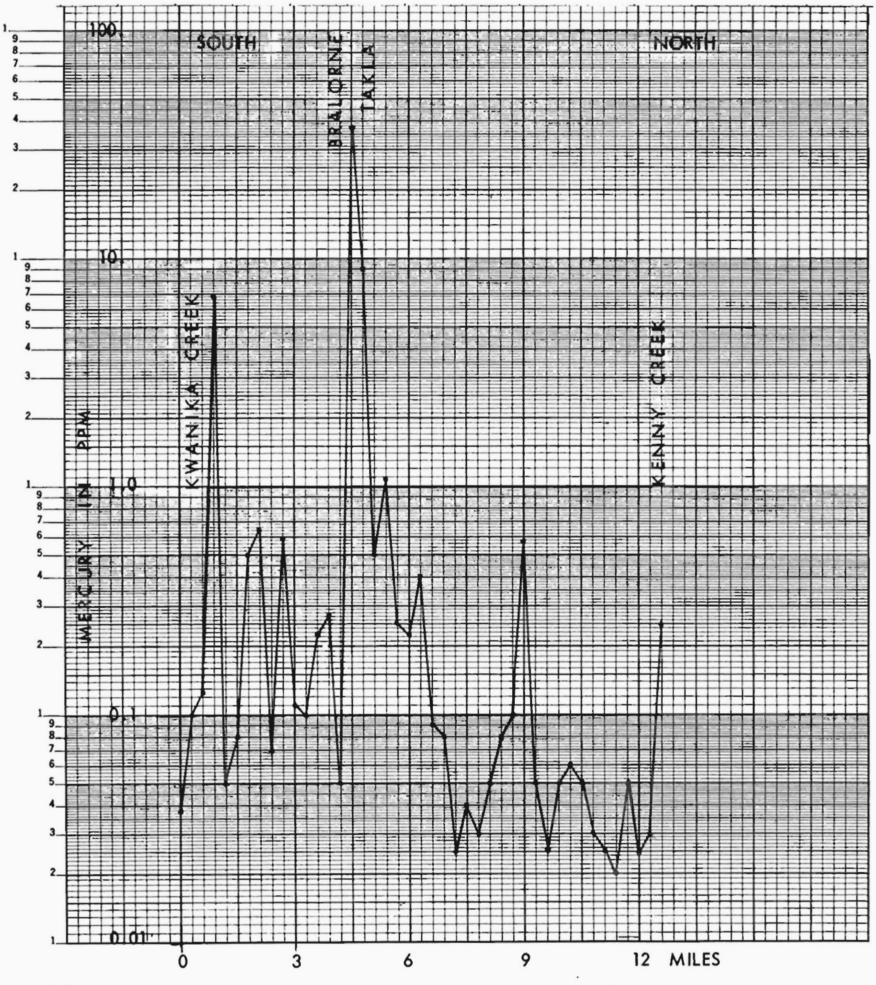


Figure 2B. Mercury content, traverse along Pinchi fault, Kwanika Creek to Kenny Creek.

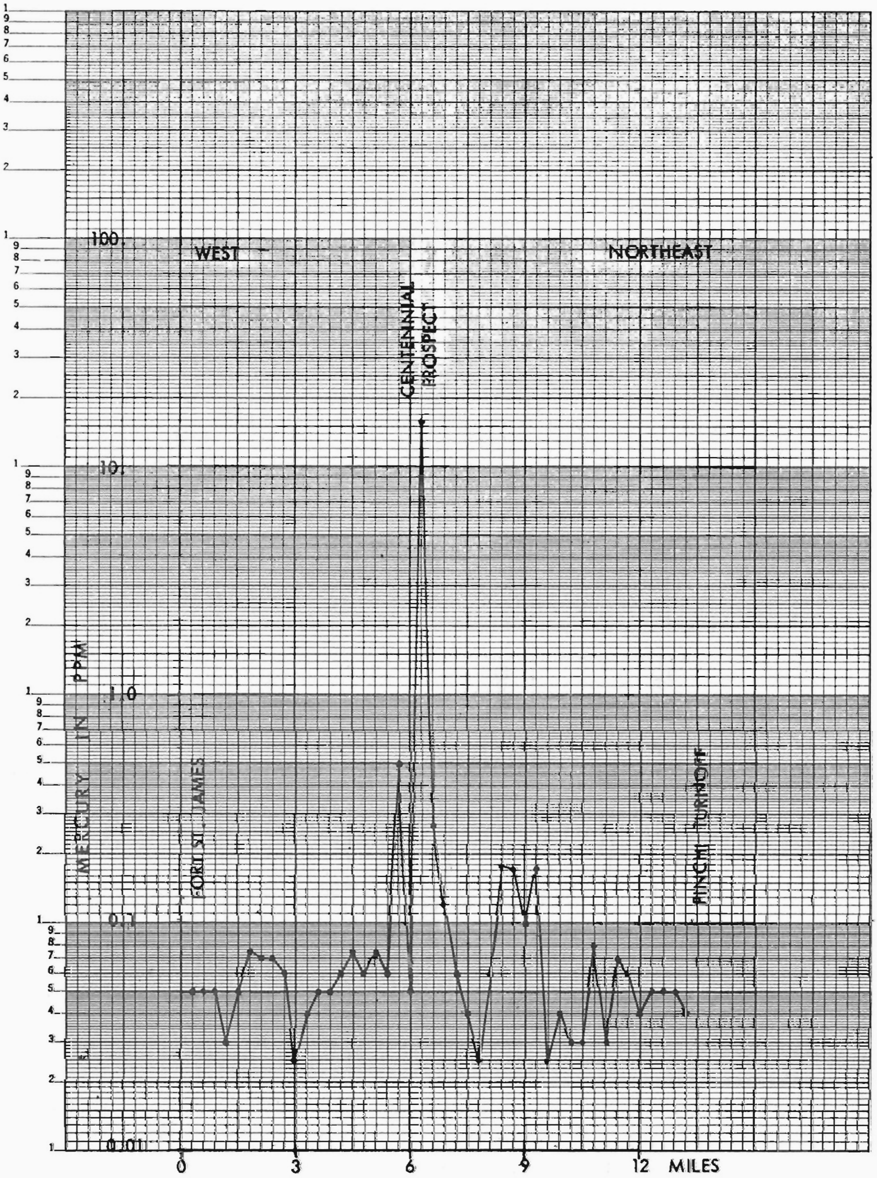


Figure 2C. Mercury content, traverse of highway, Fort St. James – Pinchi Turnoff.

to about 200 p.p.m. The preferred materials sampled were tills or outwash sands and coarse silts, or rarely regolith, but near Pinchi Lake glacial lake clays and fine silts were common. The results suggest that true clays may be fairly impervious to mercury vapour as the highest value recorded in clay samples was 0.45 p.p.m. Contamination from the surface near the Pinchi and Bralorne Takla mines was judged to be relatively slight as samples collected at 2- to 1-foot depths showed no consistent difference.

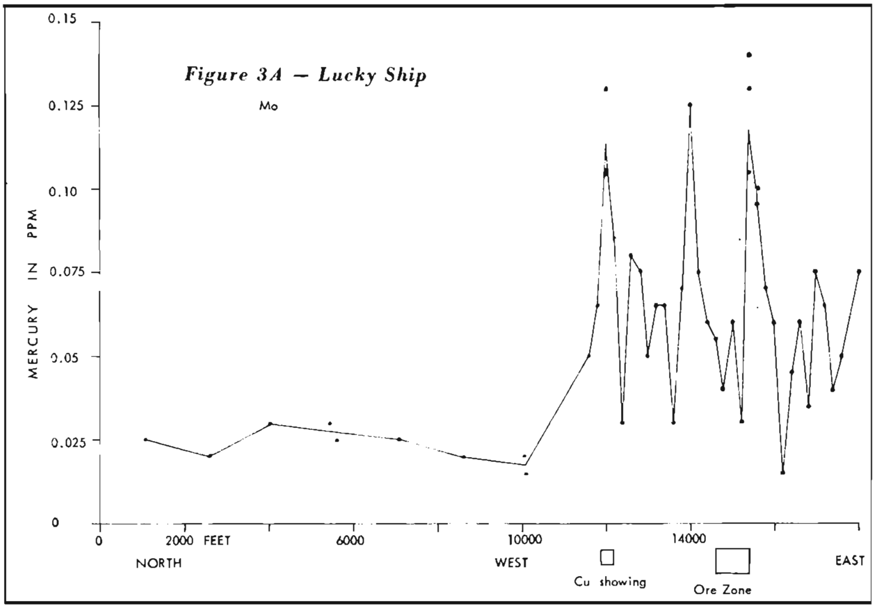
MOLYBDENUM DEPOSITS

Profiles run on molybdenum mines and prospects included Endako, Glacier Gulch, Lucky Ship, and Huber groups. The geology of these properties does not have the unity of the mercury ones, except that all are relatively sparsely mineralized. The Lucky Ship prospect is in a complex, small rhyolite porphyry plug that intrudes Jura-Cretaceous porphyritic andesites and volcanic sediments (Hazelton Group). An annular vein stockwork and silicified zone peripheral to one phase of the plug contains molybdenite with few other metallic minerals. The profile (Figure 3A) extends along the access road from the Nanika River bridge and back down across cut lines to the river flat. Most of the samples were glacial till. Background ranged from 0.01 to 0.03 p.p.m. and the peaks to 0.125 p.p.m.

The Endako mine is in a quartz monzonite, one of many phases of the Jurassic Topley batholith. Molybdenite is contained principally in veins that strike about east-west and dip 45 degrees south. There are few other metallic minerals. The profiles (Figure 3B) extend from Highway No. 16 across the orebody nearly to François Lake. The materials sampled were entirely glacial tills. The background ranged from 0.015 to 0.025 p.p.m. and the peaks over the orebody to about 0.08 p.p.m.

The Glacier Gulch prospect consists of a flat sheet-like body of granodiorite cutting hornfelsic Jurassic volcanic and sedimentary rocks (Hazelton Group). A flat vein system and stockwork with molybdenite, pyrite, and pyrrhotite extends over a wide area and considerable vertical range. Some gold-bismuth showings occur in the same vein system but remote from the molybdenum mineralization. The profile (Figure 3C) extends from the orebody to the east for 2 miles. The materials sampled were not ideal, being fine talus in the west and till in the east. Background varied from 0.02 to 0.03 p.p.m. and the values over the orebody were of this range but over the gold-bismuth showings of the same vein system they reached 0.175 p.p.m.

The geology of the Huber group consists of two adjacent small plugs of alaskite and granite porphyry intruding hornfelsic Jurassic volcanic sedimentary rocks (Hazelton Group). Between the plugs in particular, a stockwork of fractures and quartz veinlets contain pyrite, molybdenite, and minor chalcopyrite. The profile (Figure 3D) extends from Highway No. 16 across



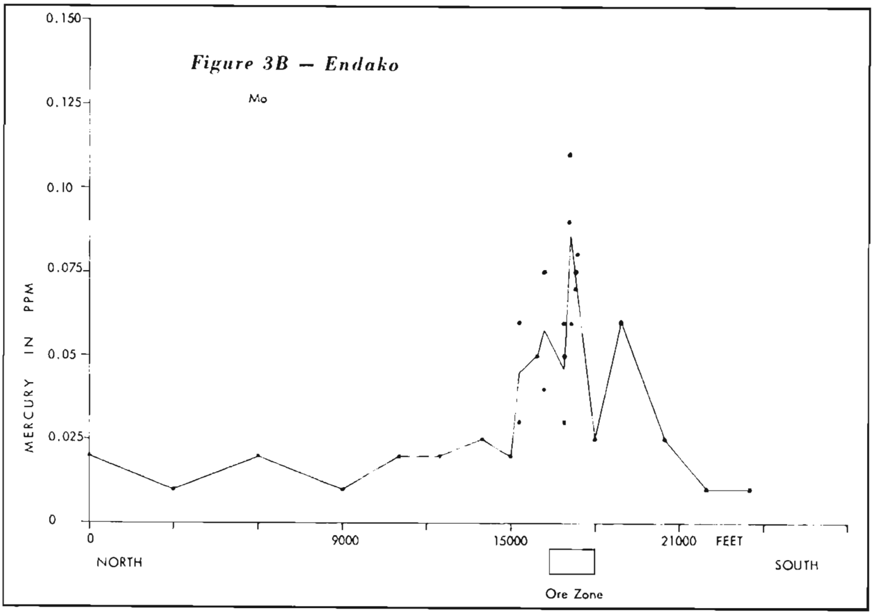


Figure 3. Mercury content profile.

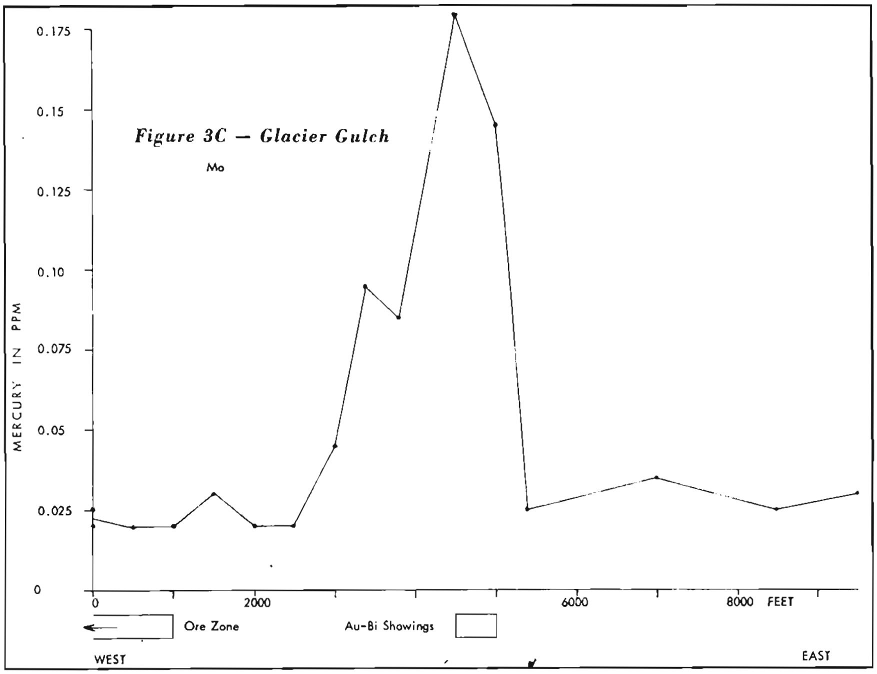


Figure 3C — Glacier Gulch

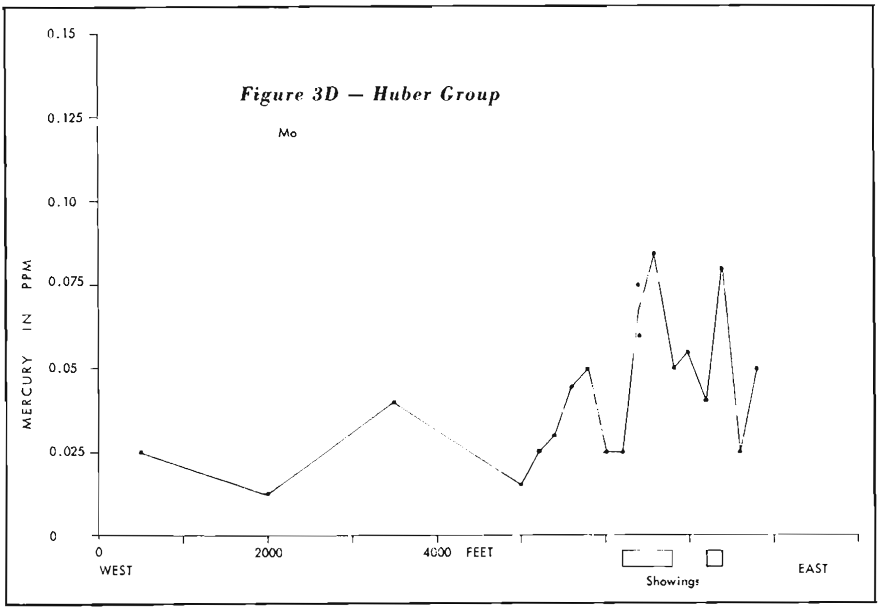


Figure 3D — Huber Group

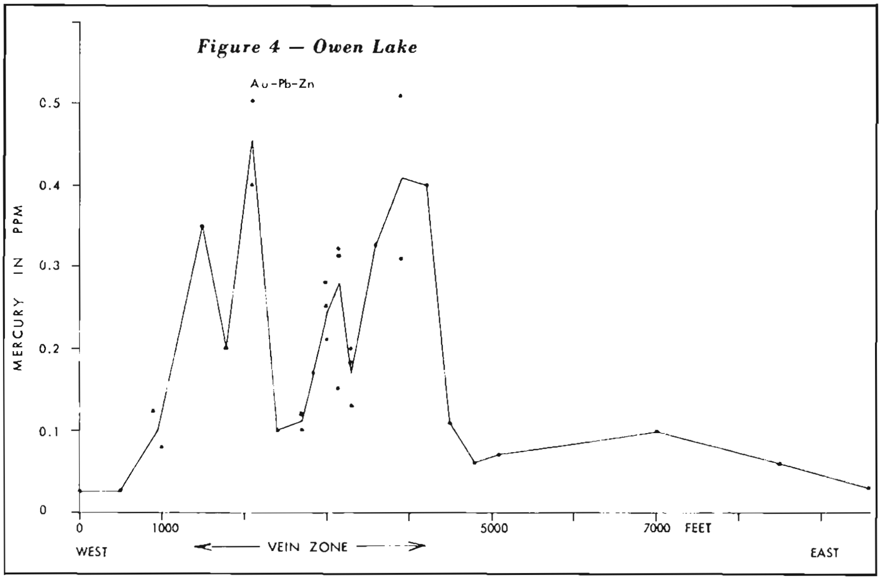


Figure 4. Mercury content profile, Silver Queen Au-Pb-Zn property, Owen Lake.

Figure 5: Mercury Halo Peaks and Backgrounds at Deposits of Selected Metals

Property	Reference
Mercury	
1. Nivloc, Nev.	Williston
2. Cerro Gordo, Calif.	Williston
3. Cordero, Calif.	Williston
4. Karaotek, U.S.S.R.	Ozerova
5. Pinchi, B.C.	Sutherland Brown
6. Bralorne Takla, B.C.	Sutherland Brown
7. Centennial, B.C.	Sutherland Brown
Gold -Silver	
8. Comstock, Nev.	Williston
9. Dixie Comstock, Nev.	Williston
Lead-Zinc	
10. Bawdwin, Burma	James and Webb
11. Eire	James and Webb
12. Gregory, Derb., U.K.	James and Webb
13. Owen Lake, B.C.	Sutherland Brown
Copper	
14. Ruwenzori	James and Webb
15. Baluba	James and Webb
16. Northwest Group, B.C.	Sutherland Brown
Molybdenum	
17. Endako, B.C.	Sutherland Brown
18. Lucky Ship, B.C.	Sutherland Brown
19. Glacier Gulch, B.C.	Sutherland Brown
20. Huber, B.C.	Sutherland Brown
21. Serb Creek, B.C.	Sutherland Brown

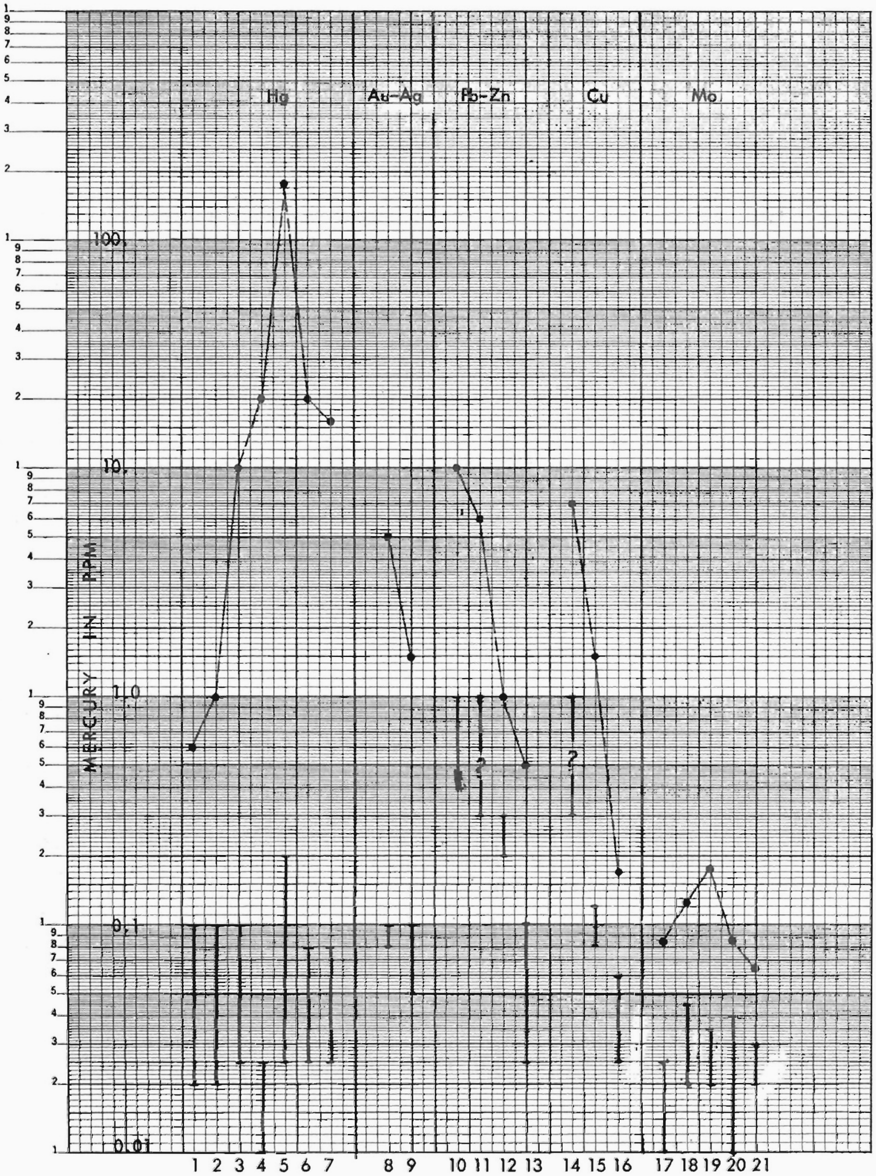


Figure 5. Mercury halo peaks and backgrounds at deposits of selected metals.

the showings. Samples were all till. Background ranges from 0.015 to 0.04 p.p.m. with peaks of 0.08 p.p.m. over the showings.

OTHER DEPOSITS

A profile was run over a small silver-lead-zinc property, the Silver Queen, at Owen Lake. Here four veins of about 6 feet width, 2,000 feet length, and at least 500 feet depth occur primarily within a large microdiorite sill that intrudes Hazelton pyroclastic rocks. The profile runs from Owen Lake across the vein zone and about a mile further east. Samples were primarily till and outwash sands. Background ranged from 0.025 to 0.1 p.p.m. and peaks to 0.5 p.p.m.

A profile was also run at a copper prospect, the Northwest group, but it was not sufficiently long to extend beyond the area of scattered mineralization. Also a profile was run at another molybdenum prospect, Serb Creek, but here all materials were either highly organic soil or loose talus, so an inconclusive profile resulted. The range of these results are shown with the others on Figure 5.

CONCLUSIONS

Secondary dispersion haloes of mercury were detected at all the properties which were examined, although the order of anomaly peaks varied greatly from mercury deposits to molybdenum deposits. Figure 5 shows the background variation and anomaly peaks for some mercury, gold-silver, lead-zinc, copper, and molybdenum deposits. The examples include all those run by the writer and many from the literature in which absolute values are given. It is clear that in most localities background ranges from 0.01 to 0.1 p.p.m. but in some others is much higher. In some of the latter, the profiles may not have extended far enough from the ore zone to truly record background judged by the horizontal dimensions shown. However in still others, background over whole regions may be so high (for example, the Crimean Highlands, Bulkin, 1962) that molybdenum peaks would not be noticed. It is also clear that the peaks for the various groups follow the theoretical sequence related to temperature of deposition.

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THE ATOMIC ABSORPTION SPECTROMETER IN THE GEOCHEMICAL LABORATORY

A.H. Debnam*

INTRODUCTION

Applied geochemical studies of rocks, soils, vegetation and waters have been made possible by the application of rapid semi-quantitative analytical procedures, either colorimetric or spectrographic, which are aimed at productivity rather than accuracy. Colorimetric methods are used for metal determinations after samples have been treated by any of a variety of extraction procedures which may selectively remove only one form or group of forms of the metals contained in the samples, from very loosely bonded metals to those incorporated in the crystal lattices of minerals. For most elements, simple buffering and complexing procedures will control pH and interferences but some metals require tedious separations. The main advantage of the colorimetric procedures is that they can be applied in the field at the point of sample collection or in a field laboratory. A disadvantage is that each metal requires its own particular set of operating conditions, making multi-element determinations rather laborious. Spectrography is probably the most rapid and efficient method for carrying out total multi-element determinations on geochemical samples, the disadvantages being high initial cost and limited portability. Spectrographic analyses are usually made in centrally located laboratories, although some mobile units for field use have been built.

In recent years a new analytical procedure which is closely related to spectrography has been developed. It is atomic absorption spectrophotometry. This method has most of the advantages of both colorimetry and spectrography with very few disadvantages. Atomic absorption is applied to solution extracts of samples and is extremely rapid, sensitive, precise and free from interferences. The method has gained wide acceptance in all branches of analytical inorganic chemistry.

THE THEORY OF ATOMIC ABSORPTION

Many geologists and chemists are already familiar with emission spectrography so the difference between emission spectrography and atomic absorption will be explained in simple terms. Emission spectrography is based on the fact that when a substance is volatilised in an arc or spark discharge some of the electrons in the metal atoms receive heat energy and jump to higher energy levels. When these electrons fall back to lower

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energy levels they emit light energy of specific wavelengths which are characteristic of the elements present. The light is spread out by a prism or grating to isolate the specific wavelengths and these are measured either photographically or electronically to give a quantitative determination of the elements of interest. Only 1% to 5% of the atoms and ions in the arc or spark are excited to emit light whereas the greater proportion remain in the so called "ground state" condition. It has now been found that these ground state atoms are capable of absorbing light of the same wavelength as that emitted by the excited atoms and this is the basis of atomic absorption analysis. The material to be analysed must be in the atomic state and this is readily achieved by spraying the sample solution into a flame rather than into an arc or spark. A light beam at one of the characteristic wavelengths of the element to be analysed is directed through the flame, into a monochrometer and onto a detector which measures the intensity of the beam. The amount of light absorbed by the flame when a sample is being aspirated is proportional to the concentration of the element in the sample. Atomic absorption is free from interferences because only the wavelength emitted by the source is measured and no element other than that being analysed will absorb this light. It is more sensitive than emission spectrography because up to 95% of the atoms are being put to work instead of only up to 5%.

ATOMIC ABSORPTION INSTRUMENTS

The instruments are made up from a hollow cathode light source, a chopper, a burner, a monochrometer and a detector-amplifier system.

The hollow cathode lamp has a cathode of the metal to be determined and emits its characteristic wavelengths. It can be either single element or multi-element and costs between \$90 and \$250. Some instruments hold up to 6 lamps with one in the operating position and the others on stand-by where they are pre-warmed to eliminate delays due to warm-up requirements. A multi-element Cu-Pb-Zn-Ag lamp has been in daily use in my own laboratory for the past 12 months.

The chopper is either a mechanical rotating disc or an electronically pulsed power supply for the hollow cathode lamp. It supplies a modulated light beam compatible with the AC amplifier and prevents the detector from picking up light given off by the flame and the atomised sample.

The burner atomises the aspirated sample solution to produce ground state atoms of the elements. It is probably the most important component of the instrument since this is where the atomic absorption takes place. Two types of burners are available, the Total Consumption or Turbulent Flow Burner and the Pre-Mix or Laminar Flow Burner. Most instruments are designed to accommodate only one type of burner although the trend is toward the use of either burner system in a single instrument. In the Total Consumption Burner the sample is aspirated directly into the flame together with the fuel and support gases, usually hydrogen and air or acetylene and oxygen. All of the sample is utilised in the flame. In the Pre-Mix Burner the sample solution is mixed with the fuel and support gases in a chamber before entering the flame. Only about 5% of the mixture is burnt, the remainder goes to waste. The gases can be acetylene-air, propane-air or acetylene-nitrous oxide. As a general rule the Total Consumption Burner will not accept coal-gas, city-gas or propane because the burning velocity of these fuels will not supply a large flame and the Pre-Mix Burner will not accept oxygen because the reaction is too violent and the flame will be blown out.

Flame temperature is important as it must be sufficient to exceed the dissociation energies of those molecules containing the metals to be analysed. The following table gives the mean temperatures found in flames commonly employed in atomic absorption:

TABLE 1

Mean Flame Temperatures in Atomic Absorption

Air-coal gas	1800°F
Air-propane	1925°F
Air-hydrogen	2050°F
Oxygen-hydrogen	2500°F
Nitrous oxide-hydrogen	2600°F
Air-acetylene	2350°F
Oxygen-acetylene	3100°F
Nitrous oxide-acetylene	2955°F

Refractory-forming elements such as Al, Be, Si, Mo, Ti, Sn require oxygen-acetylene or nitrous oxide-acetylene flames.

The monochrometer isolates the absorption sensitive lines emitted by the hollow cathode lamp, preferably using a high resolution grating rather than a prism.

The detector is a photomultiplier which indicates variations in absorption of the light from the hollow cathode lamp as it passes through the flame. The detector signal is amplified and the readout is provided on a meter or permanently recorded on a chart.

Atomic absorption instruments are available from 5 manufacturers: Jarrell-Ash, Perkin-Elmer, Aztec Instruments, Beckman and Eel. They fall into 3 different price ranges according to versatility. The least expensive is $3,000-$4,000 for use in routine analyses which do not require extreme sensitivity. The more sensitive and versatile instruments for research fall into the middle range of $7,000-$9,000. The most expensive is a multichannel instrument available only from Jarrell-Ash and selling for approximately $20,000. This machine will analyse up to 12 elements simultaneously. Special features worth noting are the multi-pass systems found in the Jarrell-Ash and Beckman instruments. To increase sensitivity Jarrell-Ash passes the light beam through the flame 5 times and Beckman 3 times. Perkin-Elmer use a double beam system where one beam by-passes the flame in order to compensate for variations in absorption due to delay in warm-up of the hollow cathode lamp. Jarrell-Ash and Beckman each offer both Total Consumption and Laminar Flow Burners whereas the other manufacturers offer only the latter type. Digital readout systems are available from Jarrell-Ash and Perkin-Elmer at additional cost.

INSTRUMENT OPERATION

In a laboratory operation the solid samples (pulverised rock or sieved soil) are extracted by any suitable procedure and the solution made up to volume. The analysis can proceed immediately if the instrument electronics have been warmed up. The meter or recorder is set at 0% absorption whilst a blank solution is aspirated into the flame. At this stage most of the light of a specific wavelength (e.g. 2139A for Zn or 3247A for Cu) from the cathode is passing through the flame with very little loss due to scattering. If all adjustments are correct a strong solution of the metal to be determined will swing the meter to a reading of 100% absorption. In fact, a solution with as little as 5 ppm. Zn can give almost a 100% reading. Next the sample solutions are aspirated and the percent absorption read on the meter or recorded on a chart as individual peaks. A set of standards are run before and after each batch of 50 samples. Standard curves can be plotted with absorption against metal concentration and the unknown values read from the curves. To eliminate tedious graphical computations it is much easier to record the results on a chart and prepare scales calibrated directly in ppm. from the standards. A sensitivity of 1 ppm. to 2 ppm. can be achieved for most of the metals required in geochemical prospecting if the samples are extracted with an acid. If samples are subjected to a fusion the sensitivity will be 5 ppm. to 10 ppm. for the common metals. Two hundred and fifty measurements per hour on solutions can be maintained throughout a normal day.

ATOMIC ABSORPTION, PRESENT AND FUTURE

Due to its simplicity, accuracy and speed atomic absorption is rapidly replacing many of the wet-chemical analytical procedures used for rock analysis, the assay of ore samples, geochemical exploration analysis and agricultural analysis. In geochemical prospecting it is particularly useful for those surveys in which multi-element determinations are required. Time-consuming colorimetric analyses are no longer necessary for metals which are difficult to analyse, with a consequent reduction in costs. For example it is now possible to analyse for the 6 elements Cu, Pb, Zn, Ag, Ni and Co for as little as $2.40 whereas by the colorimetric methods the cost would be at least $7.00. Further cost reductions should be possible with the introduction of multichannel instruments with automatic read-out suitable for computer processing of the results. Within the next few years the 10-12 element geochemical survey should be quite common.

GEOCHEMICAL DISPERSION IN GLACIAL OVERBURDEN OVER THE TYNAGH (NORTHGATE) BASE METAL DEPOSIT, WEST-CENTRAL EIRE

P.R. Donovan* and C.H. James**

INTRODUCTION

This paper is based upon the results obtained during a study of geochemical dispersion patterns in the glacial overerburden overlying the Tynagh lead-zinc-silver-copper deposit in Co. Galway, Ireland. The investigation was greatly facilitated by Irish Base Metals Ltd. who granted permission for sampling to be carried out during pre-opencast stripping operations, thus enabling a three dimensional pattern to be obtained over the ore-body itself.

The diverse nature of the glacial material, together with the general lack of knowledge concerning the mechanisms involved in its deposition, makes geochemical investigations of this type considerably more complex than those in residual soils. At one time many geologists feared that geochemical techniques of mineral exploration might prove useless in terrains covered by glacial deposits. However, a slowly increasing number of case histories from different parts of the world are showing that this is not necessarily the case.

THE TYNAGH ORE-DEPOSIT AND ITS SETTING

The geology of the central plain of Ireland, in which the Tynagh deposit occurs, consists mostly of shallow dipping Lower Carboniferous (Mississippian) limestones and dolomites with scattered inliers of Silurian and Devonian shales and sandstones. The deposit itself is located on the north side of an essentially east-west fault which brings Mississippian carbonates down against Devonian sandstones, conglomerates and shales.

The geology of the deposit has been discussed by Derry _et al_. (1965), who described the ore-body as occurring in two parts, i.e. "a boat-shaped mass of residual or secondary ore covering primary sulphide ore in limestone of Lower Carboniferous age". A typical section across the body (Fig. 1) shows that the secondary ore is widest at the suboutcrop, and narrows with depth.

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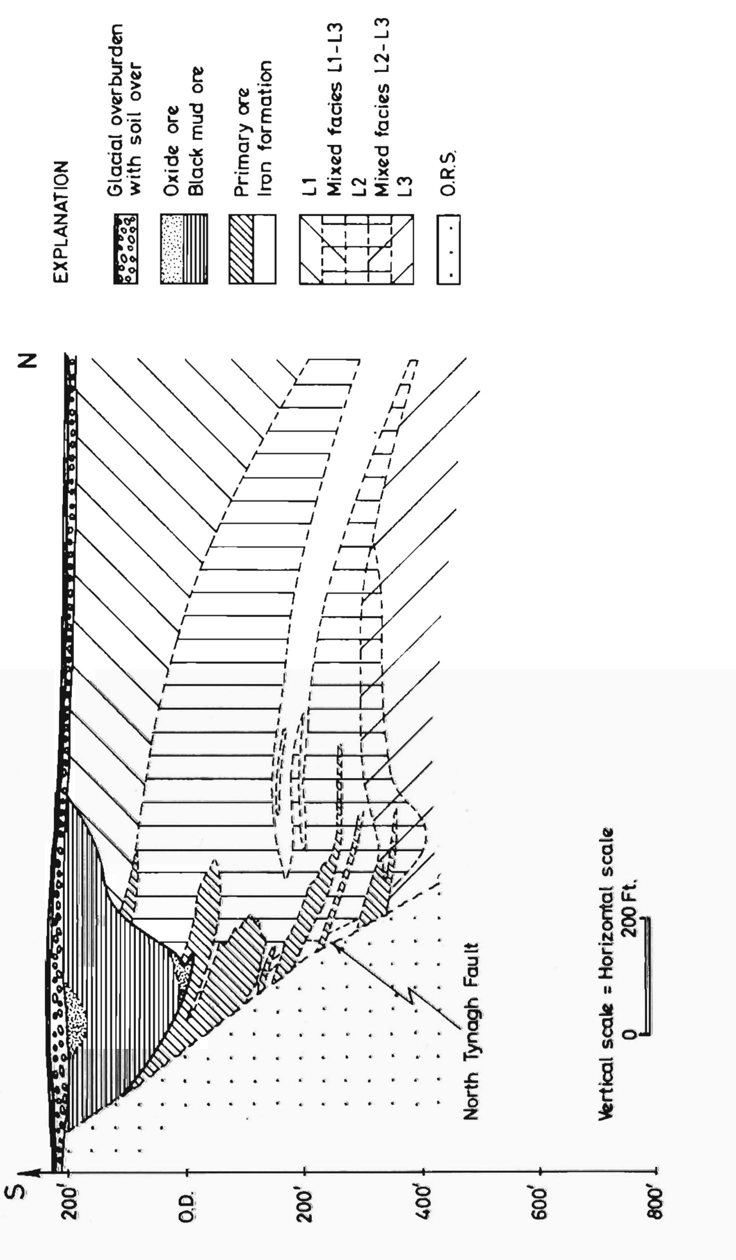


FIG. 1. CROSS SECTION THROUGH TYNAGH ORE BODY, LINE 85W. AFTER DERRY *et al.* (1965)

Figure 1. Cross-section through Tynagh ore body, line 85W. After Derry et al. (1965)

The primary ore occurs in a reef facies of the limestone where it fingers into muddy limestone, and Derry and his co-authors believe that the deposit was probably formed by solfataric solutions during local vulcanicity, although some later redistribution may also have taken place.

Of particular interest is the nature of the secondary ore, which takes the form of a black mud containing fine sulphides averaging approximately 16% lead and zinc, although sharply defined areas of secondary oxide ores occur within the black material. Derry and his co-authors believe the black sulphide-mud ore to have resulted from the supergene solution of the calcium carbonate from the mineralised limestone, causing the release of sulphides and muddy components in some parts and metal oxides in others. These then settled in or were washed into a deepening, fault-controlled gully.

During Quaternary time, the whole deposit was covered by a varying thickness of glacial material. Three major glaciations occurred in Ireland during the Quaternary period. Deposits of the earliest, the Elster, have been found only in a few localities in the south of the country. The second, the Saale, covered the entire country except for a few upland areas in the south, while the last, the Weichsel, redistributed most of the earlier glacial deposits north of the Tipperary end-moraine, its southern limit. A subsidiary centre existed in Cork during this time.

Boulder trains occurring north of the Tipperary end-moraine are often compound since they were formed during both the Saale and Weichsel Glaciations, and perhaps even during the Elster. In the case of the Tynagh boulder train, it is thought that the ice moved essentially southwards during the Saale and eastwards during the Weichsel glaciation. In the case of the Galway granite, on the other hand, the ice moved essentially eastwards during the Saale period and southeastwards and southwards during the Weichsel, although the pattern of movements is more obscure due to the greater area covered by this fan (Fig. 2).

The surface geology in the immediate vicinity of the ore-body consists entirely of Weichsel glacial deposits, except in a few places over the Old Red Sandstone inlier where the bedrock is exposed. East-west drumlinoid hills, including one overlying the Tynagh deposit, were formed during the advance stage of the Weichsel ice. The remaining smaller drift hills are of erratic orientation and are thought to be kames formed during the retreat stage of the ice. A few east-west trending eskers also occur.

During post-glacial times two basin peat bogs developed to the north and south-east of the Tynagh deposit. There is evidence that these grew out of lakes or fens since lacustrine deposits, containing fresh-water lamellibranchs, have been found in places beneath the peat.

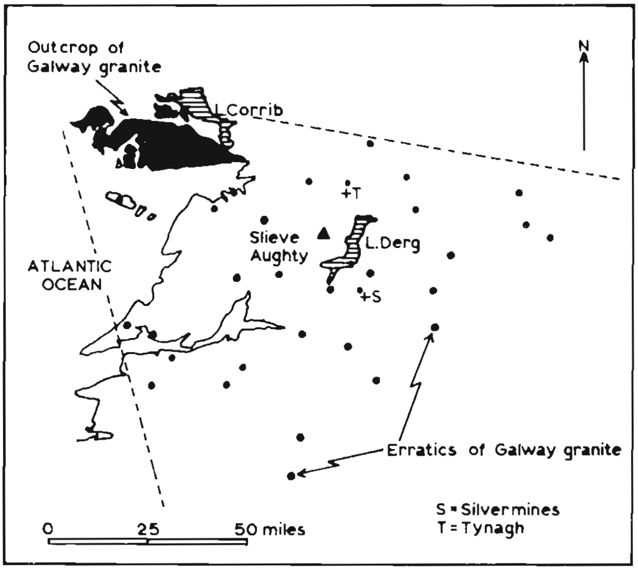


FIG. 2a. BOULDER FAN OF GALWAY GRANITE IN WESTERN EIRE.
(From Charlesworth, 1953,)

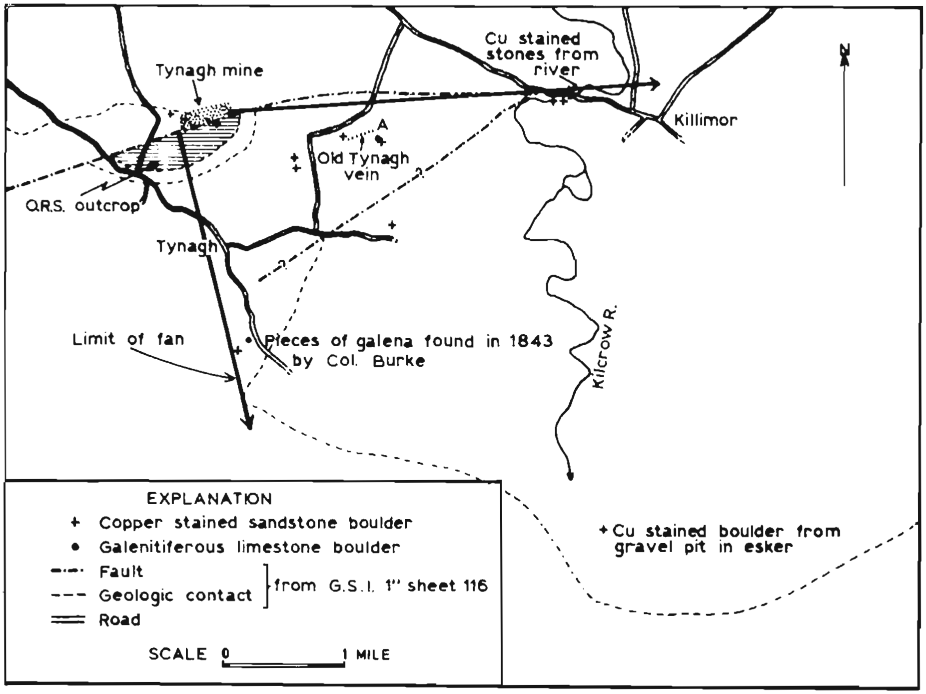


FIG. 2b. GLACIAL DISPERSION OF MINERALIZED BOULDERS FROM TYNAGH.
(Based on unpublished data of the Geological Survey)

At the time of these investigations, 90% of the land outside the bog areas was pasture, and 10% of the fields were cultivated (mainly for root crops and cereals).

The drift over the ore-body itself was found to be composed entirely of unstratified boulder clay or till, varying in thickness from 10 to 50 feet, and derived largely from limestone. The top 8 to 10 feet was a light grey-brown colour, and below this was commonly medium to dark grey. The till was all of the same age and lithologic composition, the colours corresponding with the oxidized and unoxidized portions, related to the position of the water-table. Soils now occur at the surface of the till throughout the area.

TECHNIQUES EMPLOYED

Soil and till samples were collected from surfaces exposed during the stripping operations by means of a trowel, a shallow pit being dug in order to avoid any contamination from the earth moving equipment. Outside the mine area, samples were collected by auger. Fragments larger than 1 inch in diameter were discarded in the field.

All samples were air dried at temperatures below 100°C. Soil, till and ore samples were sieved to minus 80-mesh following a light crushing to break up aggregates. Peats were ground in a pestle and mortar and then sieved to minus 80-mesh.

For analysis of copper, lead and zinc, a 3:1 mixture of nitric and perchloric acids was added to 100 mg. of sample and evaporated to dryness. This destroyed virtually all the organic matter. The residue was then leached in 0.5M HCl, from which solution copper was determined by diquinolyl, and lead and zinc by dithizone (G.P.R.C., 1964, 1962a, 1962b). Mercury was determined by an atomic absorption technique on a twin-cell apparatus developed by the Applied Geochemistry Research Group at Imperial College, London (James and Webb, 1964).

RESULTS

Investigation of the till

Size analysis of tills following wet dispersion showed that approximately 70% of both oxidized and unoxidized till material was minus 80-mesh in size, clay size particles forming approximately 28% of the sample in each case. Each of the metals analysed, i.e. copper, zinc, lead and mercury was found to concentrate to varying degrees in the clay fraction. This feature may be related only in part to sorption effects, however. Clay size material forms about 30% of the black mud ore itself, while a further 40% of the ore material consists of silt size fragments. These latter particles may be expected to at

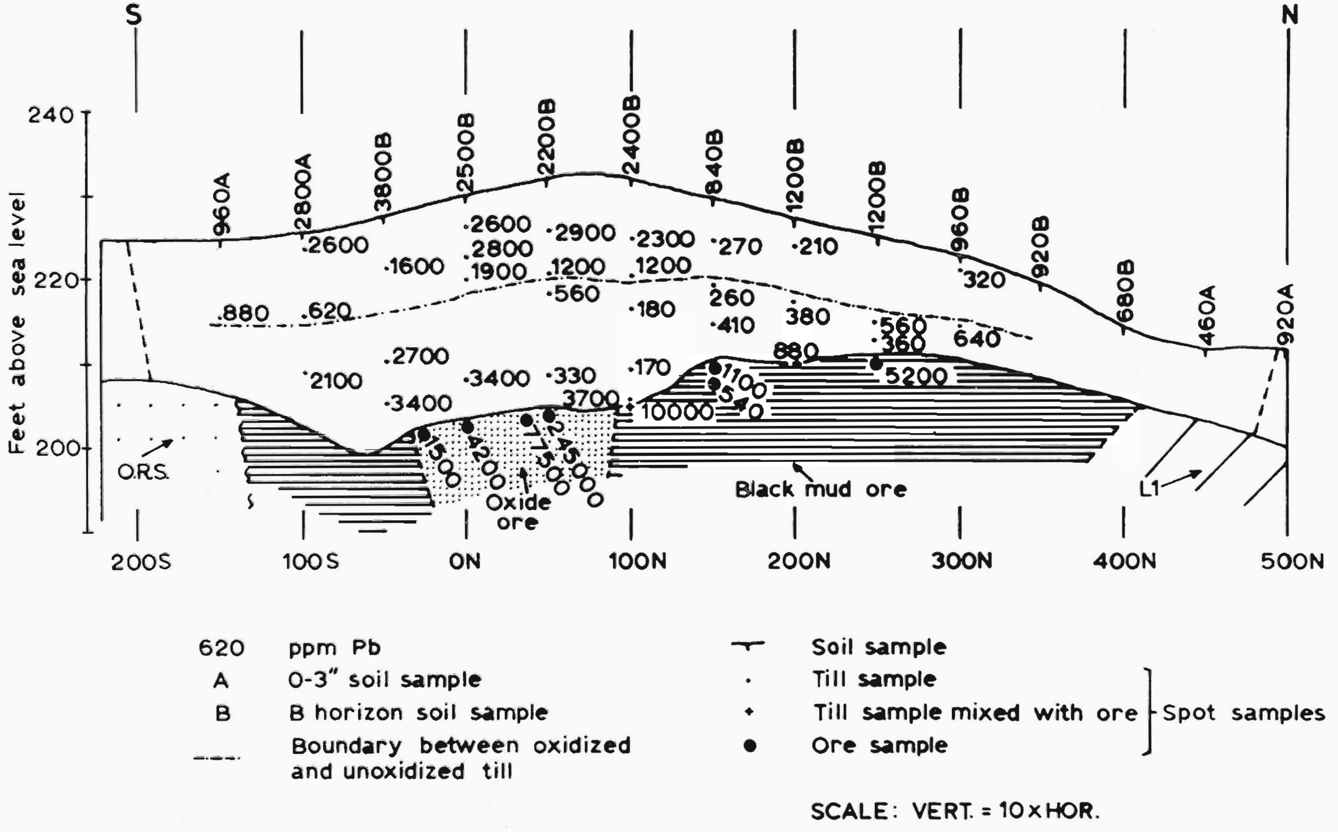


FIG. 3a. CROSS-SECTION 85W, TYNAGH - DISTRIBUTION OF LEAD VALUES.

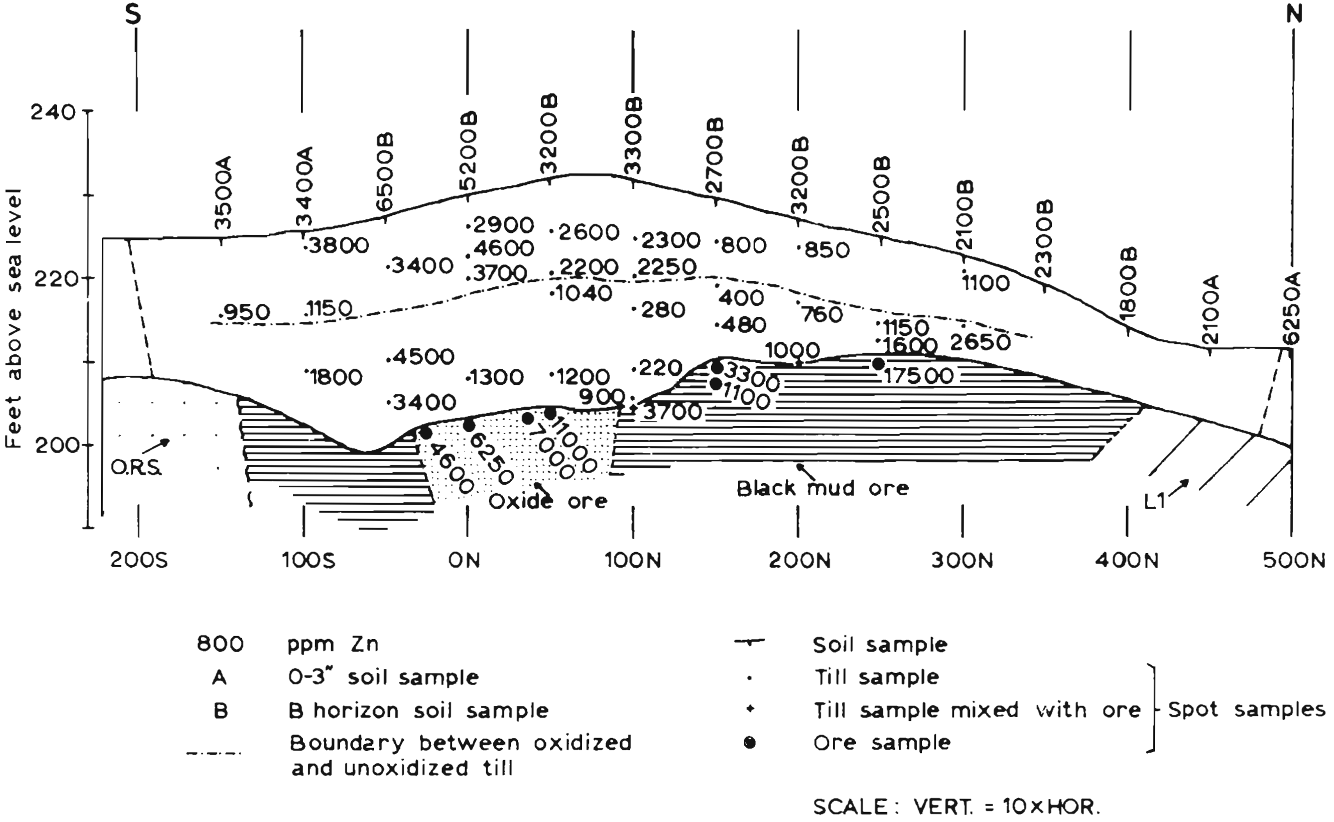


FIG. 3b. CROSS-SECTION 85W, TYNAGH - DISTRIBUTION OF ZINC VALUES

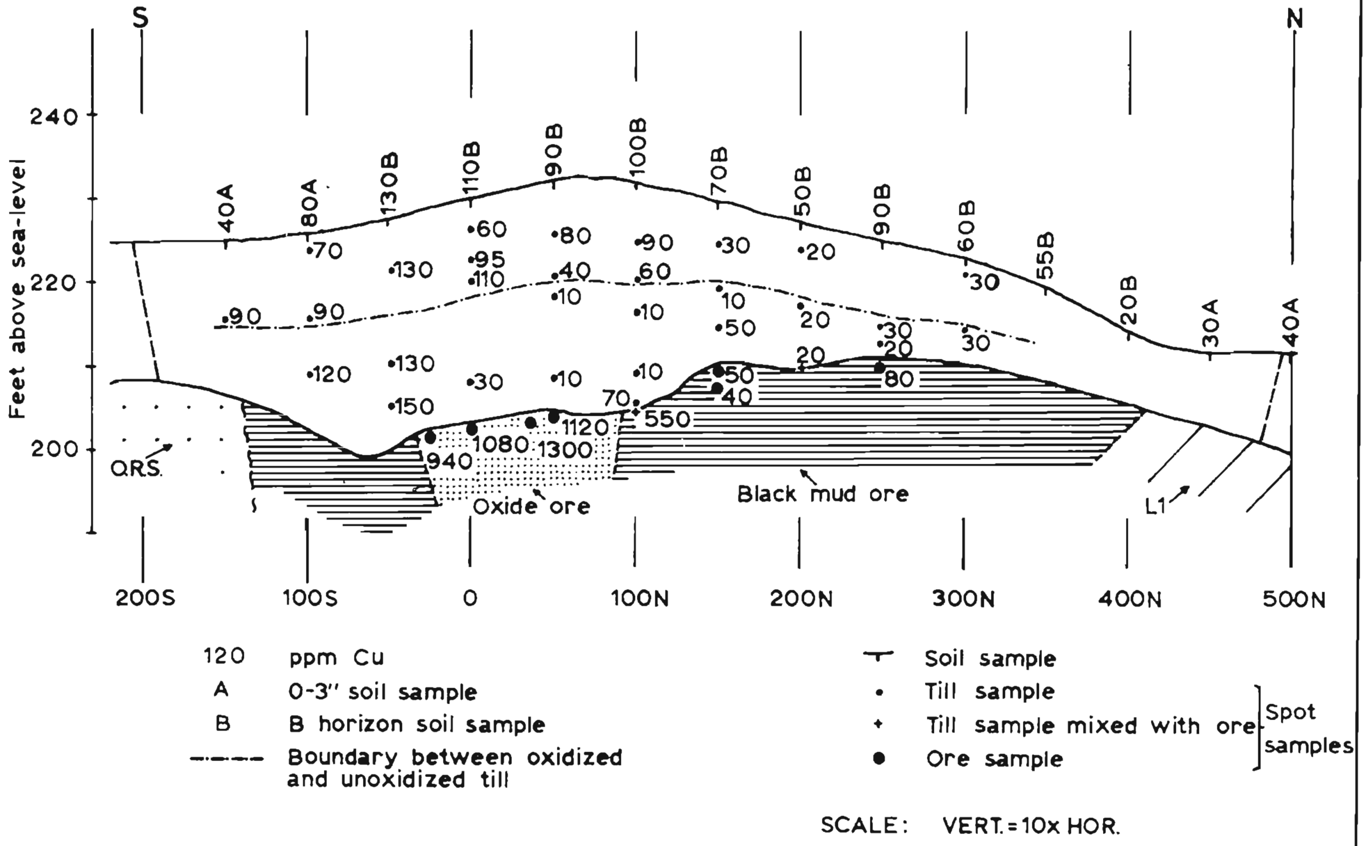


FIG. 3c. CROSS-SECTION 85W, TYNAGH - DISTRIBUTION OF COPPER VALUES.

least partially break down to clay size particles on weathering.

Dry sieving of similar, but undispersed tills, demonstrated that only minor variations of metal content occur in the undispersed size fractions smaller than 20-mesh. This is almost certainly due to the fact that clay and silt size particles form larger accretions. Thus the minus 80-mesh fraction used during routine investigations were representative of the samples as a whole.

The results obtained for the pH of the minus 80-mesh material from two profiles through soil and till to ore, showed that in all of the till samples the pH values fell within the range 8.3 to 8.5. The ore occurring immediately under the base of the till was slightly less alkaline (pH 7.85 to 7.9) and had presumably been modified by the alkaline environment above, since the pH of samples of secondary ore not in contact with the till was found to range between 3.9 and 6.3. It is significant that samples from the base of the till showed no signs of having been neutralized by acid solutions moving upwards from the underlying ore.

Figure 3 a, b and c illustrates the results obtained for samples collected from a typical geochemical cross-section across the centre of the ore-body. In this section, the results for the metal contents of the till ranged from 10 to 150 ppm for copper, 220 to 4600 ppm for zinc and 170 to 3700 ppm for lead. Here, as in the other sections, the outstanding feature of interest is the erratic distribution of high and low metal values. The distribution of the high values for each metal appears to be quite independent of the oxidation state of the till, and there is no general increase in metal values towards the base of the overburden.

The metal contents of the soils overlying the till in the section range from 40 to 130 ppm copper, 2100 to 6500 ppm zinc and 840 to 3800 ppm lead, but there appears to be no direct correlation between the values in the soil and those in the underlying till. It will be noticed that while the higher values are of a similar magnitude in both the till and the soil, in the case of the lower values, those in the till are somewhat lower than those in the soil.

Due to the thickness of the till, complete profiles from surface to ore were difficult to obtain. However, three channel sample cross-sections across the ore-body were eventually sampled. These also showed that the metal values within the till are very erratic - e.g. in one, 81W (Fig. 4 a, b and c) the results ranged from < 5 to 130 ppm for copper, 120 to 6400 ppm for zinc and 60 to 2500 ppm for lead. Once again the metal values in the soil were generally higher than those in the underlying till, and as in the earlier sections no consistent increase in metal values towards the base of the till was observed, although in several profiles, the ore was many times richer in metal than the till

FIG. 4a. DISTRIBUTION OF LEAD IN CHANNEL PROFILES THROUGH CROSS SECTION ALONG LINE 81W. (MINUS 80-MESH MATERIAL)

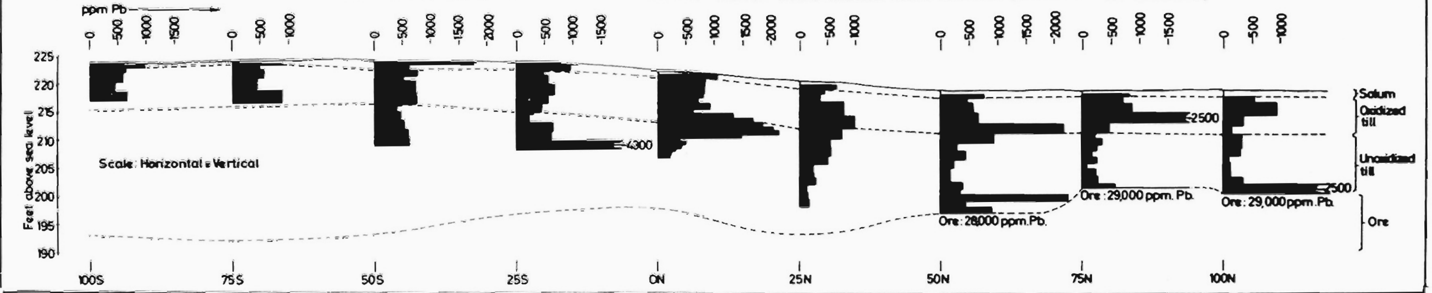


FIG. 4b. DISTRIBUTION OF ZINC IN CHANNEL PROFILES THROUGH CROSS SECTION ALONG LINE 81W. (MINUS 80 MESH MATERIAL.)

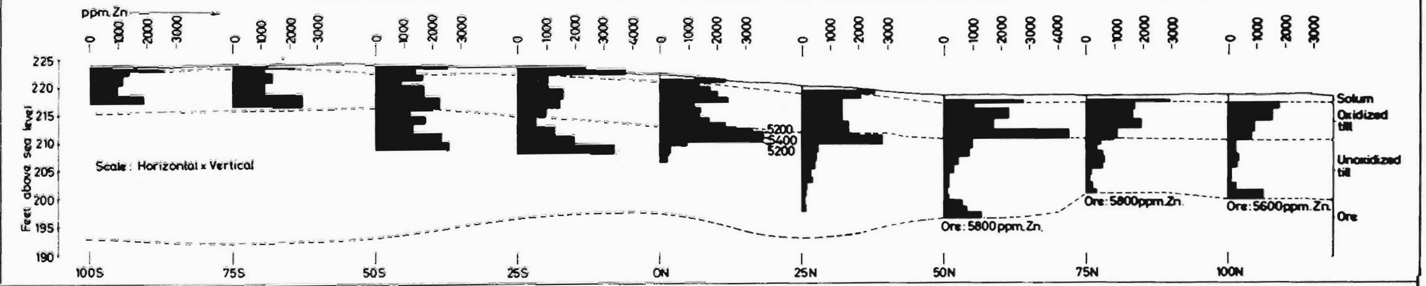
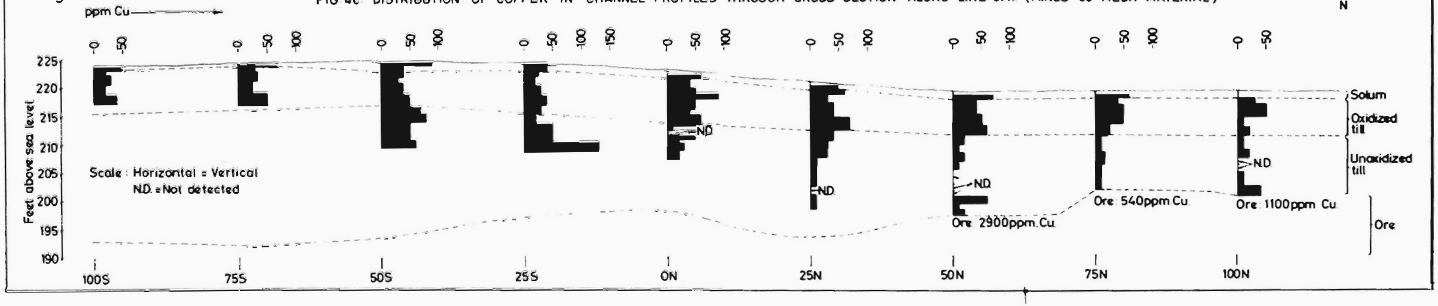


FIG 4c. DISTRIBUTION OF COPPER IN CHANNEL PROFILES THROUGH CROSS SECTION ALONG LINE 81W (MINUS 80-MESH MATERIAL)



DEPTH, FEET	HORIZON	DESCRIPTION	MERCURY CONTENT
			PPB Hg
0.70-1.00	Solum	Brown loam (B horizon)	390
1.00-2.35	Oxidized till	Grey-brown till, mainly L1 fragments	490
2.35-4.00		" , a little sandier	510
4.00-5.70		" , some Fe+++ blebs	420
5.70-7.60		" , some yellow lst.	200
7.60-8.70	Unoxidized till	Med.-dk. grey till, L1 & L2 fragments	290
8.70-9.75		" , some bn. lst.	500
9.75-10.85		" , L2 boulders	800
10.85-11.95		" , some sst. pebbles	490
11.95-13.00		" , "	420
13.00-14.10		" , "	340
14.10-15.30		" , mainly L1 frags.	190
15.30-16.60		" , rare Fe+++ blebs	460
16.60-17.40		" , "	600
17.40-18.90	Ore	Black mud mixed with oxides	18000

Table 1. Mercury contents in channel sample profile, solum-till-ore Line 81W, 75N.

DEPTH, FEET	HORIZON	DESCRIPTION	MERCURY CONTENT
			PPB Hg
0.00-0.75	Solum	Brown loam, A horizon	610
0.75-1.70		Brown loam, B horizon	1900
1.70-2.90	Oxidized till	Grey-brown till, mainly L1 fragments	350
2.90-4.35		" , "	440
4.35-5.70		" , sticky	560
5.70-7.20		" , L1 and L2 fragments	270
7.20-9.25		" , "	890
9.25-10.60	Unoxidized till	Med.-dk. grey till, "	700
10.60-12.10		" , "	450
12.10-13.60		" , "	760
13.60-14.90		" , "	600
14.90-16.00		" , "	890
16.00-16.40	Ore	Rubbly baritiferous orange oxides, trace of Cu staining.	9500

Table 2. Mercury contents in channel sample profile, solum-till-ore Line 73, 30W.

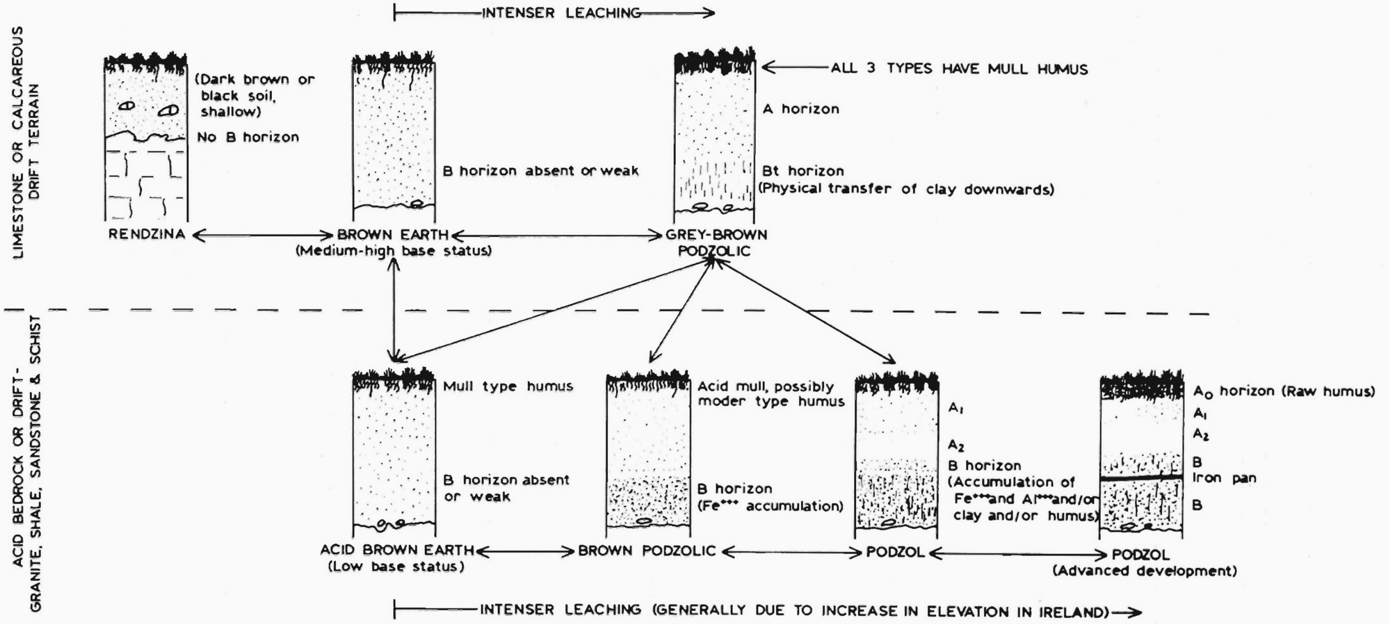


FIG. 5. TYPICAL SOIL PROFILES ENCOUNTERED IN FIELD AREAS, WEST-CENTRAL EIRE.

Figure 5. Typical soil profiles encountered in field areas, west-central Eire.

overlying it.

Cold extractable analyses for zinc (G.P.R.C., 1962c) were carried out on a number of samples of both till and soil. The results obtained indicated that in the majority of such samples, between 10 and 20% of the total metal was readily soluble. This figure might suggest that a relatively high proportion of the metal is held in exchange positions on soil colloids were it not for the fact that virtually all of the zinc present in the black mud ore was found to be readily extractable by this method, even though the metal is thought to be present mostly in the form of sulphides.

Cold extractable analysis for copper (G.P.R.C., 1962c) proved unsuccessful since the calcium carbonate matrix of the sample did not allow the buffer to control the pH of the reaction, and major interferences were encountered.

The mercury contents of till samples from two channel profiles collected over ore were found to range from 190 to 890 ppb. In one profile a strong concentration of mercury was observed in the B horizon of the soil relative to the underlying till, while in the other the soil contained somewhat less mercury than the underlying till. The ores at the base of the till contain 9,500 and 18,000 ppb mercury, although the till overlying the higher value contained slightly less mercury than the till overlying the lower value (Tables 1 and 2). There are no significant differences between the mercury contents of the oxidized and unoxidized tills in the profiles, nor is there a general increase towards the base.

Investigation of Soil

Figure 5 shows the typical soil profiles encountered in the field areas in west-central Eire. On calcareous terrain the grey-brown podzolic/brown earth/rendzina association is prevalent.

Grey-brown podzolic soils are characterized by a pronounced increase of the clay fraction in the B horizon, while in the brown earths, and rendzinas, which do not have a true B horizon, the clay fraction is constant throughout the solum. In a few places such as on the hilly Old Red Sandstone inlier south of the deposit, where the till was predominantly siliceous, acid brown earths occur, together with brown podzolics.

In the poorly drained areas gleysolic soils are common. These are mainly ground water gleys due to high watertable conditions reflecting local impermeability of the till. However, surface water gleys due to periodic flooding of streams also occur.

In areas of severe gleying, organic matter accumulates in the A horizon due to the absence of weathering of the organic compounds in reducing conditions. This gives rise to the peaty gleys, in which the surface vegetation is grass, moss, reed and sedge, rather than the true peat vegetation.

In the grey-brown podzolic profiles studies, a very slight increase in the content of copper, zinc, lead and mercury occurred in the B horizon, relative to the rest of the profile. In the brown earths copper, zinc, lead and mercury either increase slightly towards the base of the solum or are more or less constant. In most cases the enrichment factor between the solum and the till is approximately less than twofold.

Since the degree of variation of metal contents within the solum is generally less than twofold for copper, lead and zinc, it is only of minor importance which depth of soil is collected for routine soil samples. In order to avoid any surface contamination such as drill hole sludge or crop sprays, however, a depth of 9 to 12 inches was selected, 12 inches generally being the depth of the shallowest solum in the area. From the evidence available it appears that the sampling depth might be more critical for mercury.

As mentioned earlier, the range of metal values in the soil was generally somewhat higher than in the underlying till from which the soil was derived. The reason for this relative enrichment of metals in the soils may not be hard to find. Several authorities have demonstrated that a carbonate rock will yield a small amount of soil compared with a siliceous one. It can be shown that the minimum amount of calcareous till required to form 2 feet of soil would be approximately 10 feet. If the degraded till originally contained an average content of 1000 ppm metal, the content in the derived soil should be 5000 ppm if all the metal remained in the system. Thus, since it has been shown that the metal content of the soil is only twice or less than that of the underlying till, it is necessary to explain why the soil is less rich in metal than it theoretically should be, rather than finding methods by which the soil is being enriched from the underlying till under present day conditions.

Although the pH of the freely drained soils at Tynagh is usually slightly alkaline (in the range 7 to 8 pH units), and tends to inhibit the migration of metals, there is no doubt that some metal is removed as complexes by downward percolating rain water and carried away in the drainage. Some of the metal will be taken up by plants and possibly subsequently by animals. Over the centuries crops have been removed from the fields in considerable quantities and this no doubt would account for some of the metals removed from the fields. Furthermore, as the vegetation at Tynagh is generally gramineous (trees being rare except in hedgerows), the roots of the grasses and other plants are unlikely to extend into the C horizon, so that this vegetation will not replace the metals in the solum at the expense of the underlying C horizon to any great extent.

	Cu, PPM		Zn, PPM		Pb, PPM		Hg, PPM/PPB	
	LOG	NATURAL EQUIVA-LENT	LOG	NATURAL EQUIVA-LENT	LOG	NATURAL EQUIVA-LENT	LOG	NATURAL EQUIVA-LENT
Range of Values	0.7- 2.042	5-110	0.699- 2.343	5-220	1.000- 2.681	10-480	$\bar{2}.000$- 0.161	10-1450
Erratic Highs not Included in Calculation	2.439	275	2.778 2.820 3.176	600 660 5,200	3.395	2,480		
Geometric Mean	1.215	16.5	1.703	50.5	1.866	73.5	$\bar{1}.060$	114.8
Standard Deviation (s.d.)	0.314	-	0.404	-	0.357	-	0.408	-
Mean + s.d.	1.529	34	2.107	128	2.224	167	$\bar{1}.468$	294
+ (2 x s.d.)(Threshold)	1.843	70	2.511	324	2.581	381	$\bar{1}.876$	752
+ (3 x s.d.)	2.157	144	2.915	822	2.938	868	0.284	1,940
+ (4 x s.d.)	2.471	296	3.319	2,040	3.296	1,970	0.694	4,920
+ (5 x s.d.)	2.785	610	3.723	5,280	3.653	4,500	1.000	10,000
+ (6 x s.d.)	3.099	1,260	4.137	13,400	4.011	10,300	1.408	25,600
+ (7 x s.d.)	3.413	2,190	4.531	34,000	4.368	23,300	1.816	65,500
+ (8 x s.d.)	3.727	5,330	4.935	86,000	4.725	53,100	2.224	167,000
Number of Samples		92		90		92		90

Table 3. Statistical Data for Cu, Zn, Pb and Hg in Regional Soils, Tynagh Area.

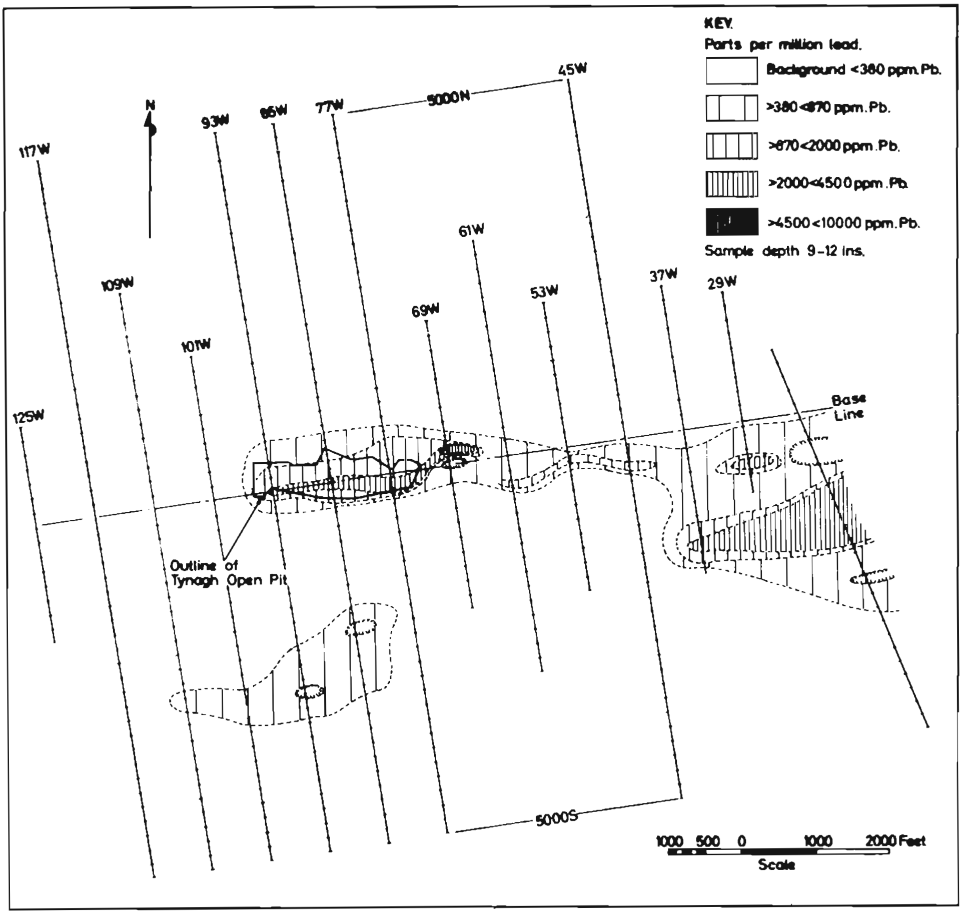


FIG. 6a. DISTRIBUTION OF LEAD OVER SOIL GRID (MINUS 80-MESH MATERIAL)

In contrast to the freely drained soils, under certain conditions copper, zinc, lead and mercury are highly concentraded in peats near anomalous metal sources. For example values of 1900 ppm copper, 77,500 ppm zinc, 4200 ppm lead and 4200 ppb mercury were encountered in peats in the immediate vicinity of the Tynagh deposit. These data indicate that where large amounts of metal are available, the degree of enrichment in peats is considerably greater than in freely-drained soils in the case of copper, zinc and mercury, but similar in the case of lead.

In some anomalous areas there was slight evidence that lead and mercury may concentrate in the surface layers of peats relative to the underlying organic material.

In routine investigations peats were sampled in the same way as freely-drained soils, i.e. at 9 to 12 inches. Generally speaking it was found that the presence or absence of peat did not appreciably affect the overall configuration of metal

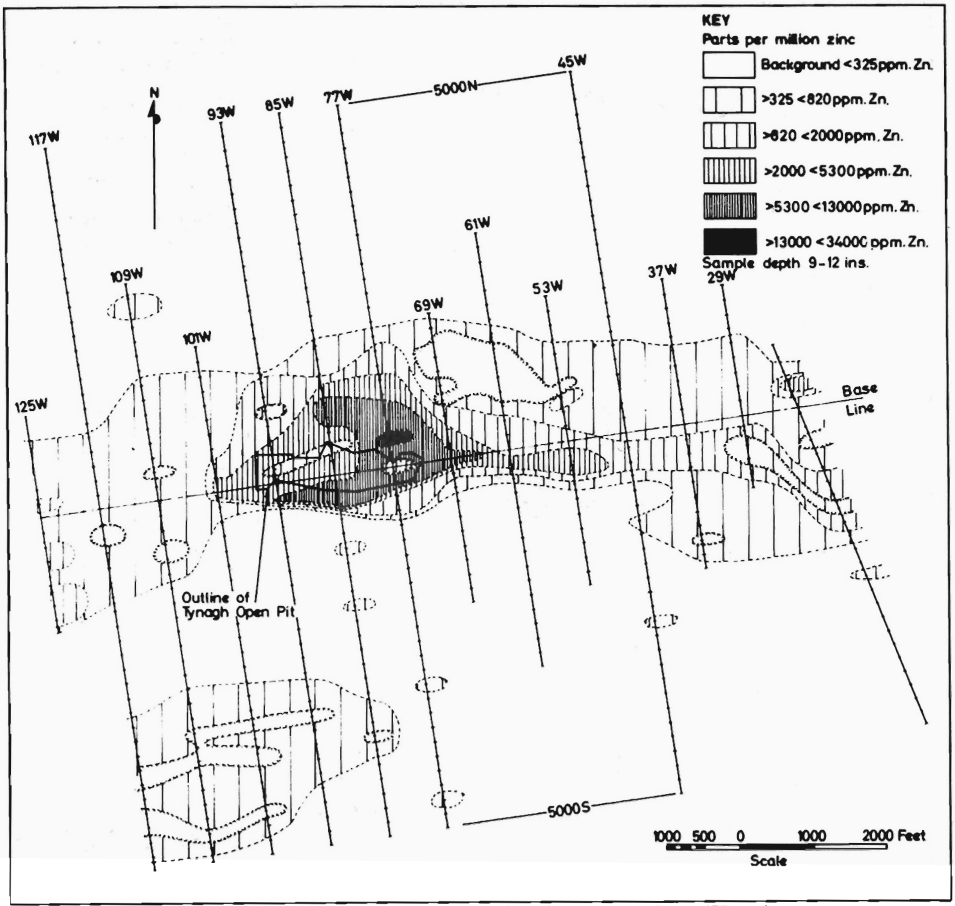


FIG. 6b. DISTRIBUTION OF ZINC OVER SOIL GRID (MINUS 80-MESH MATERIAL)

distribution in the case of copper, lead and zinc, the only effect being to enchance the anomalous values. In some background areas, however, the mercury content of peats is found to be higher than that in freely-drained soils. It is thought that this may be due to atmospheric precipitation of the metal and subsequent chelation by organic matter.

Soil Grid Around the Tynagh Deposit

Soils were collected at 9 to 12 inch depths at 200 foot intervals along north-south lines 800 feet apart. The traverse lines were laid out perpendicular to the last direction of advancing glaciation.

Threshold values (mean + 2 x standard deviation) were calculated on logarithmically transformed data for 100 samples collected over an area of 200 square miles around Tynagh within which the deposit is the only known ore occurrence (Table 3). Contour values were also calculated on the basis of the standard deviations of the same data.

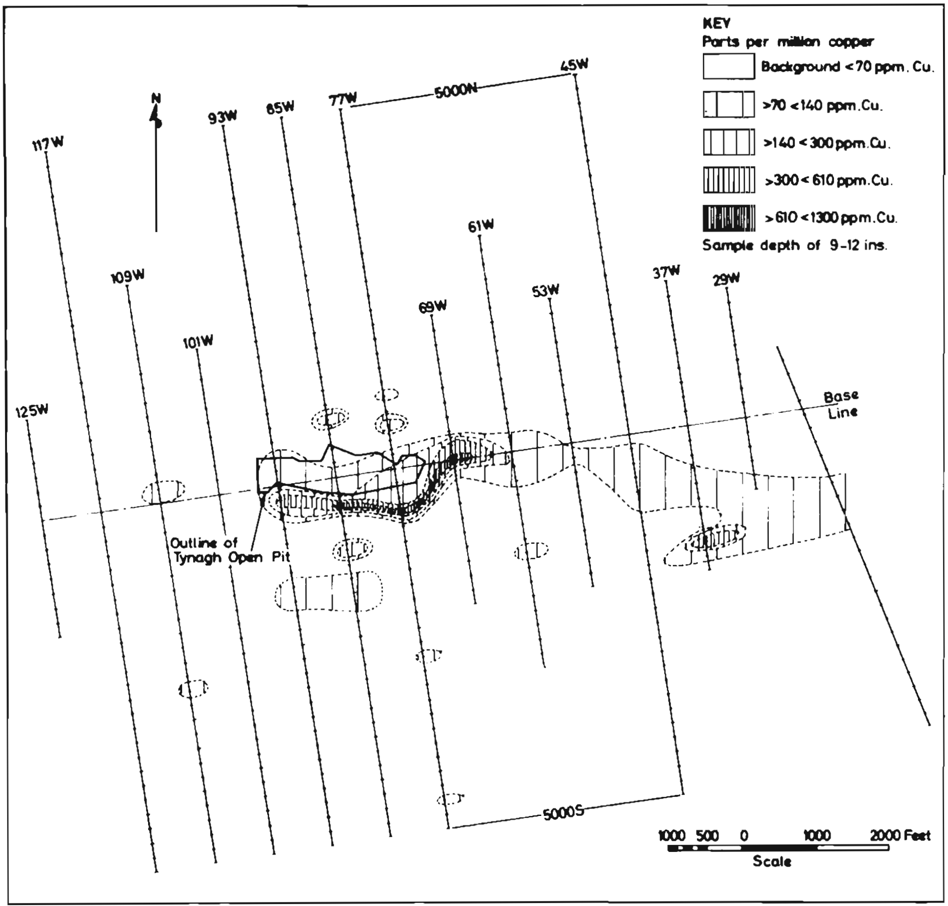


FIG.6c. DISTRIBUTION OF COPPER OVER SOIL GRID (MINUS 80-MESH MATERIAL)

Strong east-west trending anomalies, (Figures 6a, b, c, d) which were very similar in the cases of lead and copper, were detected for each of the elements. The anomalies begin at the western end of the deposit, and continue without noticeable broadening for a distance of more than a mile and a half. They could, undoubtedly, have been traced considerably further.

The results for both copper and zinc show occasional erratic anomalous points outside the main anomalies. In the case of lead no such points occur other than in the case of an unexamined anomaly to the south of the deposit. A further source of anomalous metal on Line 37 appears to be indicated by the lead, zinc and copper results. This presumed source gives rise to anomalies for each of these metals which coalesce further east with the anomaly from the main source.

The zinc results are, at first, slightly confusing and require comment. The main anomaly is considerably longer

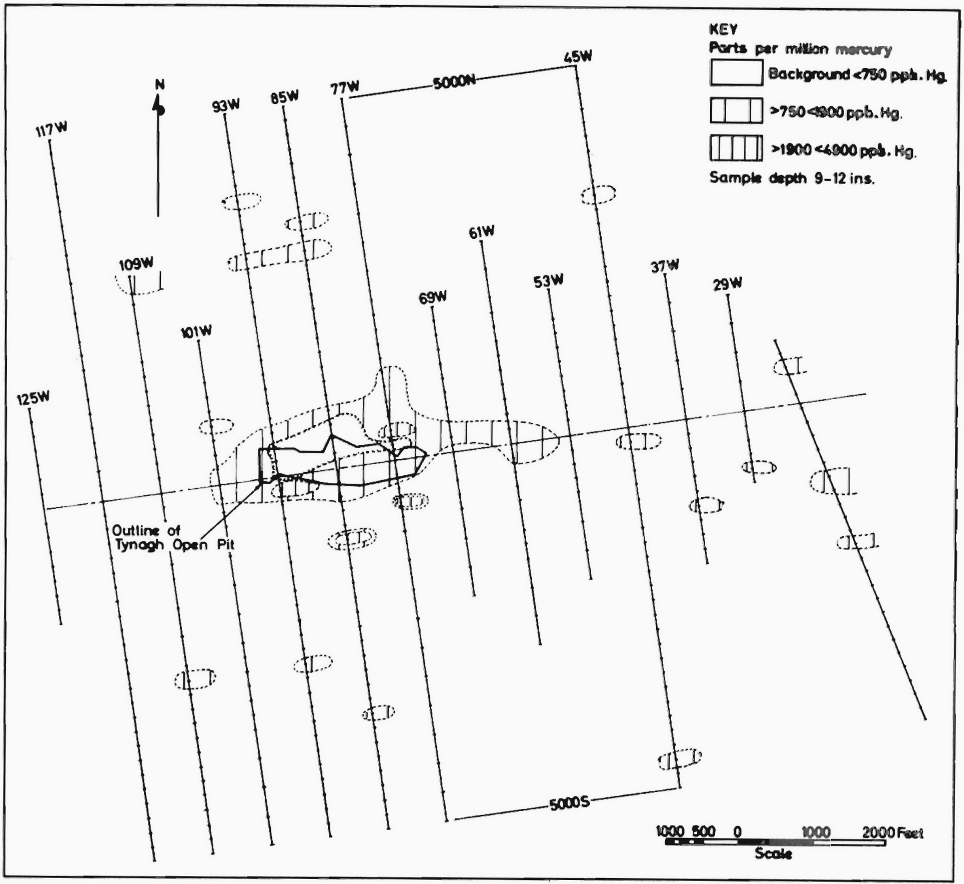


FIG. 6d. DISTRIBUTION OF MERCURY OVER SOIL GRID. (MINUS 80-MESH MATERIAL)

than that of copper, lead and mercury. Since there is no possible topographical explanation, this is interpreted as being due to another source of zinc lying to the west of the sampled area. It will be seen that the values rise westwards from the deposit. The spread of high values near the Tynagh deposit is due to the concentration of zinc in the peats. There is another large zinc anomaly to the south, as yet unexamined.

The mercury results are similar to those of copper and lead. However, there are numerous small, one-sample anomalies throughout the area, some associated with organic soils.

DISCUSSION OF RESULTS

From the results obtained during the present study it is possible to draw certain conclusions regarding the mechanisms responsible for the formation of the anomalous patterns within the till. Basically, two processes of formation are possible, i.e. syngenetic dispersion, in which the anomalous material would be laid down within the till at the time of its formation by the glacial erosion of the ore-body, and epigenetic dispersion in which the anomalous metal is introduced into the till after it has been deposited either by upward diffusion, biochemical activity or transportation by ground water.

Most of the evidence obtained in this study suggests that the former process was almost entirely responsible for the formation of the Tynagh till and soil anomalies. The completely random occurrence of metal values throughout the till is exactly the type of pattern to be expected of a distribution resulting from such a mechanism.

Further evidence of the glacial origin of the anomaly is to be found in the configuration of the distribution patterns of metals in the soils around tynagh. The narrow elongated pattern stretching away from the ore-body in the direction of the last ice-movement, and extending for a considerable distance beyond the mineralization itself, is striking evidence of the glacial origin of the anomaly.

It would indeed be extremely difficult to explain the observed distribution of metals on the basis of epigenetic dispersion. If the anomaly had been formed by these processes, it is reasonable to assume that the distribution of the metal in the till would have shown a gradational variation from the base upwards. Furthermore, the main soil anomaly would be expected to be confined to the area more or less directly over the ore (in the case of diffusion or biochemical transportation) or to a point where a transporting medium, such as ground water, comes to the surface. The fact that some peats in the vicinity of the ore are enriched in certain metals might be taken as indicating that some dispersion from the ore-body has taken place in the ground water. However, other evidence indicates that the source of this metal is more likely to be the enriched till and its overlying soil.

Since the soils of the area are mostly derived from the underlying till, a relatively close relationship between the overall pattern of distribution of metals in the soil and till is to be expected, and is in fact found. There is, however, strong evidence to suggest that some anomalous metal has been removed from both the till and soil as a result of weathering. Ground water is regarded as being the most likely agent of such a process, and evidence of its effects can be found in the peat bogs close to the mineralization which show a considerable enrichment in copper, zinc and mercury relative to background peats, but not of lead. Since lead is the least mobile of these elements, this distinction between metals is in keeping with the hypothesis of dispersion by ground water movement.

One problem created by the postulation of a glacial origin for the anomaly, is that the wide angle of dispersion of the boulder fan from Tynagh (about 80° - Fig. 2b), is at variance with the narrow pattern of the geochemical anomaly. This suggests that the two were not formed contemporaneously.

An explanation of this may be that the southward Saale glaciation hardly attacked the soft ore-body which was protected by the buttress of the sandstone hill to the south, although the mineralized sandstone was heavily eroded during this time. At the end of the glaciation, copper-stained sandstone boulders were left lying on top of the sandstone hill. In the intra-glacial period these boulders moved northwards off the hill by cryoturbation and solifluction and came to rest on top of the ore-body north of the fault. The subsequent Weichsel glaciation, moving almost due eastwards, acted in the optimum direction to erode the unprotected ore-body, and the surface boulders were incorporated into the Weichsel till.

Within the fan itself sulphide ore boulders, derived from the black mud, are far rarer than the copper-stained sandstone boulders. Although this is no doubt partly due to their softness, sulphide boulders would also have attracted more attention from the farmers clearing the fields, and building walls, and many of these may have been taken to the local smelter at the Old Tynagh Vein. The abundance of sulphide boulders within the stripped area suggests that there were originally far more on the surface within the fan area.

CONCLUSIONS

The present study has shown that geochemical methods of prospecting are capable of being successfully applied in areas of glacial terrain. Distinct syngenetic anomalies have been detected for copper, lead, zinc and mercury in the glacial tills overlying, and adjacent to the Tynagh deposit. These anomalies have been extended eastwards by ice movement and form a narrow pattern extending for a considerable distance from the sub-outcrop of the mineralized zone. As a result of this phenomenon, great care must be taken in the interpretation of anomalies in glacial areas, since only a small portion of a given anomaly may overlie the ore from which it is derived. In all such cases the key to interpretation is a thorough understanding of the glacial history of the area being prospected.

A further point of great interest is that, notwithstanding the presence of erratics, which can be shown to have travelled very considerable distances, the bulk of the matrix of the till is relatively local in origin and has probably only travelled distances of a few hundreds of yards or less.

Geochemical anomalies in the till can be clearly defined by the analysis of the minus 80-mesh fraction of soil samples collected from relatively shallow depths. In the Tynagh area, sampling at 200 feet intervals along lines spaced at 800 feet gave adequate coverage to detect the anomalies associated with the ore-body.

ACKNOWLEDGEMENTS

This project formed part of the research programme of the Applied Geochemistry Research Group at the Royal School of Mines, London under the general direction of Professor J. S. Webb.

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The writers also wish to express their gratitude to Dr. I. Nichol for presenting this paper at the Symposium on Geochemical Prospecting.

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A BRIEF SURVEY OF PROGRESS MADE IN BIOGEOCHEMICAL PROSPECTING RESEARCH AT THE GEOLOGICAL SURVEY OF CANADA 1962-65

J.A.C. Fortescue and E.H.W. Hornbrook*

INTRODUCTION

Methods of prospecting based on plants are generally divided into two groups, geobotanical methods and biogeochemical methods. Geobotanical methods involve relationships between the presence of a mineral deposit within a given landscape and the occurrence of morphological variations in common plants, or the presence or absence of indicator plant species. Biogeochemical methods of prospecting involve a direct relationship between the chemical composition of a mineral deposit and that of plants or vegetable materials which are found in the vicinity of the deposit. Both methods are generally applied in areas where the bedrock surface is covered with overburden (for a general account of these methods see Cannon, 1960 and Malyuga, 1964).

Compared with the better known geophysical methods, geochemical prospecting methods are in an early stage of development in Canada today. This is especially true of plant prospecting methods. In Russia and the United States, especially in areas where residual soils occur, geobotanical and biogeochemical methods have been used extensively, not only in the search for mineral deposits but also in prospecting for water and in geological mapping (Chikishev, 1965). In this paper we are concerned only with the use of plants for the location of metal mineral deposits.

To date there have been very few reports of geobotanical prospecting in Canada. An exception was an observation made by Shacklette (1964) who noted variations in the colour and form of flowers of common fireweed Epilobium angustifolium near uranium deposits at Port Radium in the Northwest Territories.

Biogeochemical prospecting has been shown to be feasible in many parts of Canada, largely as a result of research carried out during the past twenty years by Dr. H.V. Warren, Dr. R.E. Delavault and their numerous co-workers at the University of British Columbia. These researchers have demonstrated that, under certain landscape conditions, positive biogeochemical results can be obtained over mineral deposits containing any of at least twelve elements, including copper, zinc, lead, arsenic molybdenum and mercury (see references at end of paper).

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The biogeochemical prospecting research program at the Geological Survey of Canada

The need for systematic research in plant prospecting methods in Canada was recognized some years ago by Dr. R. W. Boyle. He suggested that the research program to be described here should be commenced by the Survey and it was he who suggested that greenhouse facilities for plant prospecting research should be provided on the roof of the new headquarters building of the Geological Survey of Canada when it was constructed in 1959.

A plant prospecting methods research program was commenced by the senior writer in November 1962. He was joined by Mr. Hornbrook in August 1964. In addition to these two full time staff the program has included the activities of three summer students during the summer of 1963, three during 1964 and four during 1965. For six months during 1964 the greenhouse was operated by Mrs. T. Dawes, and during the summer of 1965 a start was made in the field of geobotany by a graduate student from MacMaster University, Miss L. Usik. The first, orientation, phase of the program is designed to last five years and largely involves the setting up of laboratory facilities and field, laboratory and data processing methods. The second five year phase of the program, commencing in 1967, will involve systematic studies of the geobotany and biogeochemistry of areas in which known, but undisturbed, mineral deposits occur.

General objectives of the plant prospecting methods research program

Our research program is aimed at the provision of data on the scope and limitations of biogeochemical and geobotanical prospecting methods under Canadian conditions. This is a vast unexplored field of research which has only begun to be explored by Dr. Warren and his co-workers. When one considers the number of different kinds of mineral deposits and the diverse landscape types which occur in Canada, the magnitude of the problem of finding which plant species, or chemical elements in particular organs of common plants, are of value in prospecting, becomes apparent. Added to this, there is an almost complete lack of systematic data on the distribution and amount of minor chemical elements in Canadian ecosystems. Nearly all living organisms are found at or near the surface of the earth in what the ecologists call the "ecosystem". The term "ecosystem" was defined by Tansley to include both the "biome" and the habitat in which the biome lives. The "biome" is the whole complex of micro-organisms, plants and animals which live together as a sociological unit. Thus we have to establish normal values for the distribution of minor elements in defined rock, soil and vegetation systems before we can distinguish abnormalities resulting from the influence of mineral deposits.

The general objective of the plant prospecting methods research program is to carry out a number of systematic studies of the plant ecology and the rock, soil, and plant geochemistry of landscapes in the vicinity of known, but undisturbed, mineral deposits. Special efforts will be made to carry out soil and plant investigations of a given area at "an instant in time" with the sampling program and the chemical analysis program both being as comprehensive as is practical. One advantage of working near drilled but undisturbed mineral deposits is that the results of the plant prospecting research program can often be directly compared with those of geological, geophysical and geochemical methods which have been used to discover the deposit.

OUTLINE OF PROGRESS - 1962-65

In this short paper it is not possible to describe in detail all the experience gained during the past three years. We have therefore confined our remarks to (1) a description of the moveable laboratory unit, (2) an outline of collecting, chemical and statistical analysis methods used on vegetable material, (3) a description of some preliminary results of greenhouse studies, (4) a description of an investigation carried out in a peat bog away from known mineral deposits and (5) the preliminary results from two experiments carried out near known, undisturbed deposits. It should be stressed that the methods and results described here are largely preliminary and the field investigations do not represent examples of the type of more systematic studies which we shall carry out later on.

Laboratory facilities

In order to establish methods to carry out systematic studies of the minor element content of associated rocks, soils and plants, and to make systematic descriptions of landscapes from which the samples were collected, methods for the gathering of data of all kinds has had to be carefully organized. The project plan requires that laboratories be available in the field to handle processing of large numbers of mineral and vegetable samples of different kinds and that each sample should be analysed chemically for a relatively large number of minor elements. In addition, the analytical methods used must be simple enough to be carried out by summer students (who usually have little previous analytical training). The descriptive results from the field observations and the results from the chemical laboratories should be prepared in a form in which they may be readily interpreted, so that further sampling at the same "instant in time" can be planned on the basis of results obtained.

Much progress has been made towards the solution of these problems. The problem of laboratory space was solved by the design and construction of a "moveable laboratory unit" consisting of two specially designed house trailer laboratories.

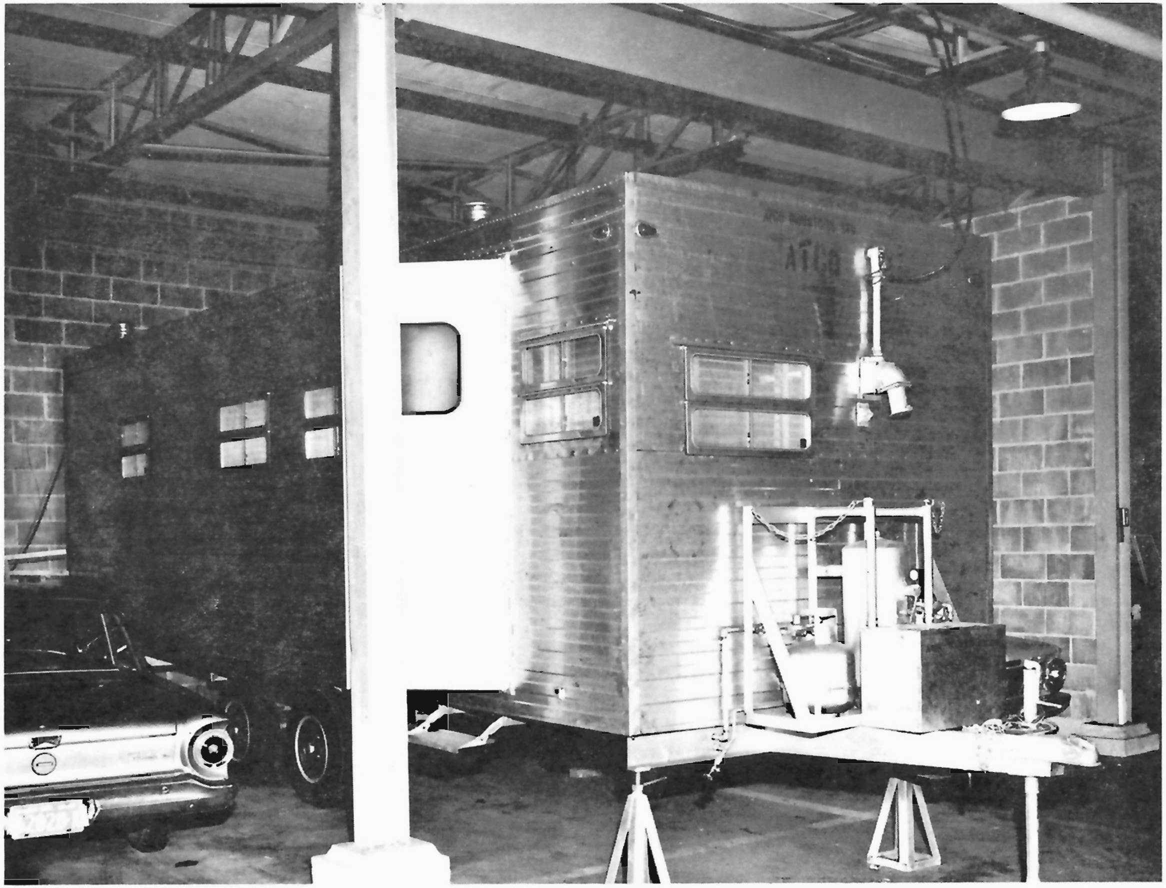

Plate I. The moveable biogeochemical laboratory unit in winter quarters. The sample preparation laboratory.

Plate II. The moveable biogeochemical laboratory unit in winter quarters.
The spectrographic laboratory.

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OPERATOR   2        METHOD   3        DATE OF ANALYSIS  57        FILM NUMBER   3        YEAR     33        SITE SET  98
                                                                                         PROJECT  39        BATCH      C


PPM METAL IN ASH         COPPER


           17500.0
           10000.0                                                              COPPER
            7500.0
            5000.0                                                 ASH P.C.     ASH          OVEN DRY
            3750.0       F
            2500.0       F                                       A  5.82        250.00       14.5500
            1750.0       F                                       B  5.56        250.00       13.9000
            1000.0       F                                       C  2.78        250.00        6.9500
             750.0       EF      L                               D  3.22        250.00        8.0500
             500.0       EF     KL    P                          E  2.21        750.00       16.5750
             375.0       EF     KL    P                          F  2.46       3750.00       92.2500
             250.0    ABCDEF  IJKL NOP                           G  3.80        175.00        6.6500
             175.0    ABCDEFGHIJKLMNOP                           H  5.41        175.00        9.4675
             100.0    ABCDEFGHIJKLMNOP                           I  5.85        250.00       14.6250
              75.0    ABCDEFGHIJKLMNOP                           J  4.74        250.00       11.8500
              50.0    ABCDEFGHIJKLMNOP                           K  3.70        500.00       18.5000
              37.5    ABCDEFGHIJKLMNOP                           L  3.37        750.00       25.2750
              25.0    ABCDEFGHIJKLMNOP                           M  3.59        175.00        6.2825
              17.5    ABCDEFGHIJKLMNOP                           N  4.51        250.00       11.2750
              10.0    ABCDEFGHIJKLMNOP                           O  3.70        250.00        9.2500
               7.5    ABCDEFGHIJKLMNOP
               5.0    ABCDEFGHIJKLMNOP                           TOTAL         8275.00      265.45
               3.8    ABCDEFGHIJKLMNOP
               2.5    ABCDEFGHIJKLMNOP                           MEAN           551.67       17.70
               1.8    ABCDEFGHIJKLMNOP
               1.0    ABCDEFGHIJKLMNOP                           SUM SQ    11464333.33     6326.53
                .8    ABCDEFGHIJKLMNOP
                .5    ABCDEFGHIJKLMNOP                           S.D.           904.92       21.26
                .3    ABCDEFGHIJKLMNOP
                .1    ABCDEFGHIJKLMNOP                           COEFF VAR      164.03      120.12
NOT DETECTED
                                                                 MEDIAN         175.00        9.47
SAMPLE NUMBER         ABCDEFGHIJKLMNOP
MASTER                 2 347 8659998 8                           MASTER       2 347 8659998 8
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PARTS/MILLION(ASH WEIGHT BASIS)

Figure 1. Computer printout data sheet for copper in a batch of 15 samples. The letters A – O refer to the samples of the same material collected from each of fifteen sample sites. The letter P refers to the value for copper obtained from a reference standard sample which is not included in the statistical measures.

These trailers are designed to be used the year round, in the field in the summer time and in a heated garage at headquarters during the winter months (Plate I & II). The sample drying and subsampling of vegetable material and the preparation of herbarium samples for geobotanical investigations is carried out in one trailer. The second trailer is used for ashing and chemical analysis of the different kinds of samples. Experience has shown that, using two operators, the spectrochemical method, as set up at present, will determine semiquantitatively on a routine basis nine elements and a reference standard in thirty samples of vegetable material during each day. The results from the spectrographic method are obtained by visual comparison of the spectrum of the unknown samples with that of a master film made with a set of synthetic plant ash base standards. The results as read off are recorded directly on special forms which allows the data to be later punched on I.B.M. cards and the cards processed by a special computer programme which provides a printout of the results. Each batch of fifteen samples generates ten pages of printout, one page for each element (Fig. 1). On each page results are shown as a histogram and as an array as parts per million on an ash and an oven dry weight basis. Simple statistical measures (for example standard deviation and mean values) are printed out for each column of data. Experience has shown that it takes half a man day to plot and record the statistical measures for a batch of samples, a job which the computer achieves in two and a half minutes!

So far both laboratories have been tested out separately on a routine basis. The sample preparation trailer was used in the Moose River area of northern Ontario last summer while the spectrographic trailer was in Ottawa. Both trailers will be used in the field during the summer of 1966. Details of a moveable spectrographic trailer similar to the one described here will be given in a publication by Holman and Durham (1966).

Methods

Space does not allow for a complete description of the field and laboratory methods which have been developed for the plant prospecting research program. Perhaps the most important innovation is the organization of the field and laboratory work on the basis of "site sets" of data. The field sampling and laboratory processing is carried out on site sets of material, each of which contains not more than fifteen samples. The number fifteen was originally arrived at by subtracting one from the total number of exposures which can be placed on a single spectrographic film. The fifteen samples included within a site set are generally derived from fifteen stations located at regular intervals along a line, or from fifteen points within a sample plot. In either case a number of batches of like material are collected within each site set. For example, in each of the twelve plots (site sets) located in the Moose River area in 1965 the following batches of different materials were collected:

		Batch number	Number of samples
TREES	Current needles	1	15
	Current twigs	2	15
	Second year needles	3	15
	Second year twigs	4	15
	Third year needles	5	15
	Third year twigs	6	15
	Upper bark	7	15
	Middle bark	8	15
	Lower bark	9	15
SOIL	Humus	10	15
	B horizon	11	15
	C horizon	12	15
	Total	12	180

In the field it was found that it took a three man crew two days to complete the collection of the 180 samples included within a site set. Using the sample preparation trailer the same crew would take two more days to prepare air dry subsamples of the material ready for oven drying prior to ashing. In the laboratory it was found that two men could ash and spectrograph two batches of samples per day on a routine basis. In this way it was possible to balance the sample collection and preparation time with the time taken for chemical analysis of samples and, allowing for transport of the samplers to and from the field, it would be possible to complete the collection, processing and recording of all results from a site set during six man days of each two man crew. It should be stressed that these methods and laboratory facilities have been designed and set up specifically for research in biogeochemical prospecting methods. In any application of the findings of our research to practical prospecting by a mining company there would, of course, be no need for such elaborate sampling, analytical or computational methods.

After subsampling of each field batch (for example the dividing up of foliage material into current growth, needles and twigs; second year growth of needles and twigs; and third year growth of needles and twigs) the batches are oven dried overnight at 80°C. Ten gram portions of each oven dry sample are placed in 50 ml pyrex beakers and dry ashed in a muffle furnace. The muffle furnace temperature is regulated during the ashing cycle by a cam operated thermostat. This allows the temperature to rise slowly to 435°C and then remain constant until the end of an 8 hour cycle. In the case of most samples this produces a clean white ash, a 10 mgm portion of which is then placed on a sugar impregnated ½" diameter graphite platrode. A few drops of sugar solution (containing a small amount of indium as an internal standard) is used to fix the ash to the surface of the platrode. After drying, the platrode is rotated at 10 rpm for 20 seconds and sparked using a flat graphite upper electrode. The light emitted is passed through a 1.5 metre Jarrell-Ash spectrograph

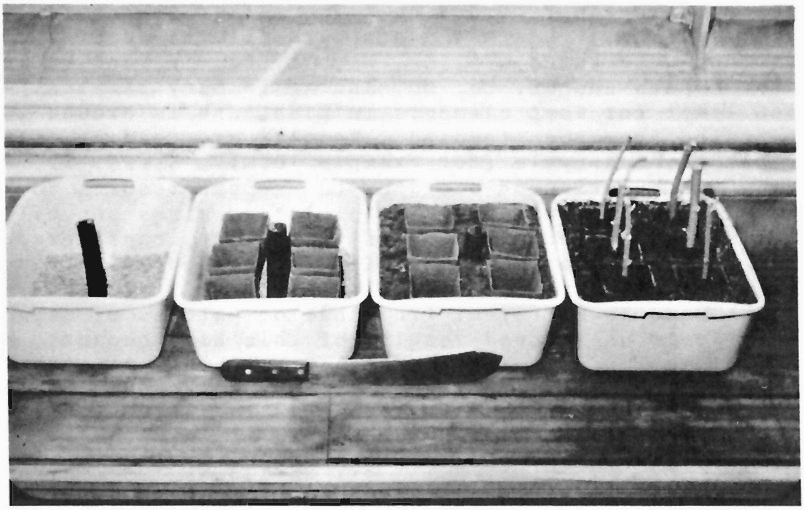

Plate III. Method used for planting out willow cuttings. Left to right: Pan with gravel layer and bottom watering tube; pan with six peat pots in position on gravel; pan with peat surrounding the peat pots; and pan with willow cuttings planted out in the peat pots.

Plate IV. General view of the greenhouse showing willow cutting experiment in progress.

and the spectrogram recorded on film. After processing the film is matched visually against a standard film as described above. This method detects Cu, Pb, Zn, Ni, Ti, Ba, Sr, and Mn in almost all ash samples and Cr, Co, Mo, and Ag in many samples. The detection limit for most elements in plant ash is around 10 ppm, as indicated from the standard. Results are read at only six intervals per log cycle (for example 10, 17, 5, 25, 37, and 75 ppm). An experienced operator can repeat results for the same element in the same unknown sample plus or minus one of these intervals. This precision is, at the moment, considered adequate for the project. Considerable bias is introduced in results for some batches owing to the fact that the matrix of the synthetic plant ash base is different from that of batches of unknowns. We are able to use biased results of this kind because, as will be shown later on, the results with a batch are relative to one another. When atomic absorption apparatus is added to the laboratory (in the near future) it is planned to carry out frequent accuracy checks on the spectrographic data. It is also planned to use this instrument to carry out checks of this kind and other more specialized analyses of plant material when the laboratories are at headquarters during the winter months.

Before the moveable laboratory unit is fully operational several problems still remain to be solved. We need to set up methods for routine minor element analysis of soil extracts, soils and rocks and we need to install and set up the atomic absorption apparatus. It is hoped that the laboratories will be fully operational for the summer of 1967.

Greenhouse experiments

A greenhouse is potentially a very important part of a biogeochemical and geobotanical prospecting methods research unit because it provides a controlled environment in which plants can be grown for detailed study. Up to now little progress has been made in our greenhouse owing to lack of staff to tend year round experiments. The feasibility of growing forest plants in the house during the summer season was established during the summers of 1963 and 1964 when preliminary experiments involving willow cuttings and birch trees were carried out.

The willow cuttings were obtained from the Petawawa Forest Experimental Station (by kind permission of the then Director Dr. C. Place). The cuttings were first planted out six at a time in plastic washing bowls using the procedure shown on Plate III. After the cuttings had rooted in the peat pots containing soil for four weeks the peat pots were transferred, in fours this time, to containers containing sand (Plate IV). Solutions containing small amounts of one or more of four minor elements (lead, nickel, cobalt or silver) at one of four levels of concentration were added to each pan. In some cases the whole treatment was added at once and in other cases treatments were added weekly over a ten week period. A second, smaller, set of willow experiments, involving single plants, was carried out to discover if it was feasible to use artificial mixtures of non-radioactive lead and strontium isotopes as tracers. Both series of experiments gave positive results. In the first case it was shown that although one treatment including all four elements at the hundred ppm level killed the plants in a few days a single treatment of one element (as nitrate) at this concentration level could be added without harm to the plants. Of the four elements, cobalt gave the most reliable results in the uptake experiments. Mass spectrographic analyses of the ash and soils in which the isotope experiments were carried out indicated that artificial mixtures of non-radioactive isotopes could be used as tracers on the scale at which the experiments were carried out.[1]

A second set of greenhouse experiments involved the development of a technique for bringing small plants and the natural soil in which they are found into the greenhouse for detailed study. This procedure was carried out as follows. A circular trench was first dug around a small tree growing in the forest. The sod containing the tree was then trimmed to fit exactly a four gallon plastic garbage can. By means of a bottomless can (of the same type as used in the greenhouse) the sod containing the plant was transferred to a clean can in which a two inch layer of pea gravel had been placed at the bottom. The plant soil and can were then moved into the greenhouse where holes were cut at the bottom of the can to allow bottom watering of the plant from a plastic pan in which the can was placed. In one experiment of this kind it was found that a small amount of Co^{66} added to the water in the pan was detectable in the different parts of the soil and in the different organs of a tree growing in it after only three months in the greenhouse.

As a result of the experience which has been obtained during these trials we feel confident that meaningful experiments along these lines can be carried out in the greenhouse later on as required.

Field investigations away from mineral deposits

Two experimental investigations of this kind have been carried out to date, one in the Moose River area in 1965 (MacLaren, 1966) and the other in the Mer Bleue peat bog during the summer of 1963. We shall deal here only with important aspects of the Mer Bleue investigation. The Mer Bleue is a typical peat bog of the type found in eastern Ontario (Graham and Tibbetts, 1961). The object of our investigation was the establishment of methods for the systematic study of the biogeochemistry of peat bogs along the lines pioneered for prospecting

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[1] The writers would like to thank Dr. R.K. Wanless for his help in this experiment and for mass spectrographic analyses made on the samples supplied by us at the end of the growing season.

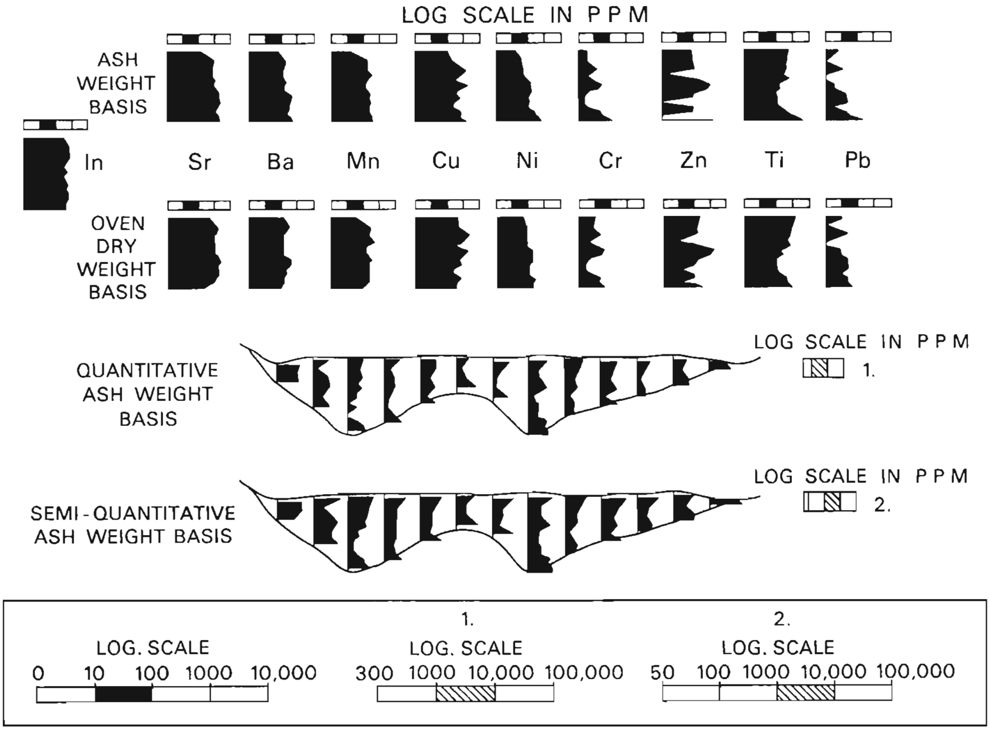

Figure 2. Results obtained from the Mer Bleue investigation I. At the top of the figure the vertical distribution of nine chemical elements in samples collected at intervals of two feet down a hole are shown. The results plotted at the top profile are on an ash weight basis and those below on an oven dry weight basis. Note the similarity of the vertical distribution patterns. The results in the two profiles near the bottom of the slide show vertical distribution patterns for the titanium content of the peat samples as determined on a quantitative or semi-quantitative basis. In this case the vertical distribution patterns are very similar.

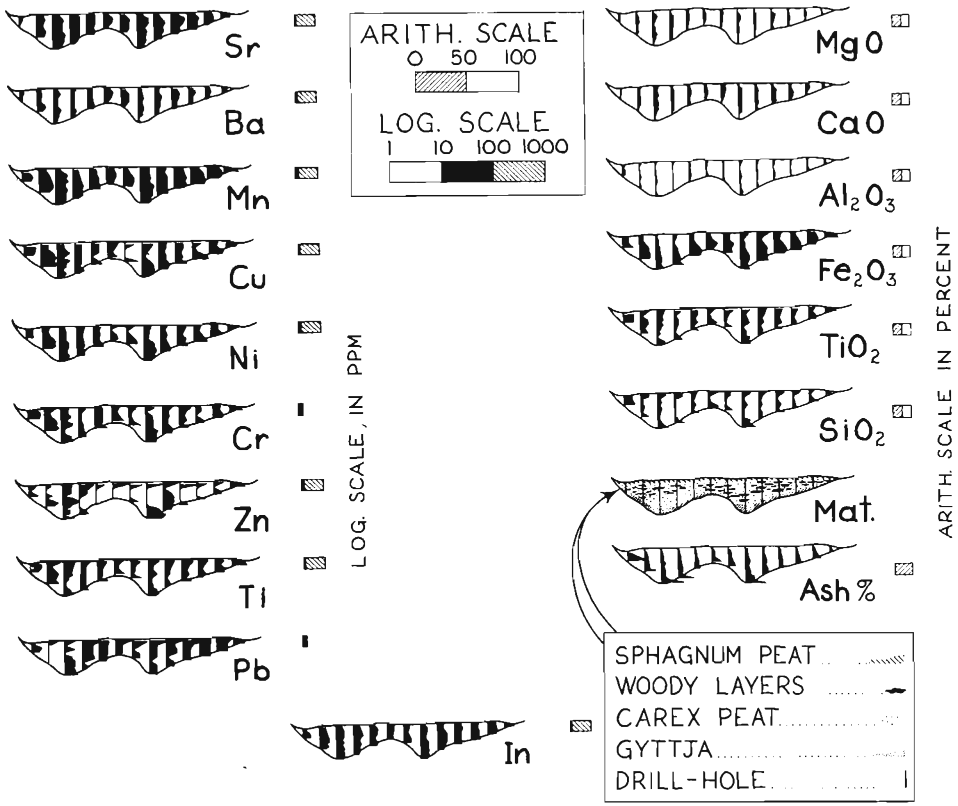

Figure 3. The vertical distribution of nine minor elements and six major elements (expressed as oxides) in thirteen holes spaced at two hundred foot intervals along a traverse across the middle arm of the Mer Bleue peat bog near Ottawa, Ontario. The indium was used as a reference standard during the determination of the minor elements by the semi-quantitative spectrochemical method described in the text.

purposes by Salmi (1950) in Finland. Sample cores were collected by means of a three inch Shelby tube sampler from sample points located at 200 ft intervals across the middle and south arms of the bog. Samples for chemical analysis were collected at 2 foot intervals down each hole. After extrusion from the sampler each core was tied in plastic sheet for transport to the laboratory. In the laboratory the cores were unwrapped and allowed to become air dry. When air dry a channel sample from the whole length of each core was collected and oven dried at 110°C. Ten gram portions of the oven dry material were ashed and spectrographed as described above. A second portion of the ash was analyzed for major elements by a quantitative spectrochemical method due to Cameron and Horton (1966). In this way ten elements (An, Cu, Mn, Ni, Ba, Sr, Cr, Pb, Ti, Ag) were determined semiquantitatively and six elements (Si, Al, Fe, Ca, Mg, Ti) by a quantitative method.

Some of the results are shown in Figure 2. The top part of the figure shows the vertical distribution patterns for nine minor elements in a single hole plotted on an ash weight basis at the top of figure and on an oven dry weight below. It is evident that either base for the results yields similar distribution patterns. For the sake of convenience we chose to express all results on the ash weight basis during this investigation. Only one element, titanium, was determined both quantitatively and semiquantitatively. The lower part of the figure shows both sets of results for the vertical distribution patterns for the titanium content of the ash of samples collected at thirteen points located on a traverse across the bog. It is evident that the vertical distribution patterns are remarkably similar although, as was discussed above, the indicated titanium content on the semiquantitative scale is subject to considerable bias. From the practical point of view of interpreting vertical distribution patterns, the results obtained from the rapid method are of almost equal value to those found by the quantitative method. Similar accuracy checks are now planned for other minor elements determined semiquantitatively.

On Figure 3 the results for the vertical distribution of fourteen elements (or oxides) in each of the thirteen holes have been brought together. Although detailed interpretation of the vertical distribution patterns for all elements cannot be carried out from this small figure two general observations can be made. The first is that each element has a distinctive vertical distribution pattern within the bog which is repeated from hole to hole across the traverse, and the second is that, in the case of zinc, relatively high values were found at the surface and near the bottom of the holes with low values in between. Detailed interpretation of these results will be made later. The main purpose of Figure 3 is to illustrate our approach to the study of the minor element content of peat bogs. In future other studies along these lines will be carried out in bogs located above mineral deposits.

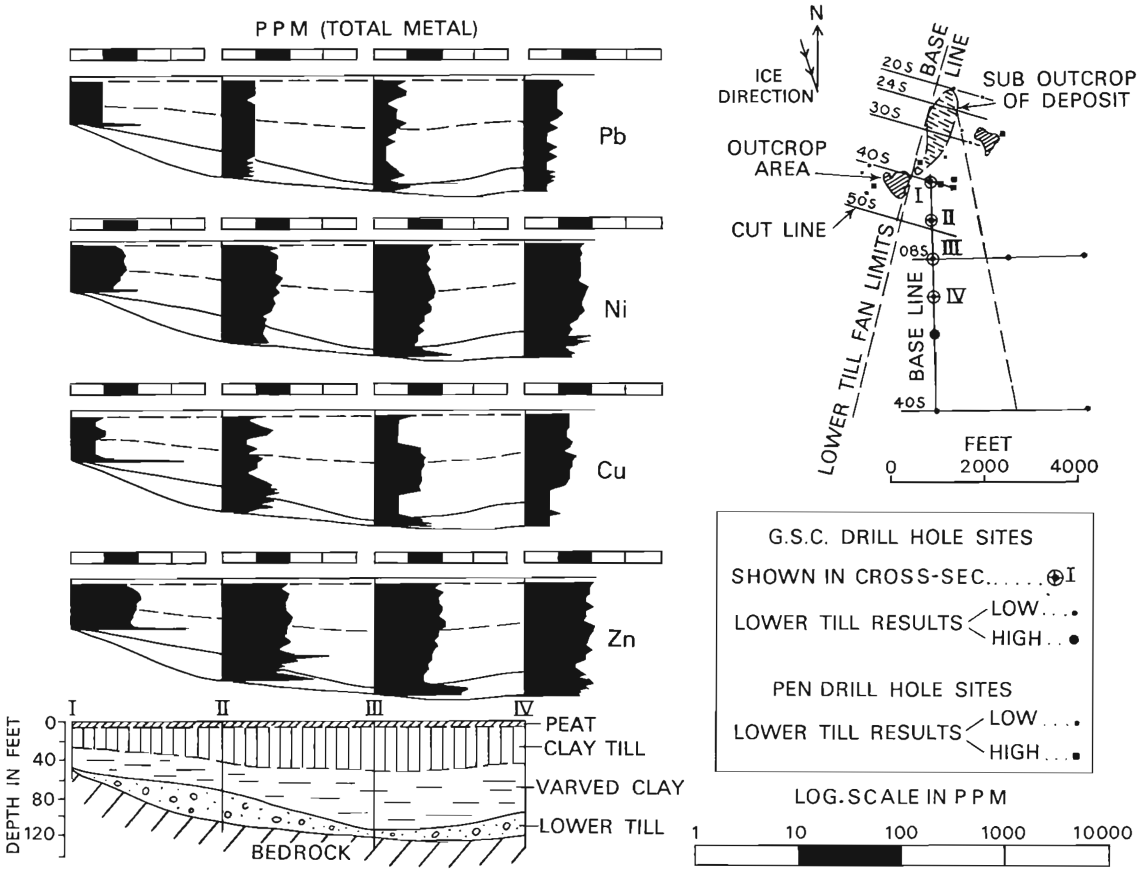

Figure 4. Sections showing the vertical distribution of lead, nickel, copper and zinc in samples of overburden collected from four holes drilled in the vicinity of the Texas Gulf sulphur deposit near Timmins, Ontario.

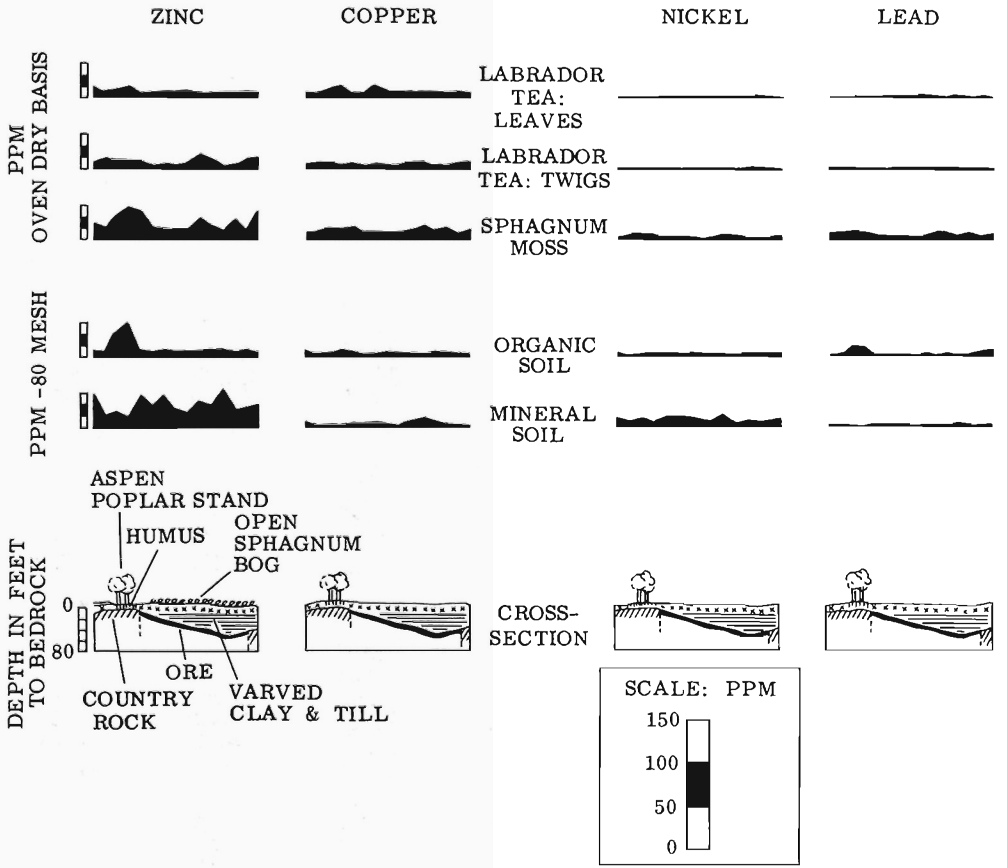

Figure 5. The distribution of lead, nickel, copper and zinc in samples of mineral soil, organic soil, sphagnum moss, labrador tea leaves and twigs collected in the vicinity of the Texas Gulf sulphur deposit near Timmins, Ontario.

Field investigations near mineral deposits

At two days notice during May 1964 we were invited to collect soil and plant samples in the vicinity of a large undisturbed mineral deposit which had just been discovered by the Texas Gulf Sulphur Company near Timmins, Ontario. Our first trip to the property ended ten days later when 500 samples of vegetable material and soils were flown out of the property by helicopter. The forests in the area from which the samples were collected were then being cut over so that it was impossible to collect more samples above this interesting deposit. Later, a number of control soil samples were collected around the cut-over area. Preliminary chemical analysis of the vegetable and mineral matter collected above the orebody gave negative results. This focussed our interest on the chemical composition of the underlying overburden. Subsequently, a number of samples of overburden, donated to us by the company, were analysed for total copper, zinc, nickel and lead. These results (Fortescue and Hughes, 1965) indicated anomalous concentration of zinc and copper in the Lower Till material directly overlying the bedrock, with background concentrations in material collected nearer the surface.

In order to follow up these preliminary findings a small scale overburden sampling program was carried out by the Geological Survey of Canada during the winter of 1964-65. In Figure 4 the location of some of the holes which were drilled are shown in relation to the presence of the suboutcrop area of the orebody. At the left hand bottom corner of the figure a generalized section of the overburden in the vicinity of the holes is shown together with histogram showing the content of total copper, zinc, nickel and lead in the samples taken from the four holes. (Samples were taken by 2" Shelby tube at five foot intervals in the clay till and varved clay material and by means of a hardwall sampler in the lower till material.) It should be noted that the chemical results (which were obtained by colorimetric analysis following total extraction by an $HF/HClO_4$ mixture) are plotted on a logarithmic scale unlike the results on Figure 5 which are plotted on an arithmetic scale. The chemical results on Figure 4 focus attention on the copper and zinc content of the Lower Till material. Strong zinc and weaker copper anomalies occur in the Lower Till material in holes I, II and III but not in hole IV. In contrast, the levels of concentration of all four elements in the varved clays and clay till material lying above the Lower Till are relatively low and constant. In comparing these results with those obtained from vegetation and mineral soil collected directly above the deposit (Fig. 5) the absence of significant anomalies in the surficial material is at once apparent. The only relatively high results here were on organic soil and sphagnum moss where, in the case of zinc and lead, some positive values were found in samples collected from the aspen poplar community compared with those collected from the open sphagnum bog community. Such variations are to be expected under normal conditions and probably are not related to the presence of the underlying mineral deposit.

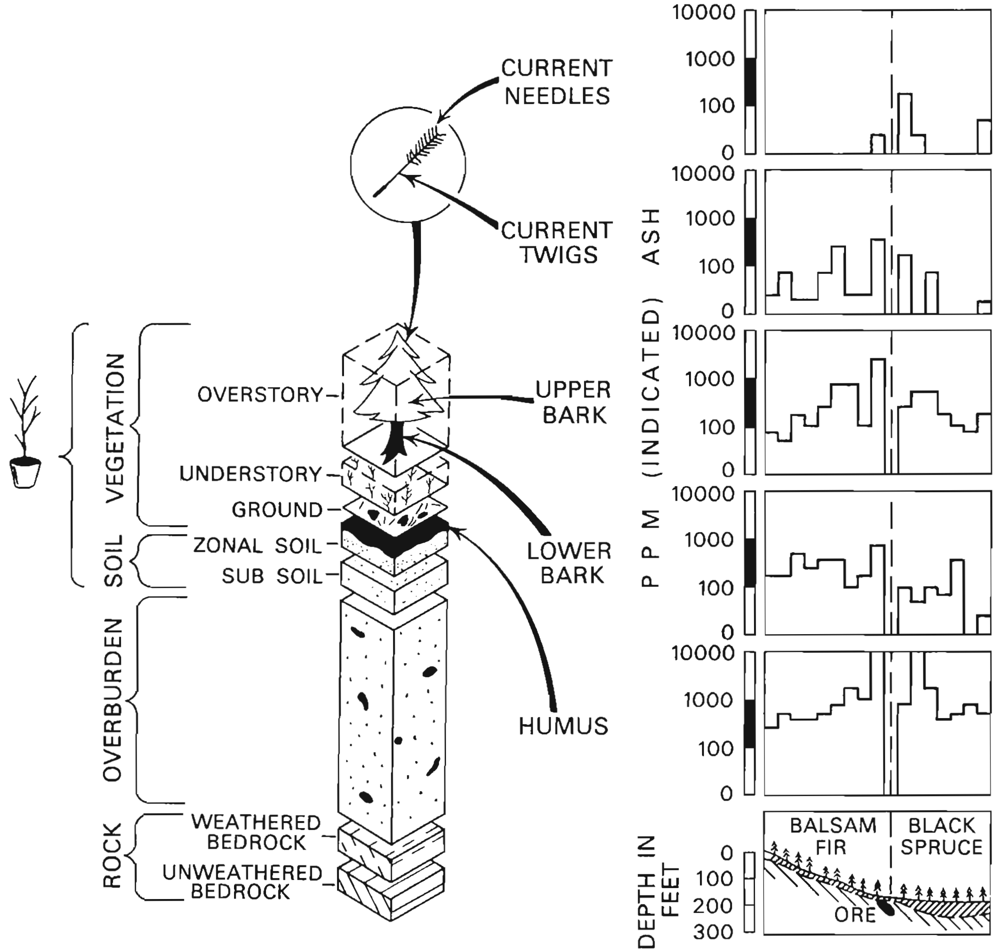

Figure 6. A prism of landscape showing the components of the vegetation and soil sampled at an undisturbed mineral deposit near Silver-mine, Cape Breton Island. Values for lead in the ash of the vegetable material are plotted above a cross-section of the landscape from which the samples were collected. Note that the word "ore" was used to indicate the presence of mineralization and has no economic significance.

The Texas Gulf Sulphur Company property near Timmins afforded us an excellent opportunity to study the geochemistry of the different components of a prism of landscape overlying an extensive ore deposit. In this case we were able to trace the copper and zinc into the Lower Till material but no farther up the prism. Because of the insulating effect of the varved clays and the overlying clay till significant amounts of copper and zinc did not migrate into the mineral soil or into vegetation. We conclude that under the local landscape conditions which obtain in the Timmins area the sampling of Lower Till is the most reliable method of geochemical prospecting. The main advantage of Lower Till geochemistry as a complement to geophysical methods under these conditions is that the Lower Till anomalies are slightly larger than the extent of the suboutcropping mineralization and that the results from the till give positive proof of the presence of specific metals within the material above bedrock.

Let us now turn briefly to an area in which biogeochemical prospecting gives positive results. In August 1963 a sampling program was carried out in the vicinity of a drilled, but undisturbed, mineral deposit at Silvermine on Cape Breton Island (Weeks, 1954, p. 104). In this area there are very few outcrops although the relatively coarse grained overburden is seldom more than a few tens of feet thick (Fig. 6). A section across the mineral deposit is shown on Figure 6 where it will be noted that a Black Spruce (Picea mariana) community occurs on the lower, poorly drained ground, and a Balsam Fir (Abies balsamea) community further up the hill.

Unlike the vegetation results plotted on Figure 5 the Silvermine results are shown on a logarithmic scale. For reasons discussed above these results are plotted as "indicated ppm" and should not be considered absolute values. In spite of this, the results show strong positive indications for lead in humus and to a lesser extent in the upper bark material (collected 2/3 of the height up the tree). As might be expected from a non-essential element such as lead, the results were erratic in the current years growth of needles or twigs. Another point of interest is that the general level of concentration of lead in the samples of lower bark taken from balsam fir trees is apparently slightly higher than that found in the black spruce. The significance of this observation is not at once apparent. More work is planned for this area during the summer of 1966 when these preliminary results will be supplemented by a more intensive investigation.

A second object of Figure 6 is to draw attention again to the need to study systematically the geochemistry of the various components of a prism of landscape in the vicinity of a mineral deposit in order to interpret the results of plant prospecting methods research. As we have seen in the case of the Silvermine results and, particularly, in the case of the work at the Texas Gulf Sulphur deposit, it is only when the geochemistry of the different components of the landscape is studied systematically that the most effective geochemical method for use in a given area can be discovered.

SUMMARY

This paper has been no more than an outline of the progress which has been made with the plant prospecting methods research programme since 1962. The progress made so far may conveniently be summarized under the following seven headings:-

1) There is a need in Canada at the present time for similar systematic studies of the geochemistry of the different components of landscapes in which known, undisturbed, mineral deposits occur in order that the relative effectiveness of different geochemical prospecting methods can be assessed under different mineralization and landscape conditions.

2) These studies must be done in sufficient detail and with sufficient intensity to explain the results obtained in terms of geochemical principles. The studies must be done sufficiently thoroughly to explain results or not at all. Partial results are misleading.

3) We have shown that it is possible to design and construct laboratories which may be used at the field for the rapid preparation and chemical analysis of vegetable material for a number of minor elements. This enables studies of specific ecosystems to be carried out at an "instant in time" which is essential if detailed comparisons of results obtained from plants growing in different areas are to be made.

4) The methods set up for the systematic collection and treatment of morphological and chemical data have indicated that, quite apart from the writeups of specific plant prospecting methods projects, our files may be used as a basis for a geochemical census of Canadian ecosystems. In this form the data will be of interest to plant ecologists and foresters as well as those engaged in general interpretation of geochemical prospecting results.

5) Preliminary greenhouse experiments have provided valuable experience in the use of chemical elements, artificial mixtures of non-radioactive isotopes and radioactive elements as tracers, or for tests of the uptake of elements by plants under controlled conditions.

6) The Mer Bleue investigation has been valuable experience in the layout and setting up of biogeochemical prospecting methods in bog areas. In particular the analytical program associated with this project has demonstrated the scope and limits of the methods we have so far developed.

7) The two investigations carried out in the vicinity of drilled, but undisturbed, mineral deposits have provided valuable experience in the methods for approaching problems of this kind. In both cases it was possible to find a simple logical explanation of our results, in one case negative and in the other positive. We believe that both negative and positive experience of this kind are of equal value to those engaged in setting up geochemical prospecting projects at this time.

In the future we plan to publish the results of progress made in the plant prospecting methods research program in the form of a series of progress reports so that the interested reader may follow our projects as they are completed.

In conclusion we thank the Texas Gulf Sulphur Company, Phelps Dodge Corporation, Kennco Explorations (Canada) Limited and the International Nickel Company of Canada for their cooperation in the search for drilled, but undisturbed, mineral deposits where geobotanical and biogeochemical research could be carried out.

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THE DISTRIBUTION AND BEHAVIOUR OF METALS IN STREAM SEDIMENTS AND WATERS OF THE KENO HILL AREA, YUKON TERRITORY

C.F. Gleeson*

Geochemical reconnaissance is attractive from the point of view of rapidly and cheaply evaluating the economical potential of an area and of outlining new and extending old boundaries of metallogenic districts. Also, these techniques have the advantage of allowing one to study regional chemical variations related to change in rock types, structure, mineralogy, etc.

The Geological Survey of Canada started its research in applied geochemical techniques in 1953 when Boyle (1955) carried out detailed water and soil surveys in the Keno Hill Area, Y.T. He followed this project with a reconnaissance water and stream sediment survey in part of Nova Scotia in 1956 (Boyle et al 1958), the following year Holman (1959) expanded the stream sediment work to cover most of Nova Scotia and in 1959 Smith (1960) extended this work into New Brunswick. Hydrogeochemical studies on uranium in the Bancroft area were done by Chamberlain (1964) in 1961, and in 1963 Tauchid (1964) studied molybdenum distribution in stream sediments and soils over a granitic body in Bathurst Area, New Brunswick. In 1964 the Geological Survey of Canada carried out its first helicopter-supported regional geochemical-heavy mineral survey. The planning, execution and discussion of the preliminary results of this work form the basis of this paper.

DESCRIPTION OF THE KENO HILL AREA

Location

The area surveyed is located about 200 miles north of Whitehorse, Y.T., it consists of a block of ground measuring about 60 miles by 34 miles and centered around Keno Hill, Yukon Territory.

Geology

Four-mile geological mapping of the region has been done by Bostock (1947, 1964), Green and Roddick (1962), and more detailed studies (1":1mi.) have been carried out by Green (1957, 1958), Kindle (1962), McTaggart (1969), Boyle (1965) and Poole (1965).

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The area studied is underlain by a series of metamorphosed sedimentary rocks, mainly quartzites, phyllites, slates and chlorite, sericite and graphite schists, as well as grits and minor limestone. The age of these rocks is uncertain but appears to range from Precambrian to upper Mesozoic (Poole, 1965; Tempelman-Kluit, 1966). A dolomite and limestone unit outcrops in the northeast part of the area. Fossils from these rocks range in age from late Cambrian to late Silurian or early Devonian (Green and Roddick, 1962). Mafic igneous sills and lenses now altered to greenstones are interlayered with the metamorphosed sediments. Quartz-feldspar porphyry sills and lamprophyre dykes are present locally. Granitic stocks cut the metamorphosed sediments east and north of Mayo Lake, northwest of Hanson Lake, south of Dublin Gulch and in the vicinity of Mount Haldane.

Skarn zones containing scheelite occur in the vicinity of some of these granitic masses particularly around Dublin Gulch, Mount Haldane, and east of Mayo Lake.

Most of the lead-silver ore deposits in the Keno-Galena Hill area occur along northeasterly striking vein faults in thick-bedded quartzite and occasionally in greenstone (Boyle 1965). In the Dublin Gulch area quartz-arsenopyrite-gold veins with a general northeast strike are present near the contacts of the granitic stocks. Also, easterly striking vein faults are mineralized with siderite, jamesonite, boulangerite, pyrite, arsenopyrite, galena, tetrahedrite and chalcopyrite. Two cassiterite-tourmaline veins occur on the right limit of Dublin Gulch near its mouth (Boyle, 1965; Poole, 1965). Northerly striking lead-zinc-silver veins are present in Davidson Range (Cockfield, 1922; Aho, 1964). In addition placer gold has been recovered from Dublin Gulch, Haggart Creek, and Duncan Creek since 1898.

The area has undergone several stages of glaciation (Vernon and Hughes, 1966) and thick glacial deposits occupy the major valleys and hill slopes below 3000 feet. Permafrost is present throughout the region.

Climate and Rainfall

The region has a sub-artic climate. The average annual precipitation is reported to be about 12 inches but in 1964 the summer was wet and over a period of 3 months a total of 10 inches of rain was recorded.

PURPOSE

The programme was designed so that the field work would be completed in one season. The chief aims of the study included:

(1) The systematic sampling of stream and spring sediments and stream and spring waters from an area of about 1900 square miles.

(2) Testing at the site for cold extractable heavy metals in the waters and sediments and recording all pertinent data on the environment in coded form on special field cards.

(3) Collecting heavy mineral samples by panning the stream gravels.

(4) Collecting rock samples for trace element studies.

(5) Stream sediments from phase one to be analysed for trace elements.

(6) Water samples from phase one to be analysed completely for anions and cations.

(7) Compilation and publication of the data in the form of geochemical maps.

(8) Computer analysis of the data.

Except for the rock analyses, phases 1 to 6 have been completed. Geochemical maps showing the heavy metal content of stream and spring waters and sediments (Gleeson et al, 1965) and the lead content of stream sediments (Gleeson, 1966) have been published. More of these maps are being prepared and should be published shortly. Computer analysis of the data is yet to be completed.

FIELD METHODS

To cover the area in the time allotted the use of helicopters was essential. Two Bell Super G2A helicopters were leased from Associated Helicopters, Edmonton, for this work. The geochemical field party consisted of 7 two-men crews, a cook and a helper, plus the 2 helicopter pilots and a mechanic. The helicopters were used as taxis to ferry the men to the heads of the creeks and at the end of the day to pick them up. About 400 hours of flying was required to cover the area.

After being set out the crews traversed the creeks on foot, took samples of stream sediments, tested the water and sediments for cold extractable heavy metals, measured the pH, and temperature of the water, and entered all pertinent data about the sample site in coded form on specially designed field cards (Gleeson and Tupper, 1966).

Generally a stream sediment sample of the finest material available was taken from the active channel at intervals of 1500 feet along all creeks. Two water samples were taken from each creek for SO_4 and Cl anion analysis. Large samples (1 liter) of water were taken from springs throughout the area and complete analyses were done on these for anion and cations. From the gravels of each creek the crews panned one or two heavy mineral samples. A total of 5900 stream sediments were tested and sampled, 5700 stream waters were tested in the field and about 700 analyzed in the laboratory, 150 spring waters and sediments were collected and 550 heavy mineral samples were obtained.

LABORATORY PROCEDURES

All sediment samples were dried, sieved to minus 80 mesh and shipped to the geochemical laboratories of the Geological Survey of Canada, Ottawa, where colorimetric analyses for Cu, Pb, Zn, As, Sb, W and Mo and spectrographic analyses for Ni, Co, Ag, Sn, Bi, B, Au, Cu, and Mo were done. The panned concentrates were also sent to Ottawa for heavy liquid separations. The heavy liquid concentrates were examined under a binocular microscope, checked for fluorescence, radioactivity, and subjected to semi-quantitative spectrographic analysis.

EXPENDITURES

Field expenditures for this operation amounted to about $82,000; of this, $40,000 was spent on helicopter charter, $23,000 on salaries, $6,500 on transportation to and from the field, $5,000 on food, about $4,000 on frieight, $1,500 on vehicle repair and gas, and $2,000 for camp supplies, field chemicals, rental of equipment etc. Hence the field cost amounted to about $43.00 per square mile. This figure does not include the cost of laboratory analysis.

RESULTS

To date a series of 14 maps have been published on a scale of 1 mile to the inch showing the distribution of cold extractable heavy metals in waters and stream sediments (Gleeson et al, 1965). Recently a map showing the distribution of lead in the stream sediment was released (Gleeson, 1965) and 11 more metal maps are presently being compiled for publication.

The results of the cold extractable field tests showed that reconnaissance sediment and hydrochemical surveys are practical and useful exploration tools for this area. With these methods most of the known lead-zinc-silver deposits were detected. In addition, numerous anomalies were found in areas that have hardly been explored. Anomalous trains varied from less that one mile to over ten miles in length.

LEGEND

CENOZOIC

TERTIARY

EOCENE OR LATER

Unit	Description
12	*Rhyolite, trachyte (flow rocks)*

MESOZOIC

CRETACEOUS (?)

Unit	Description
11	*Quartz-feldspar porphyry, granite porphyry*
10	*Granodiorite, granite, diorite*
9	*Meta-diorite, meta-gabbro (greenstone) (only the larger bodies are shown)*

PALAEOZOIC

ORDOVICIAN TO SILURIAN

Unit	Description
8	*Dolomite, minor limestone*

PRECAMBRIAN AND/OR PALAEOZOIC

YUKON GROUP (1-7)

Unit	Description
7	*Pebbly quartzite, phyllitic quartzite, slate, phyllite, minor limestone (age uncertain)*
6	*Slate, schist, quartzite, minor limestone*
5	*Quartzite, quartz-mica schist, slate, minor limestone*
4	*Quartz-mica schist, pebbly quartzite, minor limestone, skarn in vicinity of 10*
3	*Quartz-mica schist, graphitic schist, phyllitic quartzite, minor limestone, skarn in vicinity of 10*
2	*Thick-bedded quartzite, thin-bedded quartzite, graphitic schist, minor limestone, skarn in vicinity of 10*
1	*Graphitic schist, thin-bedded quartzite, quartz-mica schist, phyllite, calcareous schist and quartzite*

Drift-covered area . . . . ▭

Bedding (horizontal, inclined, vertical) . . . . + / /

Bedding inclined (direction of dip known, top of bed unknown) . . . /

Schistosity, foliation (inclined, vertical) . . . . / /

Syncline (arrow indicates plunge) . . . . ←

Anticline (arrow indicates plunge) . . . . ←

Anticline and syncline (overturned) . . . .

Glacial striae . . . .

Late fault (approximate, assumed) . . . . ~~~ ~~~ ~ ~

Geology compiled by R. W. Boyle, from published Geological Survey of Canada maps, 890A, 1105A, 43-9, 5-1956, 8-1958, 9-1958 and 15-1962, with additional field surveys by R. W. Boyle

Geological cartography by the Geological Survey of Canada, 1964

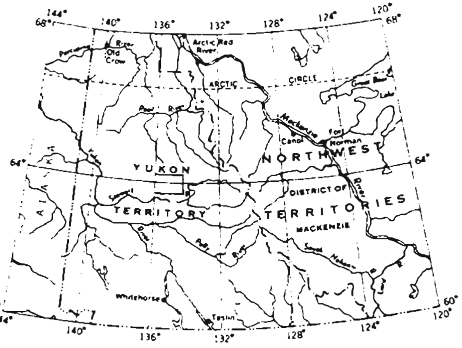
Road, all weather . . . . ———

Other roads . . . . — — —

Contours (interval 500 feet) 5000

Height in feet above mean sea-level 6250

Base-map cartography by the Geological Survey of Canada, from maps published by the Surveys and Mapping Branch and the Army Survey Establishment, R. C. E., with minor revisions by the Geological Survey of Canada



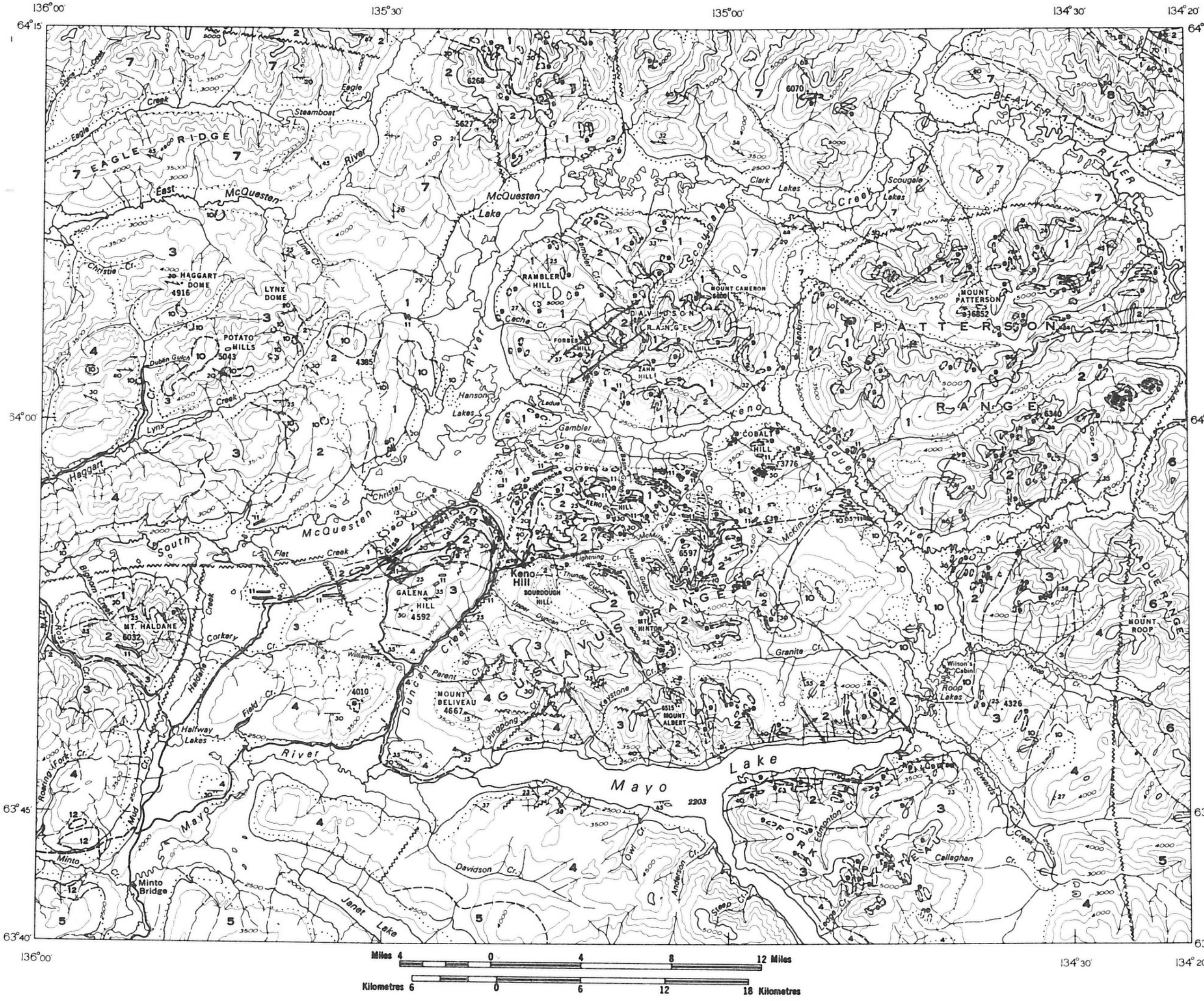
INDEX MAP

GEOLOGY

KENO HILL-GALENA HILL AREA

YUKON TERRITORY

From G. S. C. Bulletin 111, by R. W. Boyle


136°00'
135°30'
135°00'
134°30'
134°20'
64°15'
64°00'
63°45'
63°40'
EAGLE RIDGE
East McQuesten River
Eagle Creek
Steamboat
McQuesten Lake
Clark Lakes
Scougale Lakes
Scougale Creek
BEAVER RIVER
HAGGART DOME 4916
LYNX DOME
POTATO HILLS 5043
Dublin Gulch
Haggart Creek
Lynx Creek
Lime Cr.
Christie Cr.
RAMBLER HILL
Rambler Cr.
Cache Cr.
FORBES HILL
MOUNT CAMERON
DAVIDSON RANGE
ZAHN HILL
Hanson Lakes
MOUNT PATTERSON 6852
PATTERSON RANGE
Rankin Creek
6340
6268
5627
6070
4385
COBALT HILL 3776
Keno Ladue River
Allen Cr.
Gambler Gulch
Silver Basin Gulch
KENO HILL
McMillan Gulch
Faro Gulch
McNeil Gulch
Lightning Cr.
Thunder Gulch
6597
Keno Hill
SOURDOUGH HILL
GALENA HILL 4592
Christal Cr.
McQuesten River
Flat Creek
South McQuesten
Thompson Cr.
MT. HINTON
GUSTAVUS RANGE
Upper Duncan Cr.
Duncan Creek
Parent Cr.
MOUNT BELIVEAU 4667
Pingpong Cr.
Keystone Cr.
MOUNT ALBERT 6515
Granite Cr.
McKim Cr.
Williams Cr.
4010
Field Cr.
Corkery Creek
Haldane Cr.
MT. HALDANE 6032
Bighorn Creek
Ross
Halfway Lakes
Mayo River
Roaring Fork Cr.
Mud Cr.
Minto Cr.
Minto Bridge
Janet Lake
Davidson Cr.
Owl Cr.
Anderson Cr.
Steep Cr.
Mayo Lake
2203
FORK
Edmonton Cr.
Ledge Cr.
Callaghan Cr.
Edwards Creek
Roop Lakes
Wilson's Cabin
4326
Roop Cr.
MOUNT ROOP
LADUE RANGE
Miles 4 0 4 8 12 Miles
Kilometres 6 0 6 12 18 Kilometres

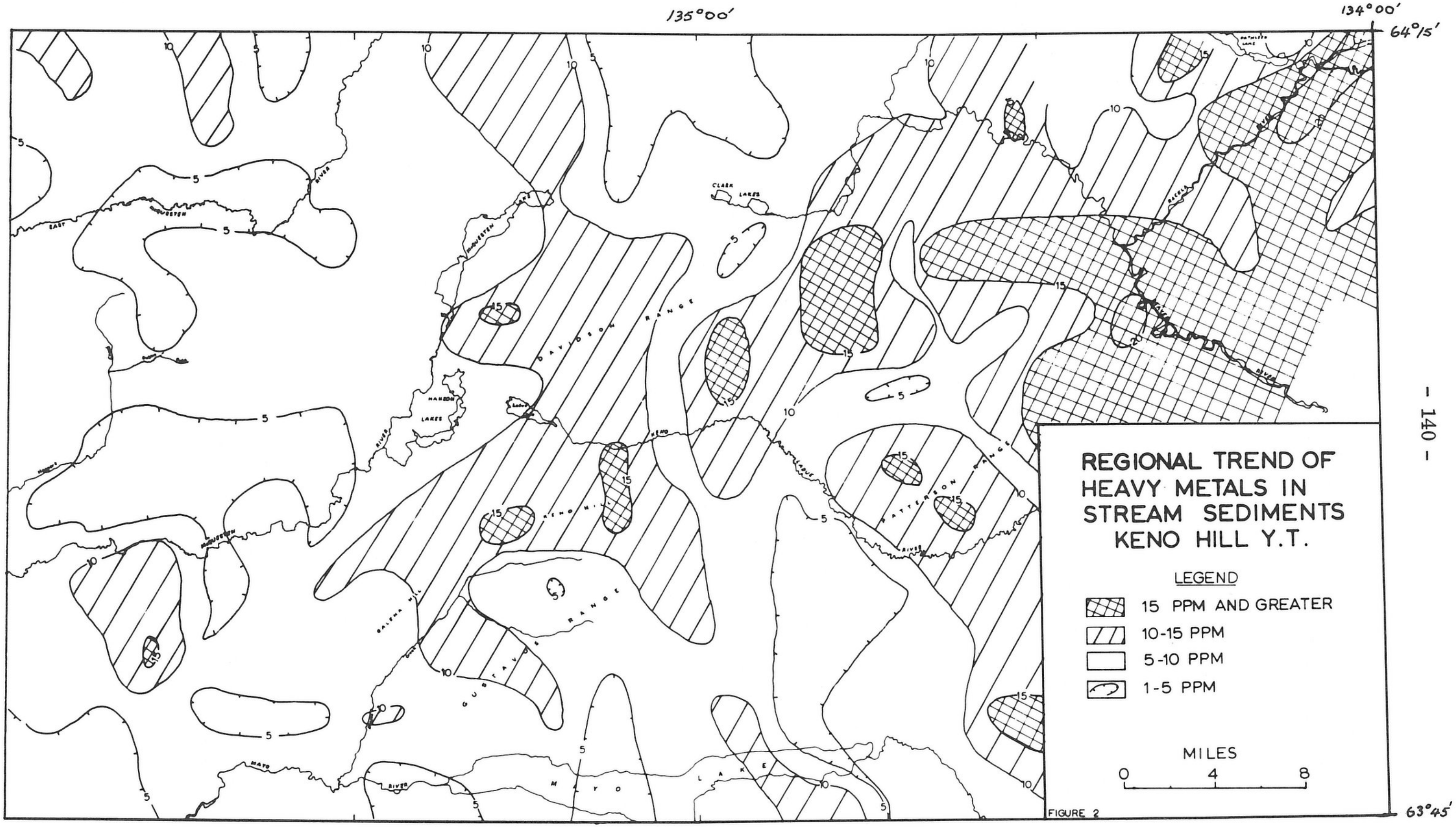


Figure 2. Regional trend of heavy metals in stream sediments, Keno Hill, Yukon Territory.

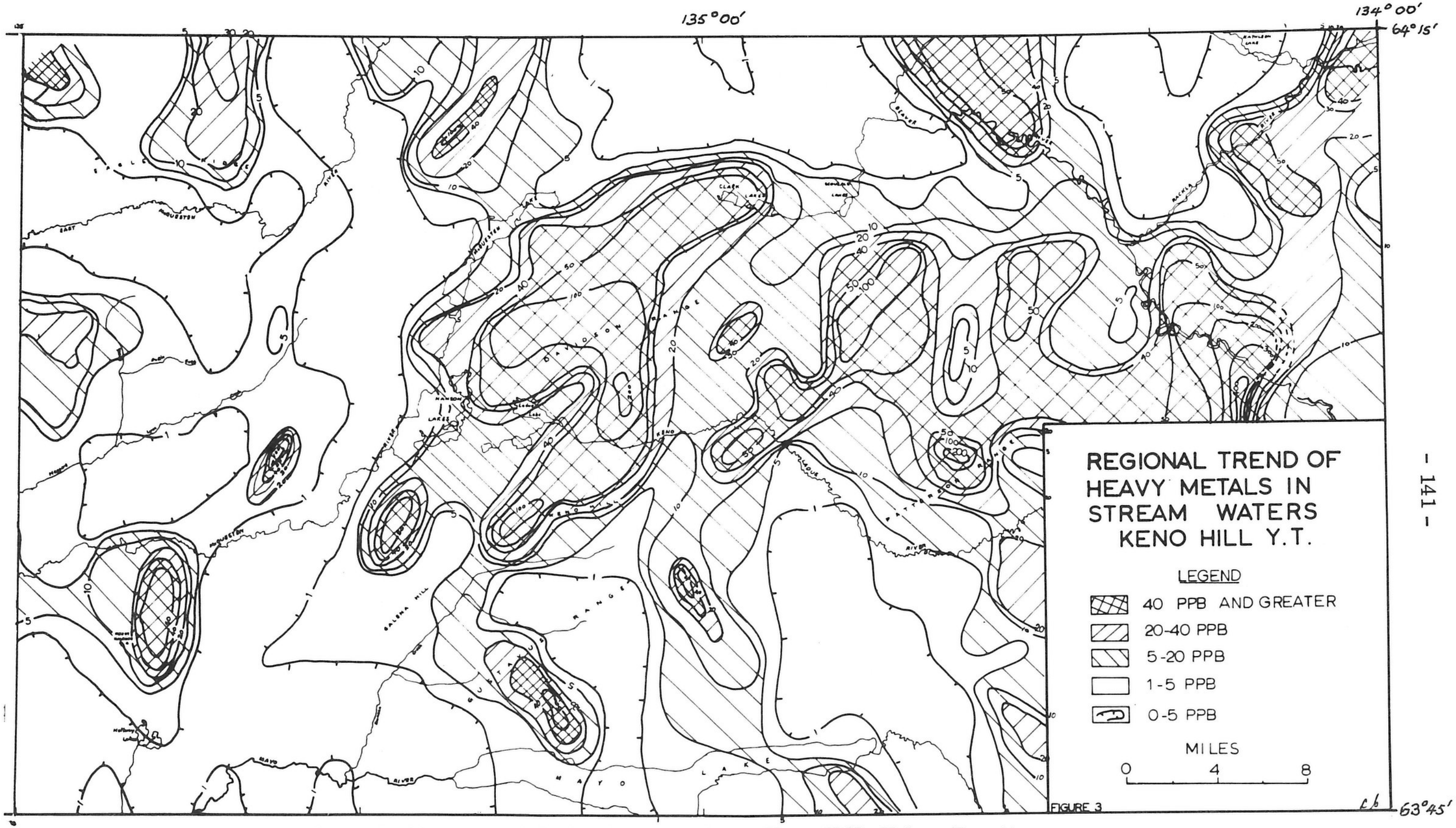


Figure 3. Regional trend of heavy metals in stream waters, Keno Hill, Yukon Territory.

The water and stream anomalies were generally coincident but certain exceptions did occur in the vicinity of some very acid springs where the cut-off of the sediment anomaly was displaced several thousand feet downstream from the water anomaly. This effect was probably due to the high acidity of the water; where the water pH is low the metals tend to stay in solution and no sediment anomaly was detected. After the sediments were analyzed in the laboratories it was found that most of the anomalies found with the field tests were due to zinc.

The area was divided into 2½ mile squares and with the aid of a computer the arithmetic means of the cold extractable heavy metals values of the sediment and water samples within each square was calculated. These values were then contoured and regional trend maps constructed (Figures 2 and 3).

The general pattern of regional trend lines on the sediment map (Figure 2) reveals highs over the producing areas in addition to highs over the phyllitic and quartzitic rocks to the north, central and eastern parts of the area. An isolated high occurs over Mount Haldane where again massive quartzite and phyllite are present in addition to several small Pb-Zn-Ag showings. There is a marked decrease in the regional trend to the west (Dublin Gulch Area). This change reflects the low trace element content of zinc in the rocks in the western sector of the area. Even the known mineral deposits of the Dublin Gulch area contain relatively little zinc; essentially the veins are rich in Pb, As, Sb, and Au. Another prominent low occurs in the north central part of the area. The rocks here are reportedly similar to those north of Dublin Gulch. To the southeast a low is present over the Mayo Lake granite stock. The values over a band of dolomitic rock in the northeast are fairly high. This is particularly interesting because this area is also high in lead (Gleeson, 1966).

A surprisingly similar picture is shown by the regional trends of the water map (Figure 3). Again there is a strong trend of highs to the east and lows to the west and north central parts of the area. The Mayo Lake granite is overlain by a low and the quartzites and phyllites are generally covered by highs. The band of dolomite in the north east is better defined by the water results than by the sediment regional trends. Highs occur over Mount Haldane and there is also a moderate increase over the Pb-Sb-As showings in the Dublin Gulch area.

As information becomes available similar maps will be drawn for all elements. However, by using the results of only a cold-extration field test, strong trends and regional relationships to rock types can be shown and favorable areas for prospecting quickly delineated.

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SOME OBSERVATIONS ON THE DISTRIBUTION OF METALS IN SWAMPS IN EASTERN CANADA

C.F. Gleeson* and J.A. Coope**

INTRODUCTION

The behaviour of trace metals in swamp environments has been studied by numerous observers in different parts of the world. Lovering (1927), Forrester (1942) and Eckel (1949) have described native copper in peats in Montana and Colorado which has been precipitated from copper-bearing waters draining areas of copper mineralization. Webb and Tooms (1959) have studied concentrations of copper in dambos in the Copperbelt area of Zambia. They conclude that, away from the main points of groundwater seepage, copper tends to concentrate in surface horizons. Cannon (1955) has reported abnormal concentrations of zinc in peaty deposits overlying the zinc bearing Lockport dolomite in New York.

In Yukon Territory, Boyle (1957) found that zinc carried into bog areas by surface waters was concentrated in abnormal amounts in the peats. Ermengen (1957) also noted that the peat bogs in the Chibougamau area of Quebec concentrated zinc. Holman (1959) reported on a copper-rich swamp near Sackville, New Brunswick that has concentrated copper from spring waters emerging from a cupriferous Pennsylvanian sandstone. Further north in New Brunswick Hawkes and Salmon (1960) have described concentrations of iron in live and decomposing organic matter in a swamp overlying a copper bearing iron sulphide deposit in the Bathurst area.

In his studies of the trace-element distribution in Scottish peats, Mitchell (1954) collected profile samples in swamps overlying rocks containing background quantities of metals. Mitchell found the quantities of copper, zinc, lead and nickel in the peats tended to increase with depth.

Salmi (1950) collected surface samples from 50 swamps throughout Finland and discovered that the bogs situated in the vicinity of sulphide orebodies contained more copper, zinc and nickel than the bogs in areas of no known sulphide mineralization.

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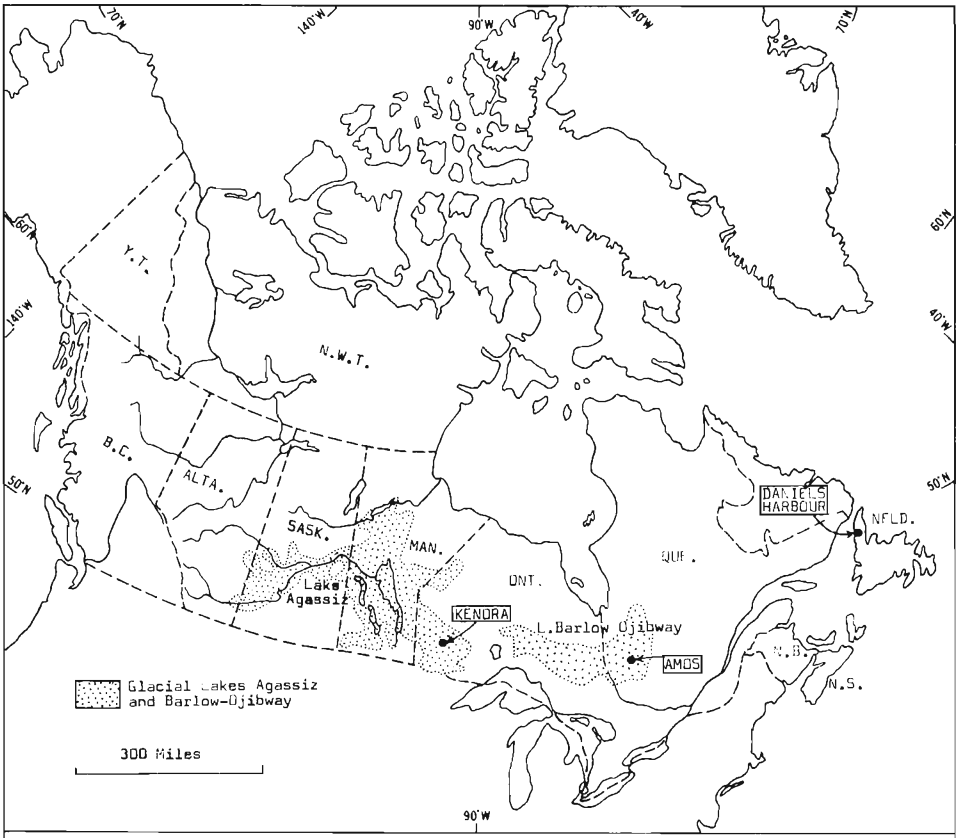


LOCATION MAP

Figure 1

After more detailed studies of trace-element distribution in swamps in the Otanmaki and Vihanti districts, Salmi (1955, 1956) found that the most important elements contained in the vanadium-bearing titaniferous iron ore and copper-zinc deposits underlying the swamps were present in anomalous amounts in the peats. Maximum concentrations occurred over or down-drainage of the suboutcrop of the orebodies in areas where the peat is underlain by up to 40 feet of sand and till. Iron, manganese, molybdenum and lead tended to be concentrated in the upper layers of the peat, while nickel, vanadium, titanium and cadmium were present in the greatest concentration near the base of the peat. In Norway Hvatum (1964) has shown that Pb, Zn and Mo concentrated in the upper layers of peat and Co, Cu and Mn are generally found in maximum concentrations at the top and bottom of the peat bogs that he sampled.

The present paper describes results obtained from geochemical investigations in poorly drained areas near Kenora, Ontario, Amos, Quebec and Daniel's Harbour, Newfoundland. The physical characteristics of the swamps and the vertical distribution of trace-elements in the swamp profiles in these three areas are essentially similar.

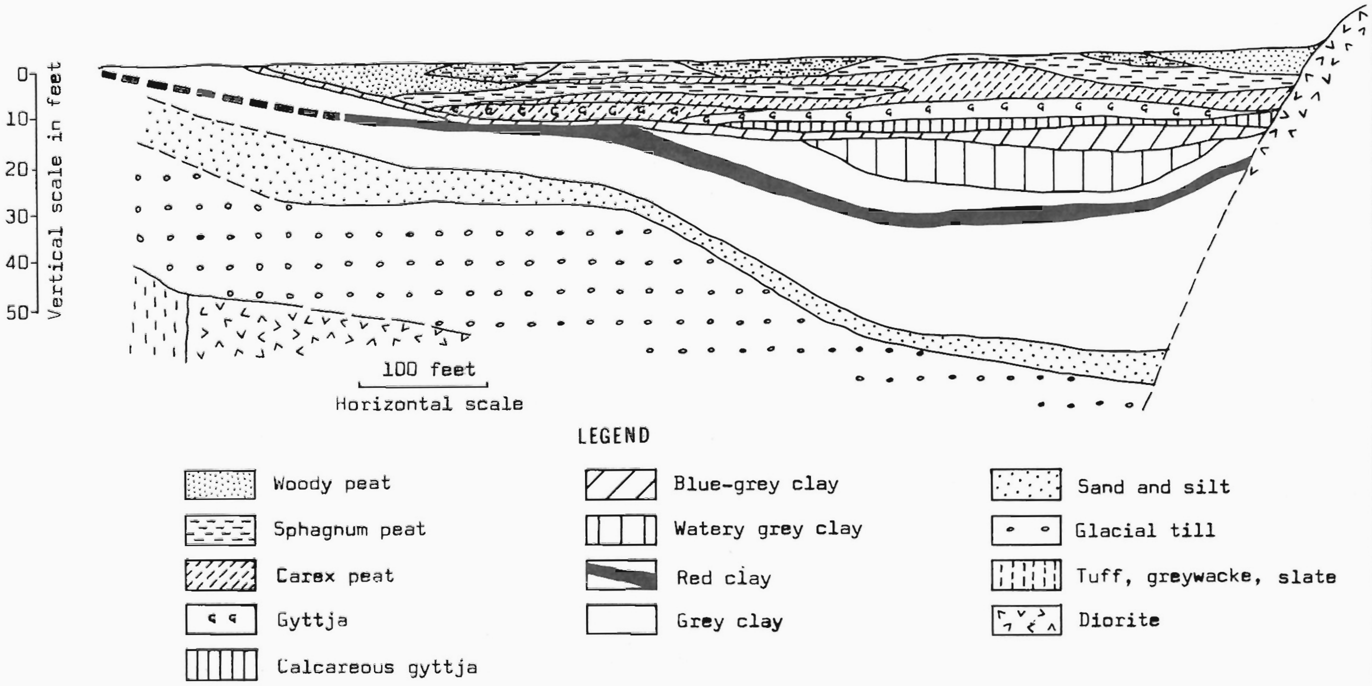
BLACKY BAY AREA, ONTARIO

Blacky Bay is located on the south shore of Crow Lake, 70 miles southeast of Kenora, Ontario, and 6 miles east of Lake of the Woods (Fig. 1). Burwash (1933) described the area as a dissected peneplain with gently rolling hills rising 200 to 300 feet above the level of Crow Lake.

In the vicinity of Blacky Bay the oldest rocks are andesitic lavas and amphibolites. These volcanics are overlain by a series of clastic sediments including greywacke, spotted slates and conglomerate. These, in turn, are overlain by fragmental volcanics, tuffs and rhyolite. All the rocks are of Precambrian age.

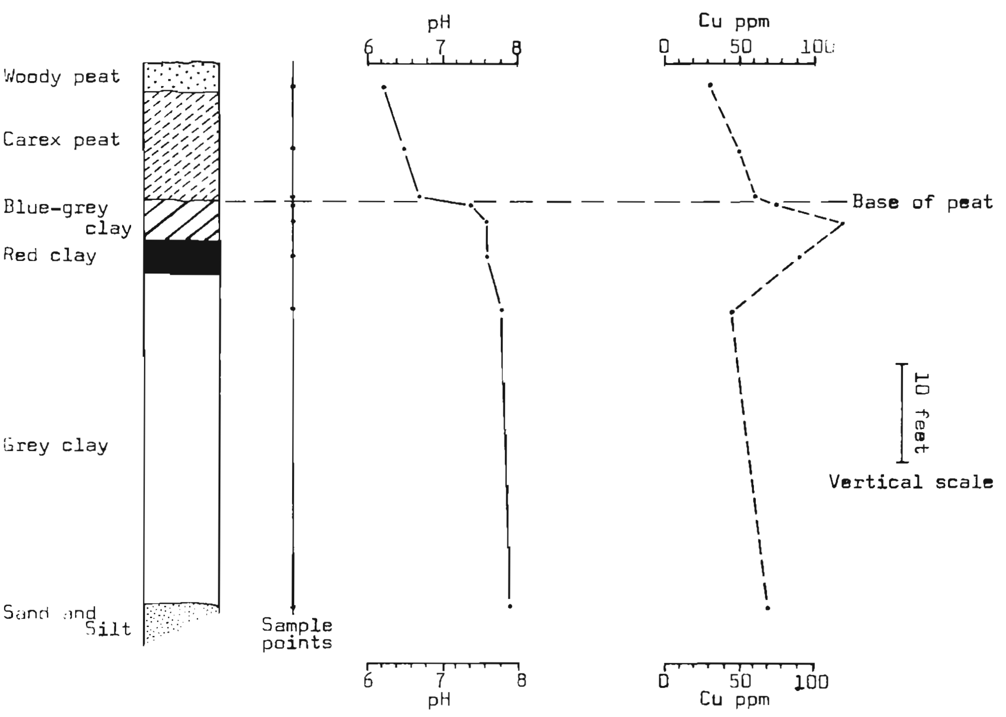
A body of granite intrudes the area immediately to the south, and the contact metamorphic effects associated with this intrusion are believed to be responsible for the development of amphibolites in the older volcanic series. Diorite sills and dykes, porphyritic diorite sills and glomeroporphyry sills post-date the granite and cut the volcanic and sedimentary rocks.

The rocks of Blacky Bay form part of the south limb of an east-west trending syncline. Dips are very steep northerly or vertical. One major fault trends north-northeasterly and numerous shears parallel the regional trend of the rocks. Calcite has been deposited along one of the larger shears but minerals of economic significance are unknown in the area.



SWAMP PROFILE-BLACKY BAY BOG

Figure 2



VERTICAL VARIATIONS IN pH AND COPPER CONTENT OF
SWAMP PROFILE BLACKY BAY BOG

Figure 3

During the Pleistocene epoch, the Crow Lake area was heavily glaciated and flooded by the waters of Lake Agassiz. Burwash (1933) correlates surficial sands and gravels present in the area with deposits formed along beaches and in shallow bays of this once-extensive lake. Overlying these coarse deposits are layers of silt and glacial clay. Since the glacial epoch, peat has formed on the surficial deposits in shallow basins of Crow Lake and at many levels above the lake.

The Blacky Bay bog occurs at the east end of Blacky Bay and measures approximately 3,000 feet by 1,000 feet. The greater part of the bog is covered by coniferous forest, but the portion bordering the stream and the lake is more open and swampy. The bog is bordered on the north and south by low hills rising 100 to 150 feet above the bog surface.

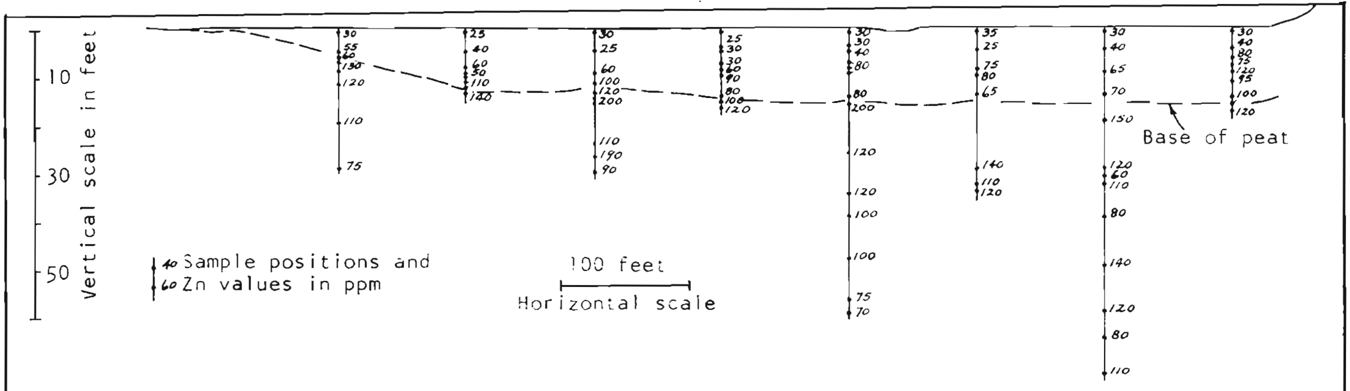
Composition and Structure of the Blacky Bay Bog

The structure of the Blacky Bay bog is illustrated in Fig. 2. The peat can be divided into five types: (a) calcareous gyttja, (b) gyttja, (c) fibrous carex (sedge) peat, (d) fibrous sphagnum peat, (e) woody peat. The maximum thickness of peat is 28 feet and the average thickness 15 feet.

Immediately beneath the peat is a bluish-grey sticky clay one to five feet in thickness. This clay is usually compact but locally it grades into a very watery grey clay, the thickness of which varies from 5 to 20 feet. A layer of more compact grey sticky clay underlies the blue-grey and watery clay and also varies in thickness between five and twenty feet. Under the grey clay is a continuous horizon of compact and sticky red clay which is one to five feet in thickness. Beneath this is a thick layer (6 to 30 feet) of sticky compact grey clay. The latter grades into silty and sandy fractions 5 to 20 feet thick, and these in turn are bottomed by glacial till composed of coarse sand and boulders. The till rests on bedrock of diorite and interbedded tuff, greywacke and slate.

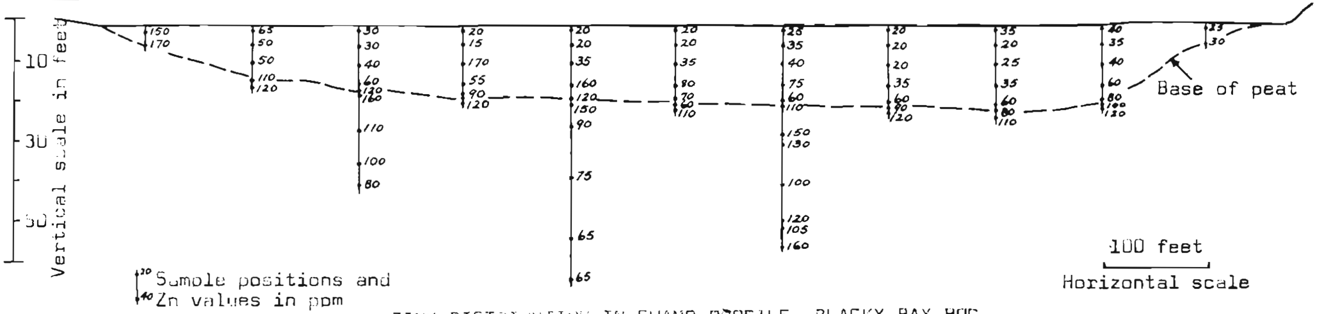
The clays are probably of glacio-lacustrine origin laid down when the area was occupied by Lake Agassiz. X-ray diffraction investigations have indicated that these clays are composed essentially of rock-flour. Quartz, feldspar, biotite, chlorite and amphibole have been identified, together with various micaceous minerals.

Determinations of pH on swamp profile samples have indicated that the top layers of peat in the bog are slightly acid (pH 5.5 - 6.8) and that, with increasing depth, the pH gradually rises. The underlying clays are consistently alkaline, with values varying from pH 7.0 - 7.1 immediately beneath the peats to pH 8.0 in the bottom sandy layer (Fig. 3).



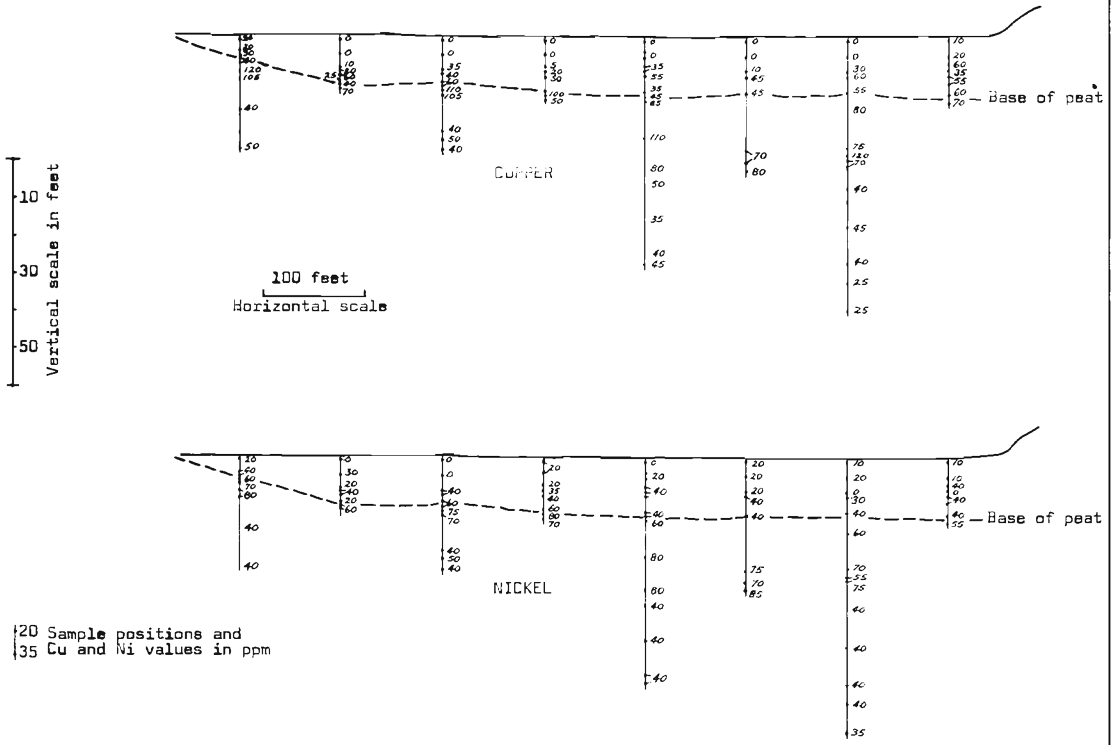
ZINC DISTRIBUTION IN SWAMP PROFILE, BLACKY BAY BOG

Figure 4



ZINC DISTRIBUTION IN SWAMP PROFILE, BLACKY BAY BOG

Figure 5



COPPER AND NICKEL DISTRIBUTION IN SWAMP PROFILE
BLACKY BAY BOG

Figure 6

Generally, as the degree of humification increases so does the pH. Baszynski et al. (1954) and Salmi (1955) have studied the rate of decomposition of organic matter and concluded that, during decomposition the pH increases because of liberation of bases and decomposition of organic acids. Increasing pH with depth is common in many swamp environments and Salmi (1958) has found that there is often a distinct correlation between the pH of peats and the underlying rock types.

Trace-Element Distribution

Samples of peat were obtained using a Hiller Peat Borer at intervals of 5 feet from the surface. The deeper sampling of the glacial deposits was done with a model B-27 Mobile Drill mounted on an M-7 Bombardier Muskeg Tractor. A total of 14 drill holes were completed with the power drill and in most instances samples were collected at 5 foot intervals in each hole, to depths up to 65 feet.

The peat and clay samples were analysed for copper, zinc and lead using the method of Bloom and Crowe (1953). Nickel determinations were made using the method described by Bloom (1957).

Zinc (Fig. 4)

In all profiles there is a tendency for zinc values to gradually increase from surface to the bottom of the peat. The surface peats contain 20 - 40 ppm Zn while the lower layers above the clay contain 60 - 100 ppm Zn. Maximum zinc values are recorded in the upper layers of clay beneath the peats where values range from 140 to 220 ppm Zn. Below this upper layer the zinc content decreases and is usually a minimum (61 to 80 ppm Zn) in the sandy horizons at the base of the profiles.

This general distribution is repeated throughout all sections of the swamp. Irregularities in the general pattern do occur, however, but they are very local and infrequent. (Fig. 5)

Copper and Nickel (Fig. 6)

The vertical distribution of copper and nickel follows the same pattern as described for zinc. Surface copper values are 0 to 20 ppm Cu an in the lower peat horizons the content ranges between 40 and 60 ppm Cu. The upper layers of clay beneath the peat usually contain the greatest amount of copper (80 to 150 ppm Cu). The clays and coarser sediments lower in the profiles contain only 40 to 60 ppm Cu.

The nickel content of the upper peats falls within the range 0 to 20 ppm Ni, while the deeper, more decomposed, peats contain 20 to 40 ppm Ni. Contents of 60 to 80 ppm Ni characterize the upper clays with values dropping off in the deeper horizons to 20 to 40 ppm Ni.

Lead

The content of lead in the profiles is very small and seldom occurs in concentrations greater than 10 ppm Pb. The limited sensitivity of the analytical method used did not allow significant differentiation of the lead content of the different swamp horizons.

HARRICANAW RIVER AREA, QUEBEC

The Sawyer Bog is located near the northern boundary of Maizerets township one mile east of the Harricanaw River and 35 to 40 miles north of Amos, Quebec (Fig. 1). In the vicinity of the Harricanaw River the topography is gently undulating and swampy conditions are characteristic.

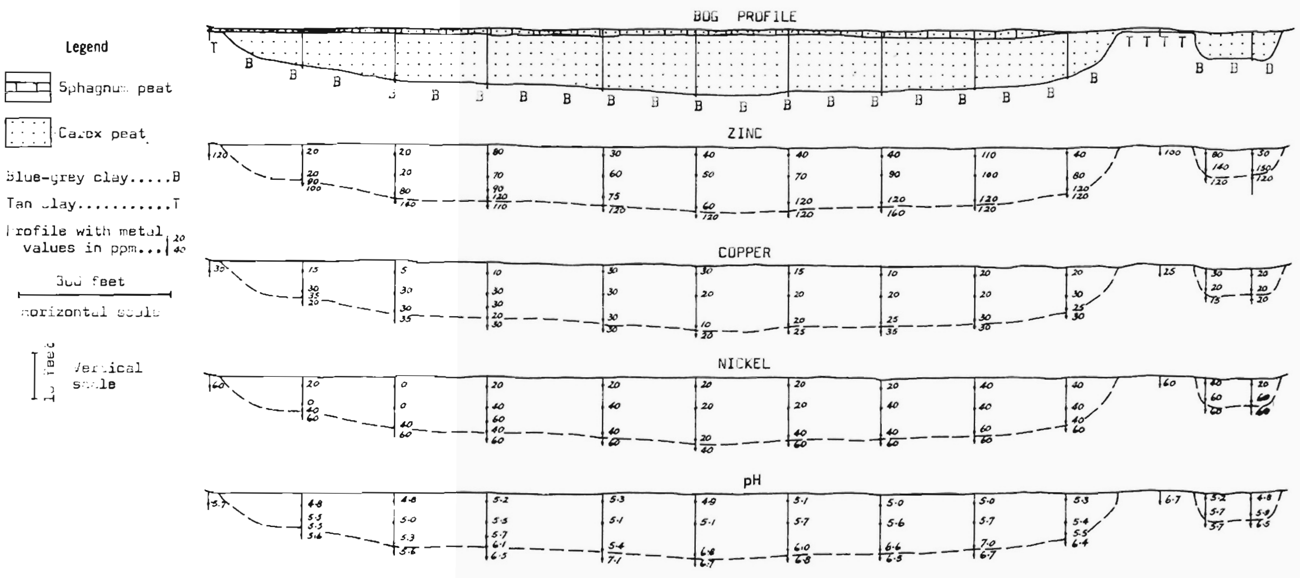
The geology of the area has been described by Wilson (1937), and in more detail by Tiphane (1959). Lake Barlow-Ojibway inundated the area in Pleistocene time and thick accumulations (20 - 200 feet) of glacial clay and silt were deposited which effectively mask large areas of the Precambrian bedrock. Most of the area is underlain by altered intermediate to basic volcanics. Minor amounts of peridotite and a few feldspar porphyry and diabase dykes are present. Large granitic bodies occur in the northeastern and southern parts of the area.

Disseminated pyrite and pyrrhotite are present in most of the volcanic rocks and slates in the Harricanaw River region. Tiphane (1959) records the presence of pyrite with galena in a shear zone along the Coigny River to the south, but no mineralization of economic significance has been found in the vicinity of the Sawyer bog.

The Sawyer bog is about one half mile long and between 1,000 and 1,200 feet in width. It is an open, wet, neva type of bog that drains northwards along a slow-moving stream. Widely spaced and stunted black spruce and larch trees grow in the swamp, the latter being characteristic of the wetter central sections. A dense shrub cover reaching one to three feet in height extends over ninety percent of the bog surface.

The peat layer varies between 5 and 10 feet in thickness. Two types of peat - sphagnum and carex varieties - occur, the carex being dominant. Sphagnum peat is intermixed with carex in the top 6 to 12 inches of the swamp profiles. A blue-grey clay underlies the peaty horizons in the bog.

X-ray diffraction investigations on the blue-grey clay have indicated that no true clay minerals exist. The clay is essentially finely ground rock flour composed predominantly of quartz and feldspar with lesser amounts of chlorite, amphibole and mica.



PROFILE OF SAWYER BOG WITH ZINC, COPPER, NICKEL AND pH VALUES

Figure 7

The pH of the upper layers of peat is more acid (pH 4.5 to 5.2) than that of the lower, more decomposed layers (pH 5.6 to 6.7). In turn, the pH of the clay, ranging from 5.7 to 7.1 is usually higher than that of the peats. This parallels the pH relationships in the Blacky Bay bog.

Trace-Element Distribution

The model B-27 Mobile Drill was not used in the investigation of the Sawyer bog and samples of only the upper blue-clay layer immediately beneath the peats were obtainable using the Hiller Peat Borer. According to Brooks (pers. comm.) there is an estimated 100 to 200 feet of overburden under the bog.

The distribution of copper, zinc and nickel is in the peat and blue-grey clay of the Sawyer bog closely resembles the distribution described in the Blacky Bay bog. Profiles are illustrated in Fig. 7. The contrast between the lower values in the surface peats and the higher values in the blue-grey clay is quite marked for both zinc and nickel. The top layers of the peat usually contain 20 - 60 ppm Zn and 20 ppm Ni whereas the clay contains 140 ppm Zn and 60 ppm Ni. The contrast for the copper is not so marked varying from 20 ppm Cu at surface to 30 ppm Cu at depth.

Daniel's Harbour Area, Newfoundland

Daniel's Harbour is a small fishing port on the western coast of the Island of Newfoundland approximately 70 miles north of Bonne Bay (Fig. 1). Inland, a broad coastal plain of low relief is underlain by a thick sequence of calcareous and, to a lesser extent, arenaceous and argillaceous rocks of miogeosynclinal origin. The strata are gently folded along east-west axes and range in age from Lower Cambrian to Middle Ordovician. The rocks are displaced by several major north-easterly and north-northeasterly high angle faults. These have been interpreted by Schuchert and Dunbar (1934) as thrust faults although Nelson (1955) considers them to be high angle reverse and normal faults.

All strata are more or less dolomitic. The more consistently dolomitic members belong to the Hawke Bay Formation (Cambrian) and the St. George Series (Ordovician), while more limy beds are generally found in the Table Head Series (Ordovician). This classification is complicated, however, by irregular, local dolomitization of all calcareous rocks including some of the more consistently limy beds of the Table Head Series.

Variations in relief in the area underlain by the Cambro-Ordovician rocks are small, maximum elevations reaching about 500 feet above sea-level. For the most part the country is poorly drained and approximately 50% of the area is covered by wet swamps and peat bogs. Numerous swallow holes are present in the carbonate rocks and some of the larger streams, in addition to the impeded waters in the swampy areas, disappear underground through these openings. A thick growth of pulpwood timber characterizes the better drained sections.

No large glacial lake extended over the Daniel's Harbour area during Pleistocene time and consequently no extensive accumulations of glacio-lacustrine deposits are present. The western coastal sections of Newfoundland were severely glaciated by ice masses moving westwards from mountainous areas to the east. During the retreat of the ice, irregular and often thick accumulations of glacial till were deposited over the whole of the coastal plain and small lakes formed in depressions. With the onset of peat growth these small lakes have developed into the swamps and peat bogs of the present day.

In 1963 the Newfoundland Zinc Corporation discovered sphalerite mineralization in St. George Series dolomites five miles east of Daniel's Harbour. Glacially transported boulders containing sphalerite are present in a train extending two miles westwards from the bedrock occurrences. Although geochemical sampling of the better drained overburden had indicated the presence of mineralization in the bedrock and glacial till, samples from peat bogs and swampy areas gave irregular and often negative results.

Nature and Composition of Swamps

A series of orientation profiles were sampled along the margins of swamps situated close to mineralization. This sampling indicated that the upper peaty and organic mud horizons are underlain by a variable thickness of compact grey clay. A maximum of three feet of grey clay was sampled with a hand auger to a total depth of four feet from surface. The thickness of the upper organic layers increases towards the centre of the swampy areas and may exceed 15 feet on the larger peat bogs.

Unlike the surveys carried out in the Blacky Bay bog and the Sawyer bog no detailed studies were made of the nature of the peat and the composition of the clays. The swampy areas near Daniel's Harbour closely resemble those in Quebec and Ontario, the central sections being treeless and of the neva type, and the marginal section supporting trees, the most typical species being black spruce. During more extensive surveys in Newfoundland it was noted that the colour of the clay layer in the swamp profiles varied with the bedrock type in the immediate vicinity. In dolomitic areas the clay is grey whereas in limestone areas the clay is bluish-grey. These colours reflect colour variations in the two types of rock. It is very likely, therefore, that the swamp clays in Newfoundland have been formed by comminution of the bedrock by glacial ice.

Determinations of pH on waters in the surface environment revealed a range of 6.5 to 7.5. No pH measurements were made on profile samples collected in the swamps.

Trace-Element Distribution

The majority of orientation samples were collected in swamps lying 1600 to 4500 feet south of the highest grade sphalerite showings. Sphalerite in bedrock and boulders had been recognized in two areas immediately bordering these swamps during geological investigations. Samples were analysed for total and cold-extractable zinc using techniques developed at the Geochemical Prospecting Research Centre, Imperial College, London (1962a; 1962b).

Profiles were sampled in a swamp lying approximately one mile east of the main showings in an area where no known mineralization occurred and where routine soil sampling had not indicated anomalous values. Analysis of a typical profile from this swamp gave the results in Table 1.

TABLE 1

VERTICAL DISTRIBUTION OF ZINC IN BACKGROUND SWAMP PROFILE, DANIEL'S HARBOUR AREA, NEWFOUNDLAND

Depth (ins.)	Description (Profile 48)	cx Zn+ ppm	Zn+ ppm	$\frac{cx\ Zn}{Zn}$
0 - 6	Peat, organic mud	0.4	20	2.0
6 - 12	Organic mud	0.4	60	0.7
12 - 18	Brown organic clay	0.8	40	1.0
18 - 24	Grey clay	0.8	105	0.8
24 - 30	Grey clay	0.8	85	0.9
30 - 36	Grey clay	0.4	80	0.5
36 - 42	Grey clay	0.4	110	0.4
42 - 48	Grey clay	0.4	100	0.4

\+ cx Zn - cold extractable zinc; Zn - total zinc

Distinctly anomalous total zinc values were detected in profiles near the smaller mineralized areas, the highest values occurring in samples close to known mineralization. The distribution of zinc in typical anomalous profiles is given in Table 2.

TABLE 2

VERTICAL DISTRIBUTION OF ZINC IN ANOMALOUS SWAMP PROFILES, DANIEL'S HARBOUR AREA, NEWFOUNDLAND

Depth (ins.)	Description (Profile 1)	cx Zn+ ppm	Zn+ ppm	$\frac{\text{cx Zn}}{\text{Zn}}$
0 - 6	Peat, roots, little organic clay	10.8	80	13.2
6 - 12	Black organic mud	7.6	190	4.05
12 - 18	Black organic mud	8.8	310	2.9
18 - 24	Grey clay, rock fragments	33.6	1,280	2.9
24 - 30	Grey clay	9.2	610	1.5
30 - 36	Grey clay, rock fragments	9.2	660	1.4

Depth (ins.)	Description (Profile 7)	cx Zn+ ppm	Zn+ ppm	$\frac{\text{cx Zn}}{\text{Zn}}$
0 - 6	Peat and roots	2.8	20	14.0
6 - 12	Brown organic clay	6.8	180	3.9
12 - 18	Grey clay	5.2	360	1.4
18 - 24	Rubbly grey clay	3.6	260	1.4
24 - 30	Rubbly grey clay	3.2	140	2.3
30 - 36	Rubbly grey clay	1.2	140	0.9

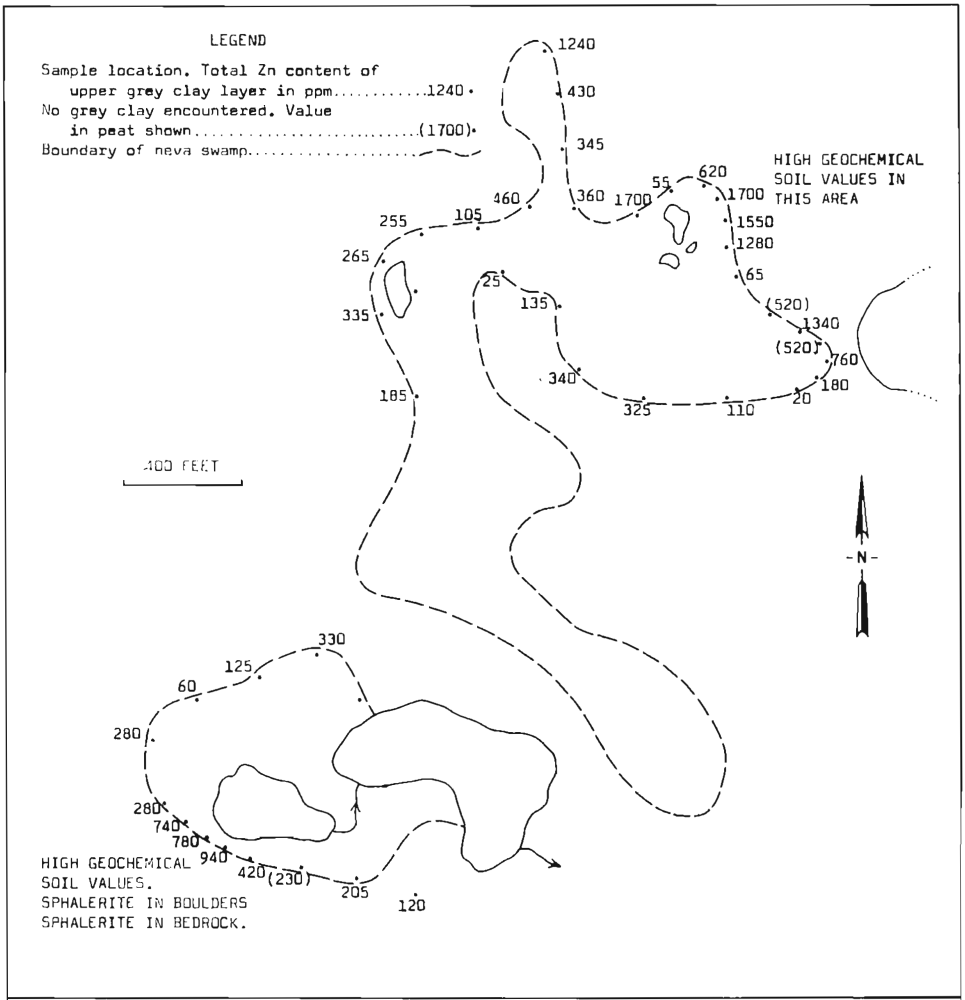
+ cx Zn - cold extractable zinc; Zn - total zinc

Profile 48 in Table 1 reflects background values in areas of barren bedrock. The distribution of zinc in the Newfoundland profiles parallels the behaviour of copper, lead and zinc in the background areas at Blacky Bay and near the Harricanaw River. The following tendencies are illustrated:

(i) Total zinc values increase with depth to the level of the upper grey clay layer. Below the top of the grey clay layer values tend to decrease. The contrast between the metal content of the surface peat samples, the upper grey clay layer and the lower clay layers is more marked in the more anomalous profiles.

(ii) The cx Zn/Zn ratio is highest in samples collected within six inches of surface and shows a tendency to decrease with greater depth. Again, this trend is more obvious in the more anomalous profiles.

The total zinc content of the top of the grey clay layer in the profiles sampled during the orientation survey is shown in Figure 8.



ZINC CONTENT OF UPPER GREY CLAY BENEATH PEAT HORIZONS IN SWAMP

FIVE MILES EAST OF DANIEL'S HARBOUR NEWFOUNDLAND

Figure 8

DISCUSSION

The previous sections have illustrated that certain trace-elements tend to become regularly distributed in swamp profiles in glaciated regions. The same relative distribution is present in both background and anomalous areas. Field and laboratory observations have suggested a possible explanation of the distribution.

The deeper drilling in the Blacky Bay area intersected the coarse glacial till underlying the clay horizons in the profiles. When this till was penetrated an artesian flow of water resulted indicating that the clay layers above the till are too impermeable to allow waters and solutions to rise through them. It is very unlikely, therefore, that the metals present in the profiles described have been derived from upward moving groundwaters.

The proximity of the highly anomalous zinc values in the upper clays to known mineralization in the Newfoundland field area indicates that the metal in the peats and clays has been locally derived, presumably by lateral movement.

The increase in metal content in the peaty horizons is paralleled by the increase in the humification of the peat with depth. Salmi (1955) notes that the base-exchange capacity of humified peat at a pH of 6.0 is 8 times greater than that of clay due to the formation of organic complexes which have a strong affinity for metals. This affinity is so strong that, according to Corwin (1950), the complexes are capable of removing copper from brass. Once formed, these complexes are usually very stable and require a vigorous extraction technique before the bonded metal can be removed.

It is very likely that the metals in the peats have been derived from the lake and swamp waters with which they are saturated. The environmental pH conditions in the peats in the three bogs described range from 5.5 to 7.5. According to Hawkes (1957) only zinc is likely to be freely soluble under these conditions, although in the natural environment it is very possible that ions of copper and nickel will be present above the laboratory-determined pH of hydrolysis of 5.3 for copper and 6.7 for nickel. Balonde and Ramsbergs (1957), after experimenting with sandy and peaty soils, concluded that the absorption of copper, manganese and zinc is predominantly a function of pH. They found that none of the trace elements were adsorbed at a pH of less than 4.0, but as the pH rises above 5.5 copper and zinc were increasingly absorbed by the peat and sandy soils.

The above observations suggest, therefore, that the metal content of the peats in the swamp environment is related to their degree of humification and the pH.

The greater concentration of metal in the clay under the peat than in the clays and sands lower in the profiles can be partially explained by adsorption of metal in the swamp waters onto the finely ground rock particles. Much of the copper, zinc and nickel was probably present in the comminuted sediments at the time of deposition but additional metal has been acquired from the lake waters. The upper clay layers have been in contact with the lake and swamp waters containing small quantities of metal for a long period allowing a maximum concentration by adsorption. The capacity for metal retention has been increased by its greater organic content resulting from the growth of plant organisms during the early stages of paludification of the swamps. In the Newfoundland area, zinc-rich material derived from nearby anomalous sources has undoubtedly contributed to the metal content of the upper clay layer. The low proportion of cx Zn in this horizon (see Tables 1 and 2) suggests that this zinc is strongly bonded to the clay size material or else is present in detrital minerals.

GEOCHEMICAL PROSPECTING APPLICATIONS

The relative distribution of zinc in the upper clay layer of the swamp profiles in the Daniel's Harbour district clearly indicates that selective sampling of this material can be used to outline nearby mineralization. Sphalerite is contained in bedrock suboutcropping in marginal freely drained areas and in boulders transported by glacial ice.

The results described from the Blacky Bay and Sawyer bogs in the Canadian Shield illustrate that trace elements in these areas tend to behave in a similar manner although present only in background concentrations. This similar behaviour in widely spaced areas of Quebec, Ontario and Newfoundland, clearly suggests that, when favourable conditions prevail, swamp sampling may be of value in reconnaissance exploration surveys for base metal deposits in glaciated regions of Eastern Canada and the Canadian Shield.

The results obtained by Salmi and Mitchell, described in the introductory sections of this paper, suggest that the same technique may be applicable in some European areas. However, as Salmi's studies indicate, surface sampling may be more satisfactory for prospecting for iron and manganese deposits.

Apart from the age of the bedrock, one very important difference between the Newfoundland area and the Blacky Bay and Sawyer bog areas is the presence in the latter two districts of considerable thicknesses of glacio-lacustrine deposits which locally deeply bury the underlying Precambrian rocks. Salmi (1955, 1956, 1958) has shown that chemical analysis of peat bog material can be used to outline base metal and iron deposits which occur beneath the swamps. Most of the swamps which Salmi sampled are underlain by 3 to 40 feet of glacial till and sand with some lenses of clay, and the mechanism by which the anomalous quantities of metals entered the peaty horizons is capillary action resulting from evaporation and transpiration of large quantities of moisture from the bog surface. It is conceivable, however, that secondary dispersion of metal from an orebody completely buried by thick and extensive sequences of glacio-lacustrine clays similar to those present in the Blacky Bay and Harricanaw River areas, would be impeded by the impervious nature of this cover. In environments similar to the Daniel's Harbour area, where swamps are interspered with areas of freely-drained overburden and bedrock, lateral movement of metal bearing materials can occur, providing optimum conditions for the development of geochemical anomalies in swamp profiles.

ACKNOWLEDGMENTS

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The Newfoundland investigations were part of a mineral exploration programme carried out by Newmont Mining Corporation of Canada in 1964. The authors thank Leitch Gold Mines Limited and the Newfoundland Zinc Corporation Limited for permission to take samples on their Daniel's Harbour property and publish the results. Grateful acknowledgments are also extended to British Newfoundland Exploration Limited whose property Newmont held under lease during their Newfoundland exploration programme and to Newmont Mining Corporation of Canada for their co-operation in the presentation of these geochemical results.

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LA PROSPECTION GEOCHIMIQUE DETAILLEE DE L'URANIUM

A. GRIMBERT - R. LORIOD*

Entre la prospection stratégique de l'Uranium destinée à repérer les régions favorables et la prospection tactique qui doit préciser la situation exacte du gisement, est apparue la nécessité d'une phase intermédiaire : la prospection détaillée, permettant de choisir les secteurs les plus intéressants au sein d'une zone favorable.

Alors que les dispersions géochimiques dans le réseau de drainage conviennent pour la prospection stratégique (1 ou 2 échantillons d'eaux et d'alluvions au km^2), et que les dispersions géochimiques dans les sols sont utilisées pour les recherches tactiques (400 à 2 500 échantillons au km^2), les dispersions géochimiques dans les eaux souterraines nous ont paru adaptées à la prospection détaillée (20 à 30 échantillons au km^2) et parfaitement capable d'apporter des renseignements sur la présence des minéralisations qu'elles lessivent dans leur parcours souterrain.

Il était nécessaire d'effectuer une enquête préliminaire pour préciser le mode opératoire et évaluer les possibilités des eaux souterraines échantillonnées aux sources, aux suintements et dans les puits.

On a choisi pour ces essais une région granitique du Massif Central français, riche en minéralisations uranifères filoniennes. C'est une région accidentée, au climat océanique, avec des vallées nombreuses drainant des précipitations atmosphériques de 1 000 mm environ réparties sur presque toute l'année.

On a retenu comme éléments à doser:

a) Dans les eaux:

- l'uranium, stable en solution dans une gamme étendue de pH.
- le radon, gaz soluble dans l'eau quelle que soit sa composition, ayant une période de désintégration de 3,8 jours.

b) Dans les "dépôts" de source:

- l'uranium, facilement fixé par les matières argilo-organiques fréquentes au voisinage des sources.

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La radioactivité γ maximale de chaque point de prélèvement a été mesurée à l'aide d'un scintillomètre muni d'un cristal de 1 x 1,5 pouce.

Le travail de terrain a comporté les opérations suivantes qui ont été réalisées sur tous les points d'eau (sources, suitements, mares, marécages) dont la densité est de 30 au km^2 environ:

1°/- Collecte des échantillons

- 50 ml. d'eau dans des sachets en polyéthylène pour le dosage de l'uranium.

- 30 ml. d'eau dans un tube à essais bouché hermétiquement pour le dosage du radon. Ce prélèvement doit être effectué à la source géologique qui peut être repérée à l'aide du scintillomètre grâce au dégagement de radon qu'elle produit.
- 100 à 150 g. de dépôt de source dans un sachet en papier fort, pour les dosages d'uranium.

2°/- Mesure de la radioactivité γ

La radioactivité maximale retenue est celle qui correspond au maximum de l'accumulation du dépôt actif engendré par le Rn; essentiellement le RaC puissant émetteur de

Les techniques d'analyses ont été celles couramment utilisées à bord de camions-laboratoires:

- pour l'uranium, la fluorimétrie, après séparation chromatographique des éléments accompagnateurs, a été retenue.

Cette méthode possède les caractéristiques suivantes:

- dans les eaux: sensibilité = 0,1 γ/l
  fidélité = ± 20% pour 1 γ/l
  rendement = 48 dosages par homme/jour.

Les résultats sont exprimés en ppm du résidu sec calculé à partir de la conductivité de l'eau.

- dans les sols, les alluvions, les dépôts de sources =
  sensibilité = 0,1 ppm
  fidélité = ± 15% pour 5 ppm
  rendement = 90 dosages par homme/jour.

Les résultats sont exprimés en ppm d'U métal mis en solution par une attaque nitrique 2,5 N.

pour le radon, dosage par scintillométrie α à l'aide d'un ballon scintillant enduit de sulfure de zinc activé à l'argent dans lequel on a récupéré par barbotage les gaz dissous dans l'échantillon d'eau.

sensibilité = 10^{-10} Ci/l
fidélité = ± 20 %
rendement = 50 dosages par homme et par jour (avec 2 ensembles de comptage).

Les résultats sont exprimés en émanes correspondant à 10^{-10} Ci/l.

L'interprétation des résultats a été faite après report des résultats sur 4 plans au 1/10 000 comportant respectivement:

- les teneurs en U des eaux
- les teneurs en Rn des eaux
- les teneurs en U des dépôts de source
- les radioactivités maximales des sources.

Afin de pouvoir comparer entre eux, d'une façon aussi objective que possible, ces quatre documents, nous avons pour chacune des populations statistiques correspondantes calculé une valeur typique et un indice de dispersion qui nous ont permis d'établir des échelles d'anomalies réellement comparables. Nous avons pris comme valeur typique la médiane (μ) qui n'est pratiquement pas influencée par les valeurs très élevées et comme indice de dispersion la moyenne des écarts (E) par rapport à la médiane. Les valeurs obtenues sont les suivantes:

	Rn 10^{-10}Ci/l	U eaux ppm résidu sec	U dépôts ppm
médiane (μ)	170	20	26
moyenne des écarts (E)	142	22	34

Les différentes coupures (C) des échelles d'anomalies ont été obtenues à partir de la relation:

$$C = \mu + kE$$

dans laquelle on a donné à k une suite de valeurs identiques, d'une population à l'autre.

L'étude des résultats obtenus sur plusieurs milliers d'échantillons a permis de faire les observations suivantes:

Reproductibilité des résultats.

Elle a été étudiée pour 139 points d'eau échantillonés à 2 époques de l'année. Les coefficients de corrélation (calculés par la méthode graphique de M. CRAMER) ont montré que la reproductibilité est médiocre pour Rn (0,6); satisfaisante pour l'U des dépôts de source (0,8); bonne pour les teneurs en U du résidu sec des eaux (0,9).

La mauvaise reproductibilité des teneurs en Rn résulte principalement de la rapidité avec laquelle ce gaz s'échappe de l'eau au contact de l'air. Il en résulte de grandes difficultés pour l'exécution des prélèvements qui à quelques décimètres d'intervalle peuvent fournir des résultats très différents.

Comparaison des résultats entre eux.

Il existe une bonne corrélation (0,73) entre la teneur en Rn et la radioactivité maximale des sources. Il semble que la radioactivité due aux produits de filiation du Rn (RaC) soit plus significative car elle traduit le débit en Rn de la source et non pas seulement la teneur en Rn de l'eau.

La mesure de la radioactivité ne présente pas le défaut de reproductibilité des teneurs en Rn dû au dégazage rapide de l'eau. Mais elle est rendue localement impossible par l'absence du matériau fixateur du dépôt actif.

La corrélation entre la teneur en Rn et la teneur en U du résidu sec des eaux est mauvaise. Le coefficient de corrélation varie de o0,3 à 0,5 suivant la nature des points d'eau retenus pour l'établissement du diagramme. Cependant on constate une concordance géographique assez bonne entre les anomalies de chaque type, avec toutefois un léger décalage des unes par rapport aux autres.

La corrélation entre la teneur en U des dépôts de sources et la teneur en U du résidu sec des eaux n'est pas satisfaisante. Ces teneurs sont parfois très différentes et il conviendra d'élucider ce problème.

Concordance avec les minéralisations connues.

A toutes les minéralisations connues correspondent des anomalies en U, Rn et radioactivité dans les sources situées à proximité (quelques centaines de mètres), qu'elles soient directement en relation avec les structures minéralisées ou qu'elles proviennent de la nappe circulant au voisinage de la surface.

Les valeurs des anomalies peuvent être différentes suivant l'élément mesuré par suite des caractères particuliers du point d'eau échantillonné, mais les anomalies uranifères sont généralement les plus satisfaisantes. Par exemple une petite source située à proximité immédiat d'un gisement connu donne une très forte anomalie en Rn (2 500 émanes) avec une radioactivité relativement faible (300 μR/h), alors que la teneur en U est intermédiaire (80 ppm U dans le résidu sec). Ce désaccord entre les résultats peut s'expliquer dans le cas présent par l'absence totale de matériaux propices à la fixation du RaC d'où le peu d'activité, alors que le très faible débit de la source entraîne une teneur en Rn anormalement élevée dans l'eau.

Une étude de chaque anomalie est donc nécessaire avant de porter un jugement sur son intérêt.

A l'issue de cette enquête, on peut donc conclure que dans les terrains cristallins:

- l'échantillonnage des sources au stade de la prospection détaillée de l'Uranium présente un réel intérêt, à condition de prélever toutes les sources:

- les prélèvements d'eaux pour le dosage de l'uranium et la mesure de la radioactivité maximale des sources sont suffisants.

- les dosages de Rn ne seront plus utilisés que dans certains cas particuliers (absence de matériaux fixateurs de dépôt actif) et pour un stade plus avancé des recherches lorsque l'eau fera défaut.

On peut également espérer, par l'étude des sources, obtenir des renseignements qualitatifs sur l'intérêt des indices qui existent à proximité et ultérieurement repérer des gisements n'affleurant pas, mais qui ont été lessivés par les eaux souterraines.

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Eh AND pH IN GEOCHEMICAL PROSPECTING

John A. Hansuld*

INTRODUCTION

The three tasks of geochemistry may be summarized thus:

1. To establish the abundance relationships of the elements.

2. To study the distributions and migration of the elements.

3. To detect the laws governing the observed abundances, distributions and migration of the elements.

Most of the work in exploration geochemistry to date has been concerned only with tasks one and two. Although petrologists have been studying the behavior of elements under high temperature and pressure conditions for years, as yet there has been very little serious attempt to quantitatively define the laws and principles governing the migration of elements in the surface or near-surface environment. Most of these environments represent aqueous chemical systems in which the environment and reactions involved may be characterized almost entirely by oxidation potential (Eh) and pH. It is possible, if reasonable assumptions are made, to evaluate the effect of changing environmental conditions on the migration of individual metals within the framework of Eh and pH as graphically portrayed by Eh-pH diagrams. Two areas of application are considered:

1. the oxidation of primary sulfides in the outcropping or sub-outcropping environment, and

2. the mobility of metals in different secondary dispersion media.

PURPOSE AND SCOPE

The purpose of this paper is to discuss the concept of Eh and pH and demonstrate, with the aid of some simple diagrams, some applications to geochemical prospecting. The scope of the paper is rather general with emphasis on practical application rather than chemical theory. Diagrams and examples are purposely kept simple in order not to confuse or discourage the novice.

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This paper is quite similar to that presented previously (Hansuld, 1966). The text is revised in places, a number of diagrams changed and the bibliography made more selective.

Eh-pH BACKGROUND

To illustrate the techniques involved and provide a background for those not familiar with Eh and Ph, we might first very briefly define the terms, describe their measurement and indicate the method of Eh-pH diagram construction.

Eh

Eh is a measure of the oxidizing or reducing tendency, or more explicitly, potential of a system. Because oxidation or reduction involves a transfer of electrons, it is fundamentally an electrical property measureable in volts or millivolts. Eh potentials as opposed to simply E or measured potentials represent specific potentials in that they are measured against or compared to the standard hydrogen half cell; thus they are said to be referenced to the hydrogen scale -- hence the term Eh. The more positive the potential, the more oxidizing it is relative to the hydrogen half cell. However, a negative Eh value does not neccessarily mean a reducing potential, only that it is reducing relative to the standard hydrogen half cell. Because Eh potentials are relative values and most measurements of natural systems on the hydrogen scale are positive, that is oxidizing, Eh is usually referred to simply as oxidation potential.

The oxidation potential of an aqueous system is determined experimentally by measuring the voltage between an inert electrode such as platinum, and a reference standard hydrogen electrode. In actual practice, a secondary standard half cell such as a calomel electrode is used as a reference electrode in place of the primary standard hydrogen electrode. It then becomes necessary to add the Eh of the reference electrode (.241 volts for a saturated calomel electrode at 25°C) to the measured potential E to get the Eh value. Therefore, Eh is in effect a calculated potential obtained by adding the Eh of the reference electrode to the measured potential E as shown at the top of Figure 1. This simple calculation is unfortunately omitted or made incorrectly in many cases, even though readings are reported as Eh. This results in some confusion when comparing data from different sources, especially when the method of measurement is not given. Contrary to common belief, there is as yet no instrument on the market whose scale is designed to read Eh directly, although one could easily be made.

pH

pH is a numerical expression of the relative acidity or alkalinity of an aqueous system. Acids and bases all owe their acidity or alkalinity to the single property of production of hydrogen or hydroxyl ions. pH refers to the concentration of these

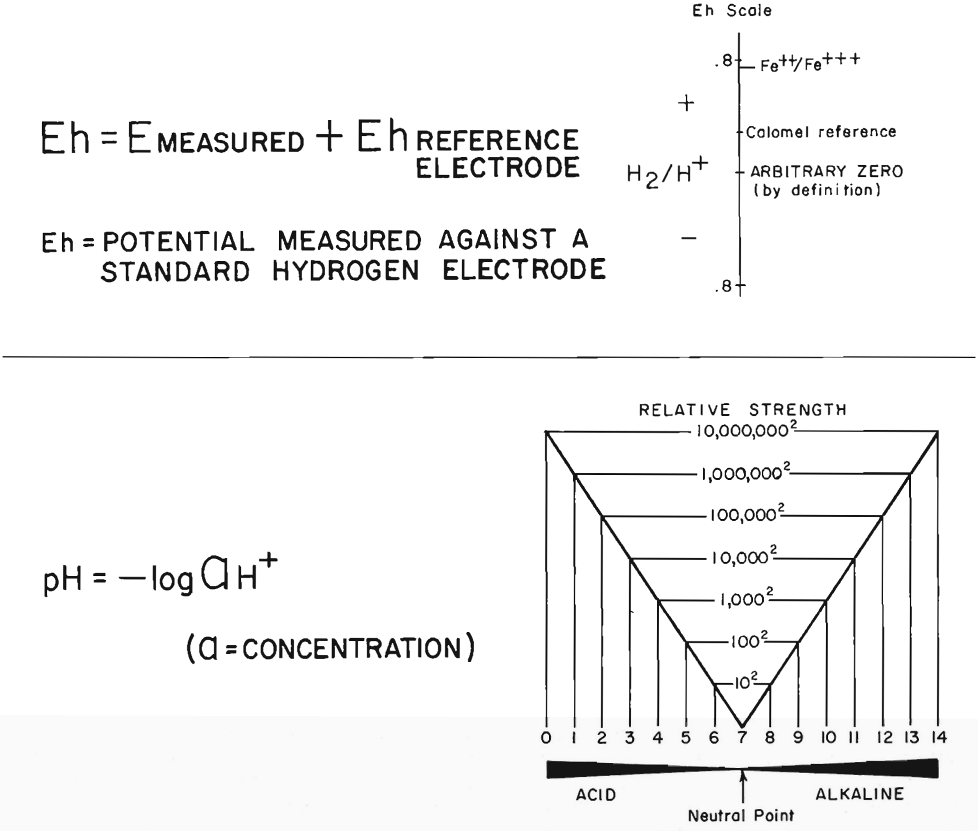
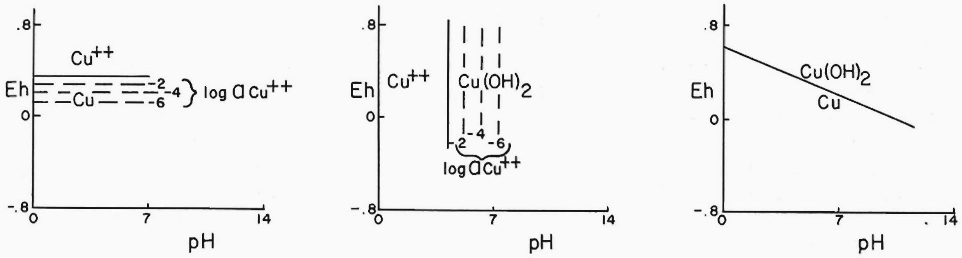


Figure 1. Eh and pH.



a) REACTIONS DEPENDENT ON **Eh**

ex. $Cu = Cu^{++} + 2e$

$Eh = .337 - .029 \log a\,Cu^{++}$

b) REACTIONS DEPENDENT ON **pH**

ex. $Cu^{++} + 2H_2O = Cu(OH)_2 + 2H^+$

$pH = 4.6 - \frac{1}{2} \log a\,Cu^{++}$

c) REACTIONS DEPENDENT ON **Eh** and **pH**

ex. $Cu + 2H_2O = Cu(OH)_2 + 2H^+ + 2e$

$Eh = .610 - .059\,pH$

Figure 2. Eh – pH diagrams.

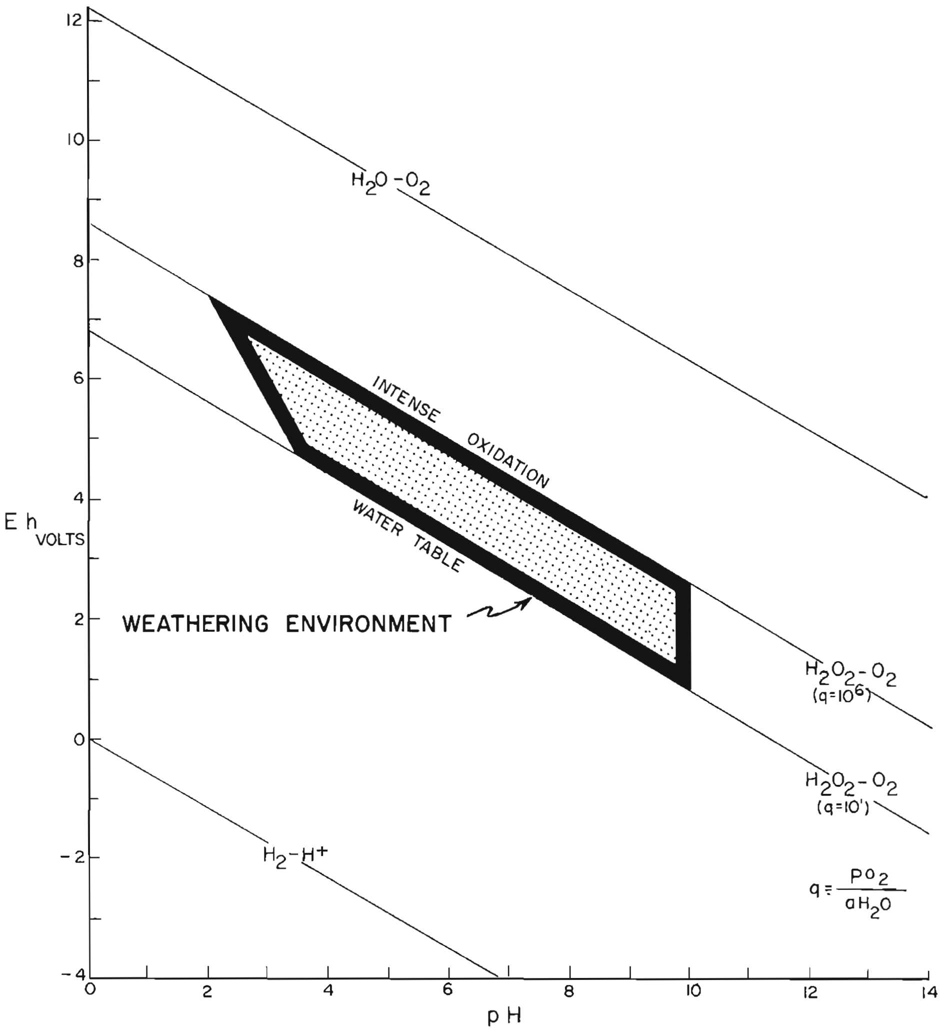


Figure 3. Weathering environment. After Sato (1960a).

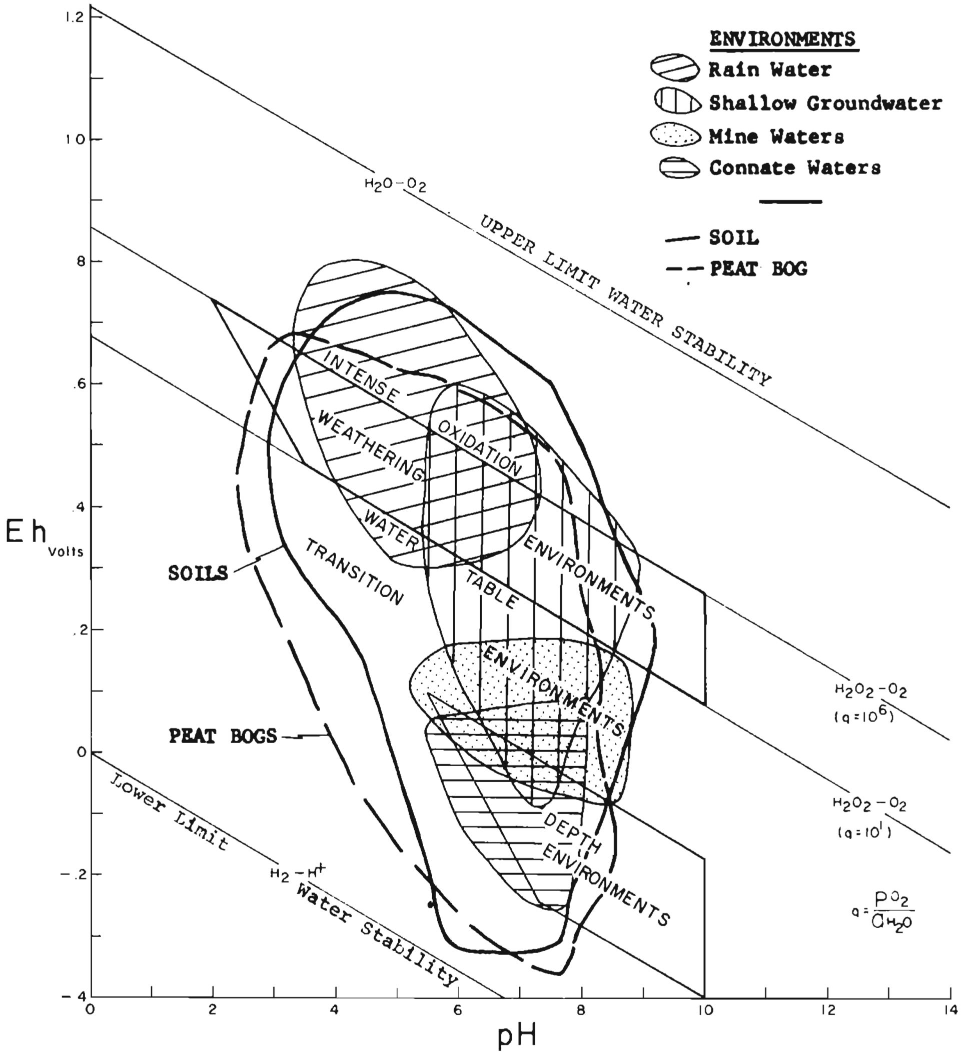


Figure 4. Geochemical environments in terms of Eh and pH. After Baas Becking et al. (1960); weathering and depth environments after Sato (1960a).

ions and is defined as the negative logarithm (to the base ten) of the hydrogen ion activity (thermodynamic concentration). From this is derived the pH scale where the neutral point is defined as the circumstance when the activity of hydrogen ion equals that of hydroxyl ion. For dilute aqueous solutions at 25°C and 1 atmosphere, this means a pH of 7. Because pH is a logarithmic function, one pH unit represents a ten-fold change. This point is commonly not fully appreciated in comparing pH values. Relative intensities between different pH units are illustrated graphically in Figure 1.

Measurement of pH is a fairly routine procedure. It is easily accomplished electronically by measuring with a high resistance potentiometric instrument, the voltage developed between a specially designed glass electrode and reference electrode. The Modern pH meter is nothing more than a vacuum tube voltmeter with scale calibrated to read directly in pH units.

When equipped with a suitable electrode pair, a pH meter can be used to measure oxidation potential. However, calculations must be made to convert pH scale readings into E and then Eh values. It is misleading to refer to a pH meter as an Eh-pH meter.

Eh-pH Diagrams

Many chemical reactions involve either or both electrons and hydrogen or hydroxyl ions. Therefore, plots of Eh versus pH provide a convenient means of describing and comparing reactions between various species under a given set of conditions. Plots of some simple reactions involving Eh, pH or both are shown on Figure 2. Changes in concentrations of dissolved species are indicated by means of dashed lines, thus adding a third variable--ionic concentration--to the diagrams.

The range of values that must be considered in constructing Eh-pH diagrams is determined by the limits observed in nature. The overall limits of aqueous environments, of course, are defined by the stability limits of water. These are given by two sloping lines at the top and bottom of the diagram in Figure 3. However, these limits are rarely met in nature and on the basis of field measurements and theoretical considerations Sato (1960a) defined a weathering environment (as shown on Figure 3) representing the probable ranges of Eh and pH values found in most secondary geochemical dispersion media.

The natural limits of a number of geochemical environments as determined from field measurements by Baas Becking et al. (1960) are shown on Figure 4. Of particular interest is the wide range of Eh-pH conditions observed in soils and peat bogs. This clearly demonstrates the need for making measurements on a specific environment under study.

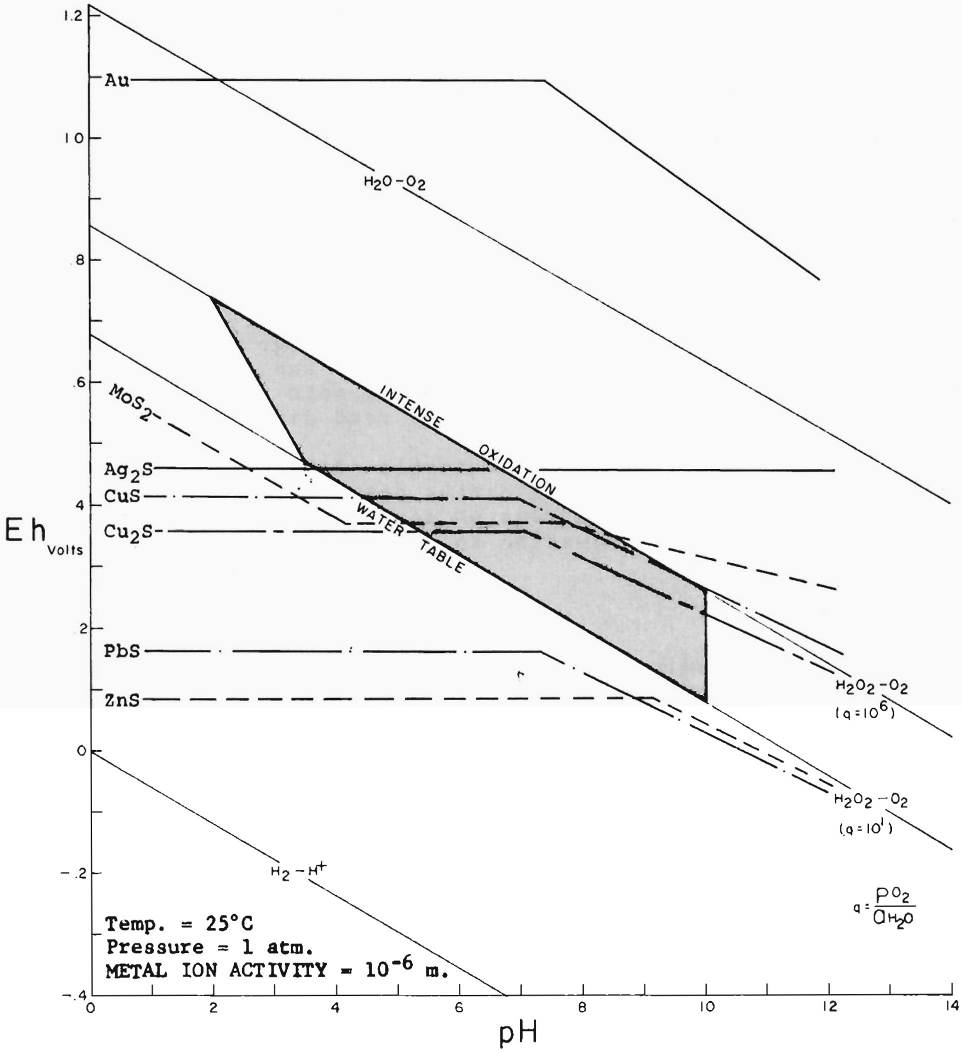


Figure 5. Oxidation reaction potentials of some simple sulphides. After Sato (1960b); molybdenite after Hansuld (1960).

APPLICATIONS

Geochemical exploration is principally concerned with movement of a particular metal or metals from its source to a given sample point. Two basic types of movement are recognized--physical and chemical.

The first problem is to decide to what extent each of these is responsible for the dispersion of the particular metal of interest. Physical movement is relatively straightforward and involves a consideration of various geomorphic erosional processes. Chemical movement on the other hand, requires a geochemical study of the outcropping or sub-outcropping environment to determine if the metal sulphide is oxidizing or not, and the various dispersion media to determine if the metal is mobile in these media. Therefore, the study may be considered in two steps: 1) oxidation of the primary sulphides and 2) mobility of metal ions.

1) Oxidation of Sulphides

Oxidation of sulphides is prerequisite to the chemical dispersion of the metals they contain. The extent of oxidation can sometimes be ascertained by visual inspection of outcrops; however it is possible to approach the problem more quantitatively within the framework of Eh and pH. Oxidation reaction potentials of a number of simple sulphides for a metal ion concentration of 10^{-6}molar are plotted in Figure 5. Note that most of these potentials become pH-dependent in higher pH regions where hydrolysis controls metal ion activities. These potentials, with the exception of that for molybdenite, are calculated from empirical data by Sato (1960b). The molybdenite potential, determined by Hansuld (1960), is tentatively considered to be mainly a function of the molybdate to acid molybdate ratio as determined by pH. The potential of native gold is included for comparative purposes.

The concentration of 10^{-6} is chosen arbitrarily to represent the minimum concentration of most metals in geologic materials. Therefore these potentials represent, for a given temperature and pressure, the minimum potential at which the particular sulphide begins to be actively oxidized. That is, in order for the sulphide to be oxidized, its environment must possess an oxidation potential equal to or greater than that of the sulphide at a given pH. For example, a potential between those of galena and chalcocite at pH 5 would indicate that in such an environment, galena and sphalerite, with potentials below that of the environment, would actively oxidize, whereas chalcocite, covellite, molybdenite and argentite with potentials above that of the environment would be thermodynamically stable. These "stable" sulphides would not liberate metal ions so that movement of metals away from the source area can only be by mechanical processes.

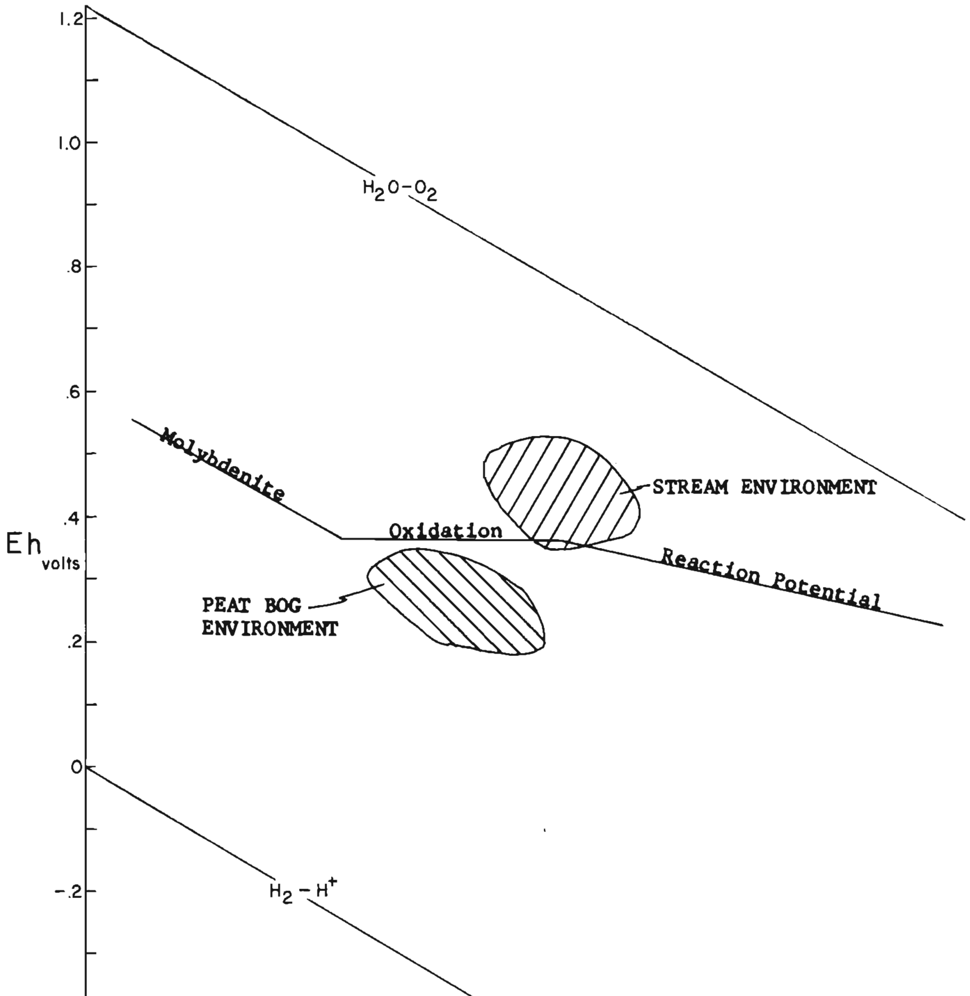


Figure 6. Eh – pH plots. Aillik molybdenite showing, Aillik Bay, Labrador.

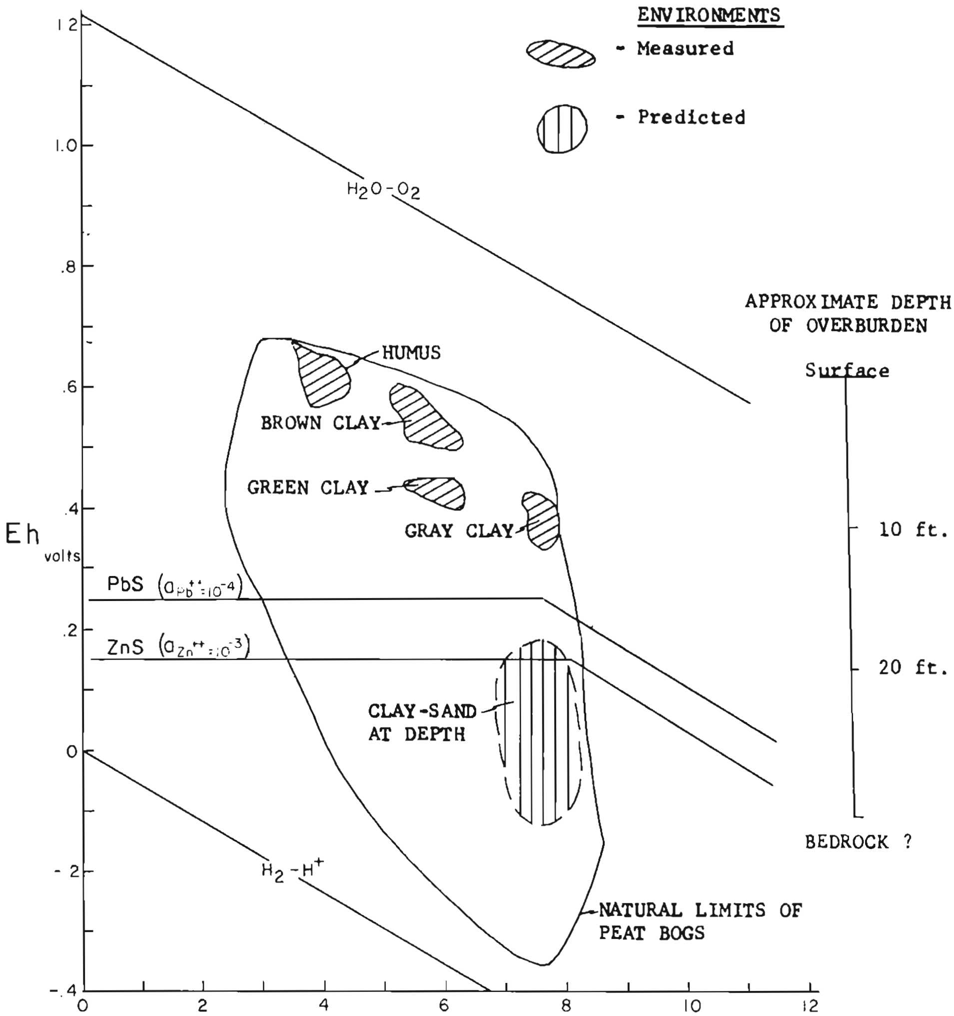


Figure 7. Eh – pH plot of peat bog environments, Mattagami area, Quebec. Measured and predicted environments plotted from measurements by Gleeson (1960); peat bog limits after Baas Becking et al. (1960); sulphide potentials calculated from data by Sato (1960b).

The significance and application of sulphide reaction potentials to geochemical exploration was first demonstrated by Hansuld (1960) in investigating a soil anomaly over the Aillik molybdenite showing in Labrador. Eh and pH measurements of the soil beneath peat bog and stream sediments were made in the field and the oxidation reaction potential of molybdenite was determined experimentally in the laboratory. These data are plotted on Figure 6. Note that molybdenite remains stable in the peat bog environment but is actively oxidized in the stream environment. Therefore, dispersion of molybdenum in soil is essentially a mechanical process and requires a detailed study of the geomorphic history of the area. Recognition of this fact was necessary in properly assessing the success and limitations of the geochemical surveys.

Another example is illustrated by data taken from a geochemical study by Gleeson (1960) in the Mattagami area, Quebec. Oxidation potential and pH measurements were made on surface and near surface humus and clays in a number of peat bogs. A typical plot of the measured field data is shown on Figure 7. Unfortunately, only pH was measured below depths of 15 ft; however, the decrease in oxidation potential measured over the first ten to fifteen feet is fairly uniform and by extrapolating these values, the Eh of clays and sand to bedrock can be predicted. The measured pH and predicted Eh values define the Eh-pH environment of clay-sand at depth. Also plotted are oxidation reaction potentials for galena and sphalerite in equilibrium with their respective metal ions at concentrations found by Gleeson in these deeper layers. Both potentials lie above the clay-sand environment and therefore are "stable" at these metal concentrations. This accounts for the surprising freshness at the bedrock interface of the sulphides, which, in most places, are found to be covered by only a thin oxide skin. The clay-sand depth environment simply is not oxidizing enough to provide sufficient metal ions for chemical dispersion and therefore is not emenable to conventional geochemical prospecting methods. The Eh-pH data offer an explanation of why conventional geochemical prospecting has proven relatively unsuccessful in the Mattagami district and other areas in the Canadian Shield covered by similar terrain, such as the Texas Gulf Sulphur Kidd Township deposit.

2) Mobility of Metal Ions

Assuming a sulphide is oxidizing, this brings us to the second step of the study--mobility of metal ions.

The behavior of a particular element or metal in a given dispersion medium is largely controlled by stability relations among its various oxidation products. Recognition of these products and their stability relations is therefore a prerequisite to a proper understanding of the observed data. Because most secondary dispersion media represent aqueous chemical systems stability relations are best expressed as functions of

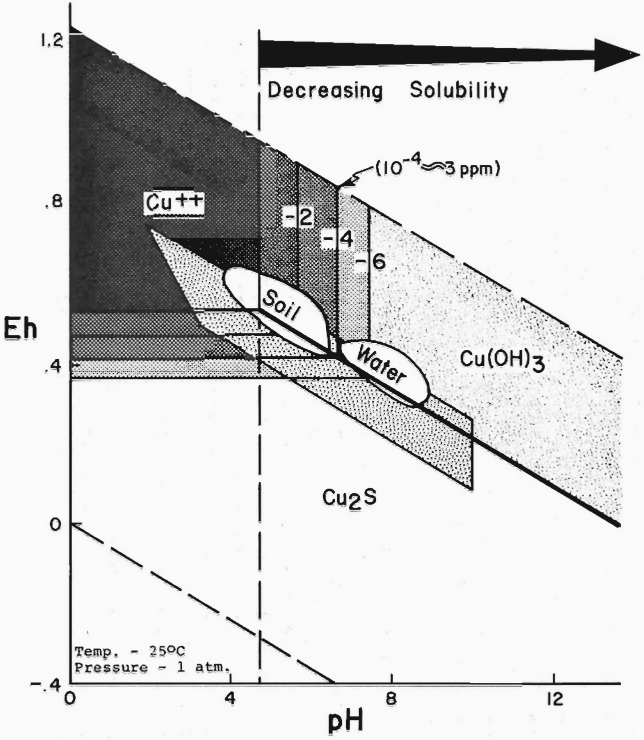


Figure 8. Some stability relations in chalcocite-water system.

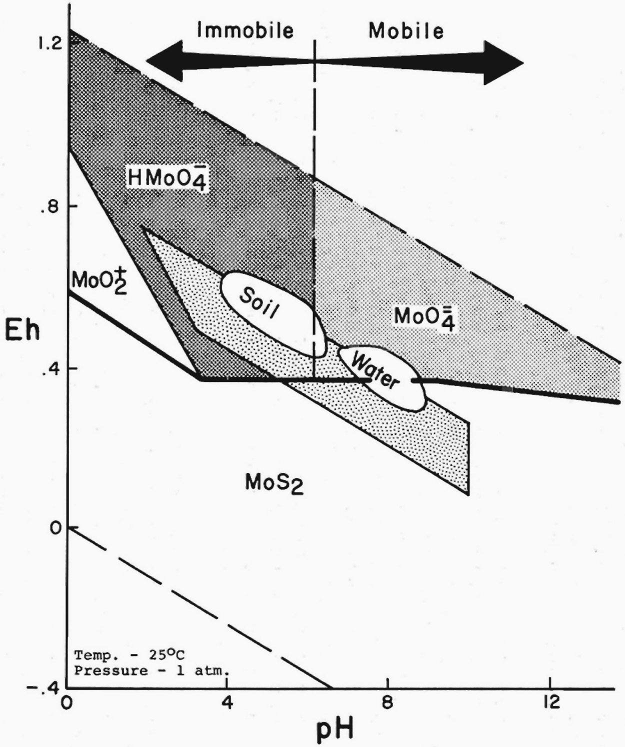


Figure 9. Some stability relations in molybdenite-water system.

Eh and pH. Thus by plotting the measured Eh-pH field of a particular environment on a stability diagram of the metal under study it is possible to make some prediction as to the mobility of the metal in that environment.

Some examples are shown by the accompanying diagrams. Because of the dearth of thermodynamic and empirical data, only the simpler chemical species of the metal are considered. Therefore, the stability diagrams given are obviously gross oversimplifications of most natural systems. In many cases, they are mixtures of theoretical and experimental data and in this respect their construction is somewhat arbitrary. However, because the emphasis throughout this discussion is on practical utility rather than theoretical exactness, these rather arbitrary presentations should not prove unduly upsetting to the pure scientist, but instead only serve to stimulate further experimentation to provide the necessary fundamental data.

Figure 8 shows some stability relations in a simple chalcocite-water system together with plots of soil and stream water environments typical of the porphyry copper deposits of the southwestern United States. The solubility of cupric ion decreases with increasing pH and to a lesser extend decreasing Eh. For example, at a pH of 6 the solubility of copper is less than 3 ppb. The decreasing solubility is depicted schematically by the arrow at the top of the diagram. Note that the copper formed in the oxidation of chalcocite is soluble only under strongly acid and highly oxidizing conditions. At higher pH's the oxidized copper is precipitated in situ as the metastable copper hydroxide. The acid character of the soils overlying mineralized bedrock implies that it should be leached of most of its oxidized copper. This explains the low copper values commonly found in soils directly over known mineralization in the southwestern United States. Similarly, the alkaline surface drainage waters, with very limited copper solubility, account for the negligible amount of copper usually found in the main drainage systems. Most of the oxidized copper has been carried vertically downward in solution by acid mine waters to eventually form supergene copper sulphides.

Figure 9 shows some stability relations in a molybdenite-water system. Of particular interest in this diagram is the boundary at pH 6 between acid molybdate and molybdate anions. The acid molybdate anion is relatively insoluble in contrast to the molybdate anion. The relative mobilities are depicted schematically by the arrows at the top of the diagram. Looking again at the soil and stream environments of the southwest we see that in the soil environment oxidized molybdenum occurs predominantly as the immobile acid molybdate anion and in the stream environment as the relatively mobile molybdate anion.

Molybdenum, because of its close association with porphyry copper type deposits, is commonly used as a pathfinder element in the geochemical search for these deposits. The basis

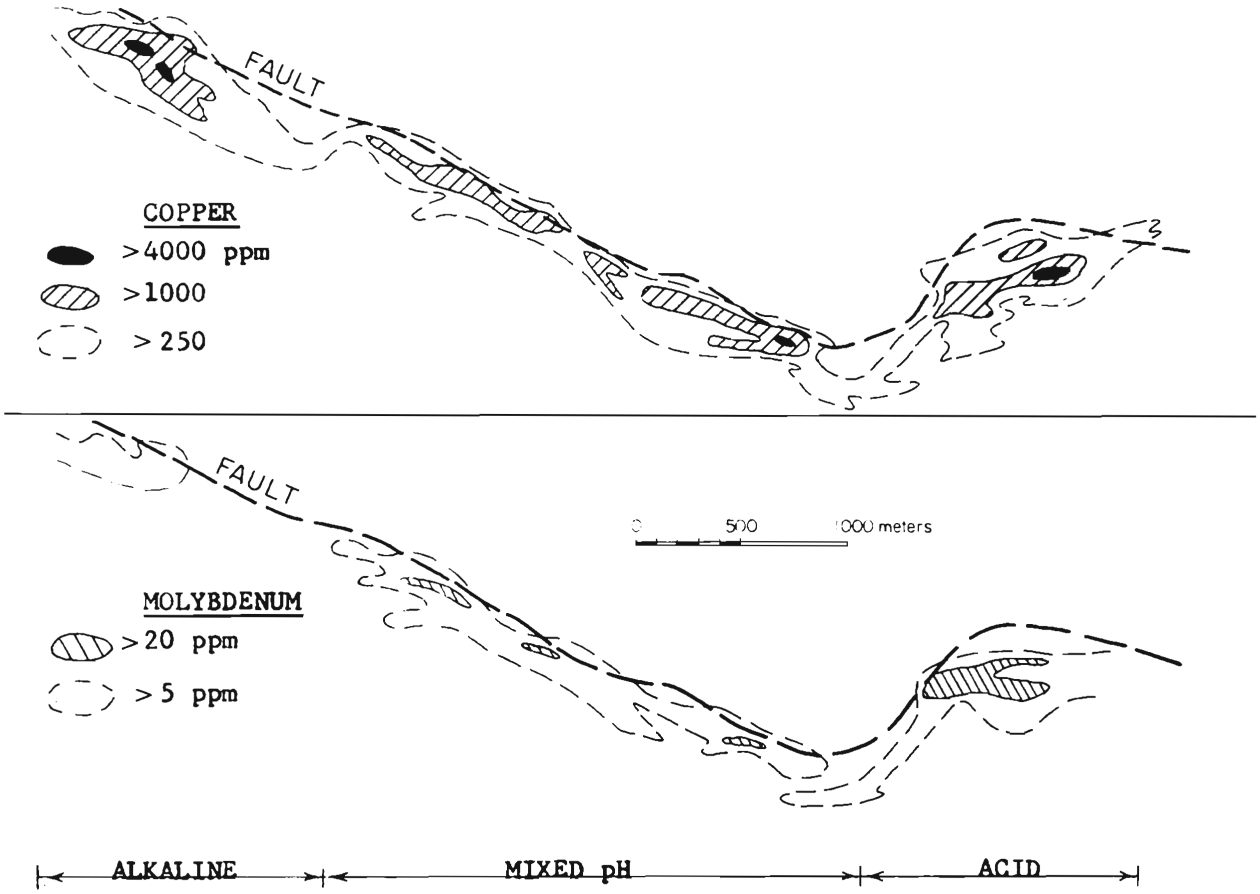


Figure 10. Distribution of anomalous amounts of molybdenum and copper, La Muda area, Puerto Rico. After Bergey (1962).

for this approach is best explained in terms of Eh and pH. A comparison of stability relations of the two metals as illustrated in Figures 8 and 9 indicates that where one metal is relatively mobile, the other is immobile. Molybdenum remains essentially fixed in acid soils where it occurs as the relatively immobile acid molybdate, whereas copper is fairly soluble and is leached away. On the other hand, in alkaline surface drainage waters, where copper solubility is extremely limited, molybdenum occurs as the relatively mobile molybdate anion. Therefore, molybdenum in acid soils can be used to define drill targets and in alkaline drainage waters as a reconnaissance tool to locate areas of copper mineralization. In general, it may be said that behavior of molybdenum in the secondary geochemical cycle is inverse to that of copper.

The importance of recognizing the relative mobilities of copper and molybdenum is well illustrated in a soil survey from the La Muda area, Puerto Rico. Figure 10 shows the distribution patterns of anomalous copper and molybdenum reported by Bergey (1962). The differences in these patterns are consistent with the observed differences in soil pH reported by Hansuld and Parker (1962). Particularly interesting is the high copper, weak molybdenum zone at the west end of the survey area. Soils there are slightly alkaline in contrast to the acid soils to the east. Although not shown on the diagram, the three small molybdenum anomalies in the central section of the survey all occur in soils locally more acid than soils in the adjacent areas. It is worth mentioning that the best copper mineralization was not found under the best copper anomaly.

CONCLUDING REMARKS

In closing, it should be emphasized that the application of Eh and pH to geochemical exploration is still very much in its infancy. Many assumptions must be made resulting in gross over-simplifications. However, if used within their limitations, they provide a convenient means of tackling the third task of geochemistry-to detect the laws governing the observed abundances, distribution and migration of the elements. As more use is made of Eh and pH to quantify reactions and environments, geochemical prospecting will become less of an art and more of a science.

ACKNOWLEDGMENTS

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Although the ideas expressed are solely those of the writer some data are taken from other sources as credited in the text. These data broaden the scope of the paper and appreciation is extended to those making this data available, either personally

or in published form; however, the writer alone assumes full responsibility for any errors or misinterpretations.

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FIELD LABORATORIES FOR OPERATION BATHURST, A COMBINED CHEMICAL AND SPECTROGRAPHIC ANALYTICAL PROGRAM

J.J. Lynch and C.C. Durham*

Operation Bathurst was a geochemical program carried out by the Geological Survey of Canada in the summer of 1965 to discover the distribution of certain trace elements in the stream and spring waters and sediments of the Bathurst-Jaquet River district of New Brunswick. The total area covered was approximately 1,200 square miles.

In order to carry out the field portion of the program, six two-man field parties were each allotted a map sheet, or a portion of a map sheet, for sampling. The parties traversed each river and stream by foot, sampling at 1,500 foot intervals. At each sampling point a number of tests were performed on both the water and the sediment. These included temperature, pH and total heavy metal measurements of the water (Boyle et al. 1955) as well as the determination of the cold extractable total heavy metal content of the sediment (Smith, 1963). Where possible, samples of water and a heavy mineral concentrate were collected at a point representative of each stream or river traversed. In addition to collecting samples and performing tests, each party recorded a number of observations concerning rock types, composition of sediment and precipitate stain.

To speed plotting of the results and to allow for possible resampling of some areas, it was found essential to perform all the sediment analyses in laboratories situated within the sampling area. These analyses utilized the facilities of three separate laboratories: sample preparation, chemical and spectrographic.

At intervals of one to seven days the field parties submitted their sediment samples for analysis. No attempt was made to analyse either the water or heavy mineral concentrates. Upon submission, the sediments were first processed in the sample preparation laboratory housed in a small abandoned farm building with a floor area of about 200 square feet.

Since the size of the analytical program prohibited the use of mobile chemical laboratories, the chemical analyses of the stream sediments were performed in the science laboratory of the Mgr. C.A. Le Blanc High School in Bathurst. The room which housed this laboratory was approximately 25 feet long by 18 feet wide. It was equipped with one fume hood and its furniture consisted of ten benches each with about 10 square feet of working area. Although the furniture and plumbing facilities were quite suitable, the electrical services were inadequate and temporary

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* Geological Survey of Canada, Ottawa.

circuits were installed around the perimeter of the room in order to accommodate equipment drawing large amounts of current. This equipment included a furnace, hot plates, stills, centrifuges, refrigerator, ovens and a hot water bath.

The analyses carried out in this laboratory were performed by six university students hired for the summer months. If seasonal employees are utilized at least two weeks must be set aside at the beginning of the program for training purposes. Failure to adhere to this practice is likely to lead to low production and erroneous results.

Analyses were carried out in batches of fifty and usually two batches per day were processed. Each batch consisted of forty-eight unknowns, one control, and one blank. The control samples were more or less similar in composition to the unknowns and they should cover a suitable range of values. In addition they should be analysed by different methods and by different analysts in order to assign specific values for the different elements. If, upon completion of a batch, the values for the control sample vary by more than the error inherent in the method (usually ±25% of the amount present) the source of the deviation must be ascertained and all the analyses of the batch repeated. Similarly, high values for blank determinations must be investigated.

The sediment samples were dried in their envelopes for approximately 36 to 48 hours at 65° C in a gas heated oven. After drying they were sized by sieving through an 80 mesh stainless steel screen. The plus 80 mesh fraction was discarded.

About 15 grams of the sieved portion were ground in a ceramic ball mill for 25 minutes. This produced a powder which was at least minus 150 mesh. Although the minus 80 mesh fraction is quite suitable for chemical analysis, the finer grained sample is prepared for spectrographic work.

After grinding, each sample was split and placed in two plastic vials. One vial was forwarded to the chemical laboratory and the other to the spectrographic laboratory. In the course of an eight hour day one man could sieve, grind, and bottle one hundred samples.

Classical methods of silicate analysis require complete sample dissolution. For some geochemical purposes, such as prospecting, this approach is unnecessary and hence many decomposition procedures render soluble only a portion of the total metal present. Since efforts were made in this program to obtain values approximating the absolute abundances of the various elements, more complete sample extractions were required than conceivably would be employed if this were purely a prospecting venture.

The analytical methods employed in the geochemical laboratories were designed so that large numbers of samples could be processed in a short period of time using seasonal personnel. Hence many of the steps included in more precise and accurate methods were modified. Two steps that were modified were sample decomposition and removal of interferences.

Since very few colorimetric reagents are specific for one element, the effects of interfering elements must be removed. This can be accomplished in a number of ways. Separations by solvent extraction, precipitation, etc. are the best but are also the most time consuming methods of removing interferences. Hence in geochemical analysis, separation is avoided unless no other means are available. Whenever possible, interferences are eliminated by pH adjustment, complex-forming agents or oxidation or reduction to other valence states.

The elements determined in the chemical laboratory were zinc, copper, lead, arsenic, antimony, molybdenum and tungsten. Three different procedures were used to decompose samples. Thus, the six seasonal employees were divided into two-man teams, each of which was concerned with the determination of those elements connected with a specific decomposition procedure.

Zinc, copper and lead were determined using the methods outlined by Gilbert (1959). A fusion with potassium pyrosulphate was employed. The zinc method was slightly modified by the addition of sodium fluoride to the acetate buffer in order to suppress any interferences due to aluminum; this modification is described by Stanton (1962).

The arsenic content of the sediments was determined using the method of Lynch and Mihailov (1963). One major modification was included which resulted in a great saving of time. Instead of fusing the sample with potassium hydroxide in a nickel crucible, the sample was heated with ammonium chloride in a test tube. Upon leaching the residue with 6 normal hydrochloric acid a solution was available for both the arsenic and antimony tests. In addition to the above modification, one milliliter of 5% potassium iodide solution was added in the arsenic procedure in order to hasten the reduction of pentavalent arsenic to trivalent arsenic with stannous chloride.

The antimony method used was essentially that outlined by Stanton and McDonald (1962).

Molybdenum and tungsten were determined using the methods of North (1956) with only minor changes to speed analysis. These included fusing the samples in batches of sixteen in an electric furnace at 800°C for 10 minutes, centrifuging the sample solutions in order to hasten clarification and employing zinc dithiol rather than dithiol, since the former is much more stable.

By employing the methods described, six analysts were capable of analysing ninety-six samples per day. Each day the results from the previous day were checked and compiled. Reports were submitted to the chief field officer once a week for distribution to the sampling parties. The results for the various elements were then plotted on appropriate maps.

SPECTROGRAPHIC LABORATORY

C.C. Durham

It is not always feasible to house chemical laboratories in mobile units. The complexities of analysis and bulk of the equipment governs the usefulness of mobile chemical laboratories. A spectrograph and its ancillary equipment, on the other hand, lends itself readily to truck or trailer mounting. Canney, Myers and Ward (1957) did in fact demonstrate that spectrographs, suitably modified, could be moved and located near sampling areas.

In 1961 R.H.C. Holman, then of The Geological Survey of Canada, designed and supervised the construction of a mobile spectrographic laboratory in which the spectrograph and accompanying equipment were completely housed in a trailer. The trailer is 24 feet long, 8 feet wide, and 7 feet high - providing 190 square feet of floor space. The shell is partitioned into four compartments: weighing room, spectrograph room, darkroom, and densitometer-comparator room.

The weighing room is situated at the rear of the trailer with benches installed along both outside walls. This compartment contains balances for the weighing of samples and buffering materials.

The spectrograph room is connected to the weighing compartment by a sliding door. The spectrograph, which is located on the right-hand side of the room is a 1.5 metre Jarrell-Ash wide angle model. It has a grating of 15,000 lines per inch, giving a reciprocal linear dispersion of 5.4 Angstroms per millimeter in the second order and a range of 2100 to 4800 Angstroms. The camera photographs 20 inches of spectrum on 35 mm film. The spectrograph is permanently supported by means of rubber shock absorbers mounted on a heavy wooden table fitted with casters in order to facilitate easy movement.

The source unit and a small refrigerator are situated on the opposite side of the room. The source unit is connected to the arc stand by overhead cables. In addition, there is bench space to provide for a small muffle furnace, hot plate, and infrared lamps. An air conditioner is mounted in the ceiling of this room.

The darkroom is equipped with stainless steel bench tops and sinks and contains a film processor, film washer, and film dryer. A water cooler, mounted over the trailer hitch, provides cold water for the film processor.

A table mounted densitometer-comparator is located in a small 6 x 4 foot room adjacent to the darkroom. The comparator is mounted on a L-shaped bench which also provides limited space for compilation of results and writing of reports.

In order that field laboratories be utilized to the fullest extent, their transportation to the field site and subsequent assembly must be performed with dispatch. For Operation Bathurst, a total of six days were required to move the spectrographic laboratory from Ottawa to the field area and to ready it for analysis.

The spectrographic method used in this project is essentially that outlined by Myers, Havens, and Dunton (1961). A ten milligram sample was mixed with twenty milligrams of graphite and transferred to a carbon electrode. Twenty milligrams of a buffer mixture were added to cap the charge. The buffer mixture consisted of one part calcium carbonate and four parts graphite.

In order to promote smooth burning of the stream sediment sample, a two step oxidation procedure was employed. After being loaded into the electrode, the samples were ashed at 450°C for one hour in a small muffle furnace. Upon cooling, 2 drops of a saturated solution of magnesium nitrate in absolute ethyl alcohol were added to each electrode. The electrodes were then heated under infrared lamps for at least five minutes.

Using the sample electrode as the anode the samplees were then arced to completion under the conditions listed in Table 1.

TABLE 1

CONDITIONS FOR SPECTROGRAPHIC ANALYSIS

Electrodes - 3/16 carbon.
Gap - 5 mm.
Excitation - D.C. arc, 15 amperes, 220 volts.
Slit - 15 microns.
Slit height - 1mm.
Light intensity - 6% neutral density filter
27% rotating light attenuator
Exposure time - complete sample consumption.
Emulsion - Kodak Spectrum Analysis Film No.1
Developer - Kodak D-19

After developing the exposed film, the resulting spectra were compared visually with the spectra of a standard film. The standard film was prepared by arcing synthetic mixtures containing known amounts of the various trace elements in the range 0.5 part per million to 10,000 parts per million.

Table 2 shows the elements determined, the lower limits of detection and the warelengths of the analytical lines used.

TABLE 2

ELEMENTS DETERMINED IN SPECTROGRAPHIC ANALYSIS

Element	Detection limit (ppm)	Wavelength (A)
Tin	10	3175.02
Silver	0.5	3280.68
Nickel	2	3414.76
Cobalt	10	3453.51
Chromium	10	4254.35
Barium	70	2277.02
Manganese	30	2949.20

By employing the methods and equipment described, three operators were capable of analyzing 75 samples per day. All analyses were checked and compiled on a day to day basis, and at the end of each week reports were submitted to the head of field work for distribution to the field parties. The results were then plotted on the appropriate maps.

During the months of June, July and August, 3,550 samples were processed in the three laboratories. In all, a total of 49,700 analyses were performed by a staff of nine seasonal employees and two staff members. At the termination of the summer, all analytical work was completed, and all of the elements analyzed were plotted on maps.

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AUTOMATIC DATA PLOTTING AND MATHEMATICAL AND STATISTICAL INTERPRETATION OF GEOCHEMICAL DATA

Ian Nichol, R.G. Garrett and J.S. Webb*

INTRODUCTION

Regional geochemical surveys aimed at delineating areas of favourable mineral potential as well as providing information relating to the fundamental geology of the area yield considerable volumes of analytical data presenting formidable problems of data handling, presentation and interpretation.

Hitherto, data handling and plotting have been carried out by laborious manual methods, with the data being presented as a series of single element maps and interpreted subjectively. Due to the difficulty of assimilating more than a few variables simultaneously, it is probable that only the more obvious features have been recognized and subtle though significant features of the data have remained undetected.

This contribution sets out to introduce methods of automatic plotting and objective interpretation of geochemical data using mathematical and statistical procedures currently being employed at the Applied Geochemistry Research Group at Imperial College. The techniques are exemplified solely by problems to which they have been applied. Detailed consideration of their significance and their application to regional geochemical problems in general will be discussed in a later paper.

DATA PLOTTING

Preliminary studies of automatic data plotting have been carried out using a Stromberg-Carlson 4020 (Figure 1). The S-C 4020 consists of a tape reading and decoding system, a cathode ray tube and a 35mm camera. A computer programme, run on Imperial College's I.B.M. 7090/1401 computer, converts the original data into a plotting format and writes a tape of plotting instructions. The tape is read by the S-C 4020 which converts the input into characters which are projected on the cathode ray tube. The plots on the tube are then photographed by the 35mm camera. Simultaneously, the S-C 4020 produces an 8 in. x 8 in. reproduction of the plot on photosensitive paper (Figure 2). Jobs normally taking a number of hours to complete by hand can be carried out in a matter of seconds. A prototype example of a symbol map from the S-C 4020 with the drainage superimposed is illustrated in Figure 3.

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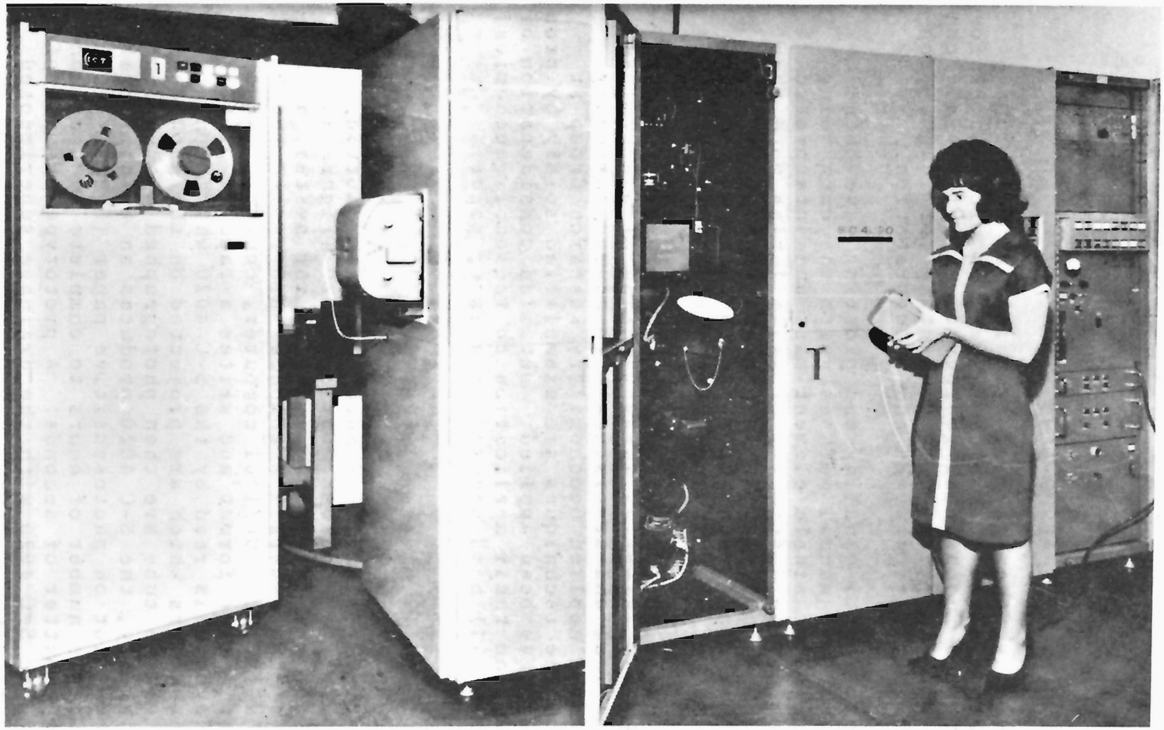


Figure 1. Stromberg-Carlson 4020 (after Jones 1966).

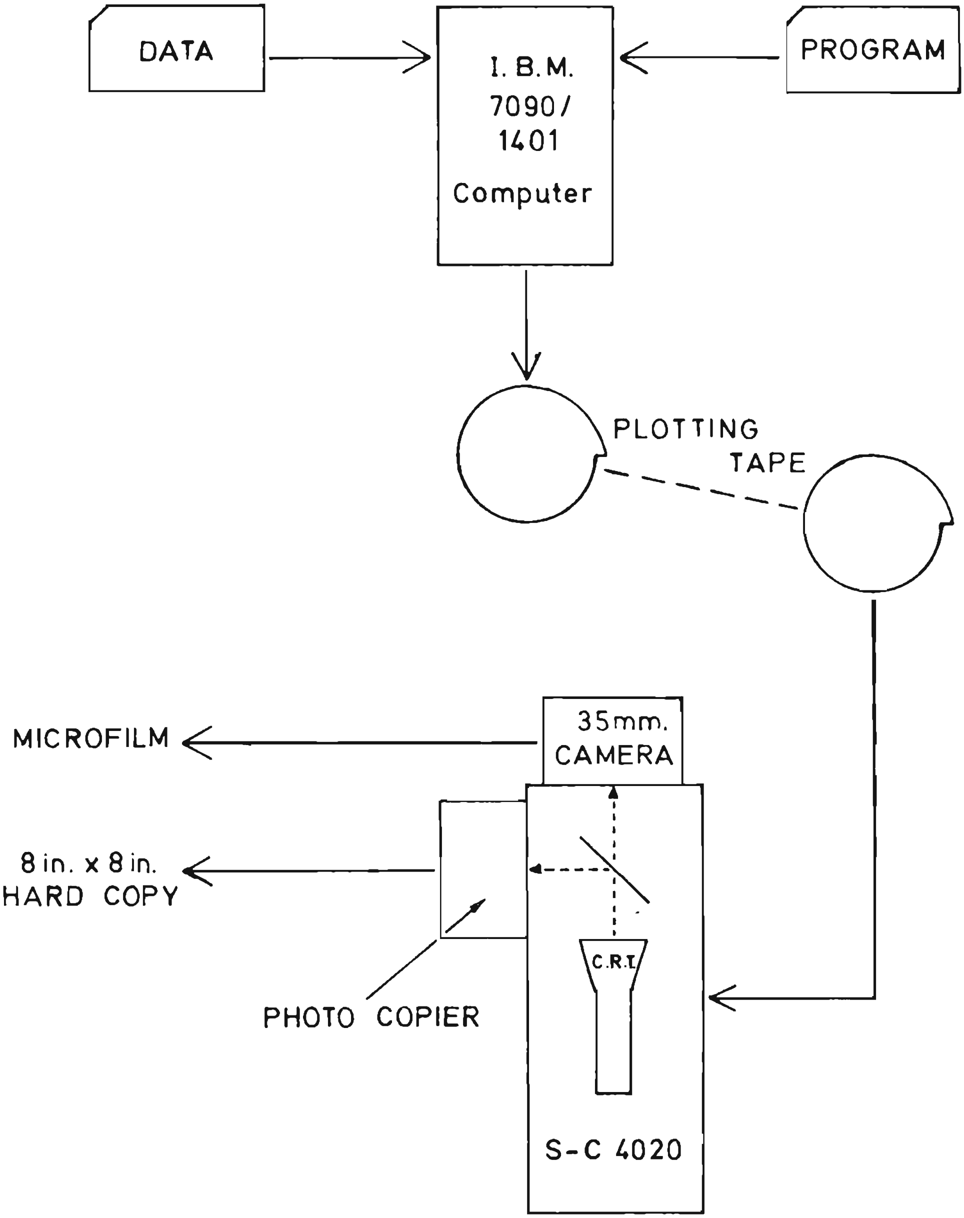


Figure 2. Flow Diagram for automated data plotting using the Stromberg-Carlson 4020.

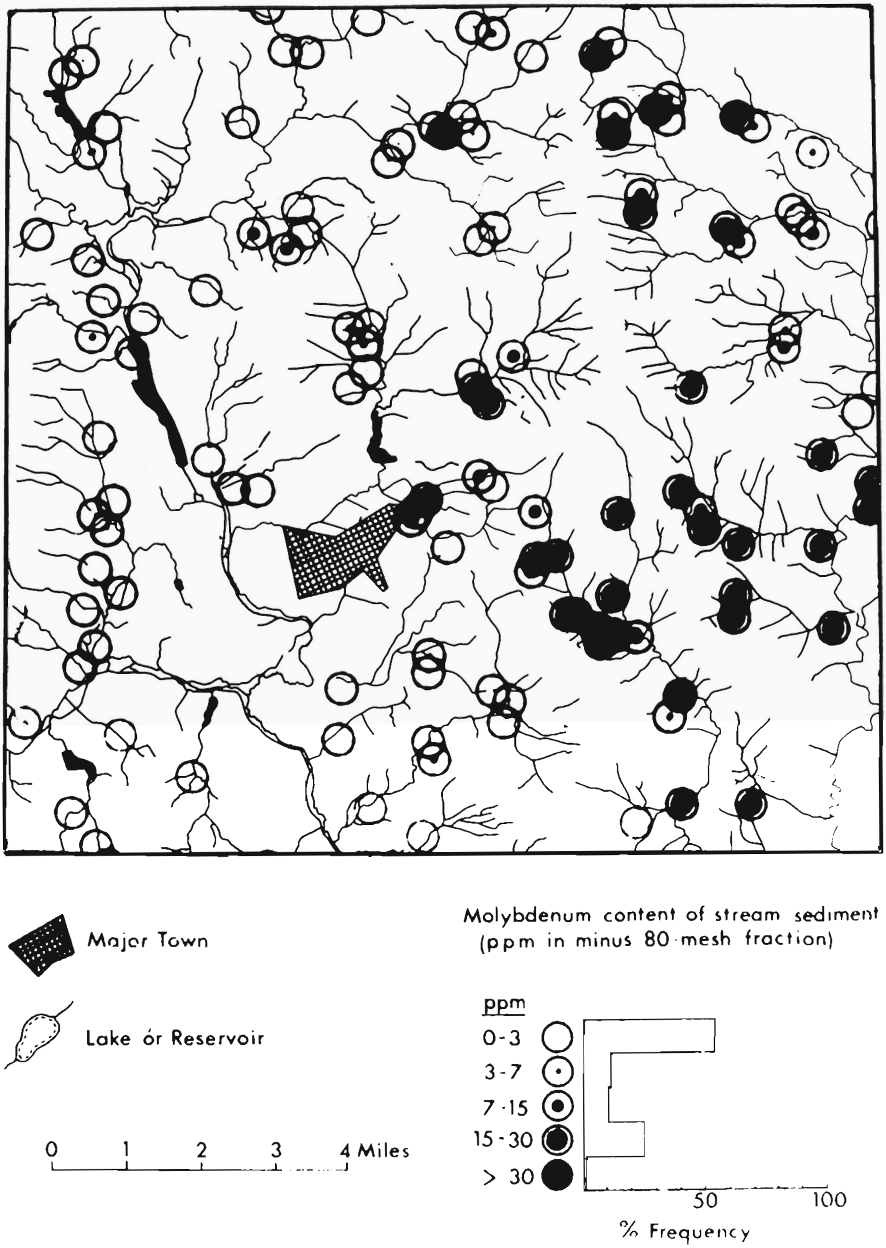


Figure 3. Prototype example of automatic plotting of geochemical data using the Stromberg-Carlson 4020 with the drainage superimposed.

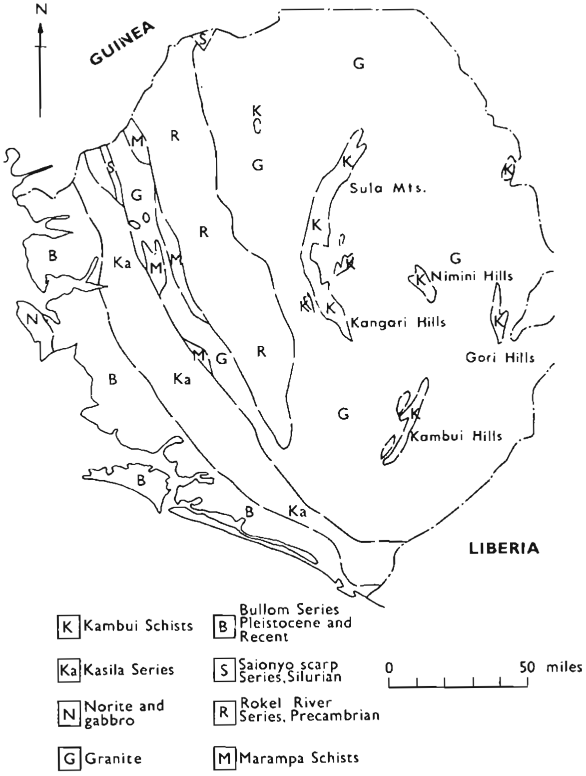


Figure 4. Geological map of Sierra Leone (after Geological Survey of Sierra Leone).

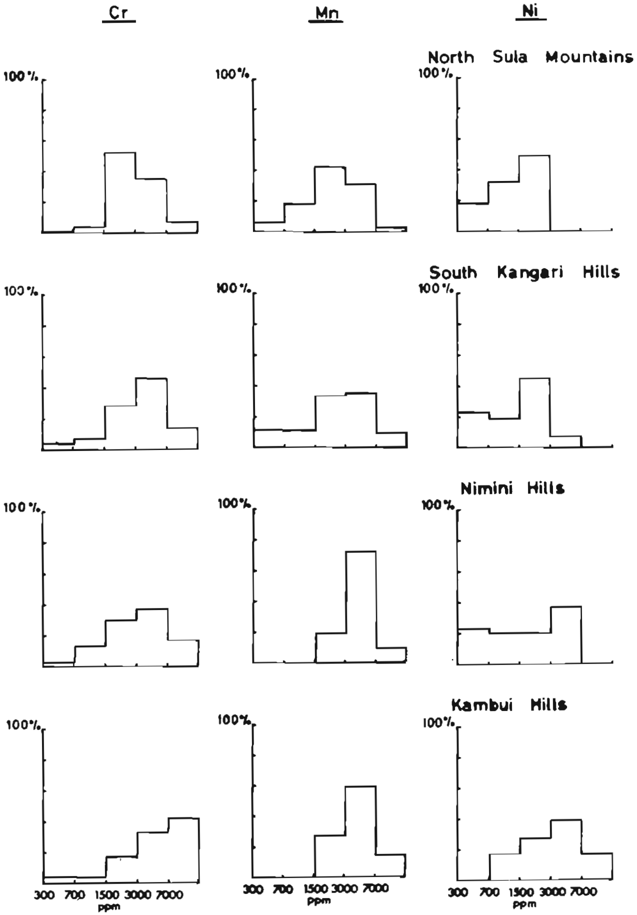


Figure 5. Distribution of Cr, Mn and Ni in stream sediments associated with ultrabasic rocks.

DATA INTERPRETATION

Before passing on to a consideration of various methods of interpretation in some detail, it is necessary to digress briefly to describe the geological background of the data used in this paper. A programme of regional drainage reconnaissance was initiated in Sierra Leone in 1960 over mineralized schist belts surrounded by granite gneisses (Figure 4). The geology of the different schist belts is similar in many respects but the metallogenic associations differ. Although the data are complex, differences in the fundamental geochemistry of the schist belts are also apparent (Garrett, 1966). For instance, Cr, Mn and Ni are present in greater amounts in stream sediments over a given bedrock type in the schist belts of the S.E. than those in the central part of the area (Figure 5). Subsequent reconnaissance of 15,000 sq. mi. of the surrounding gneisses, based on some 200 sample sites, indicated the existence of a pronounced trough in the distribution of a number of elements passing through the central schist belt, with higher metal contents to the N.W. and S.E. (Figures 6 and 7). The central low and S.E. high region corresponds with the geochemical differences noted between the individual schist belts (Figures 5, 6 and 7). In the case of manganese, the differences in the mean metal content across the area are relatively clear cut, but in the case of nickel they are much less distinct.

The precise requirements of interpretation posed by the data considered here are (a) to distinguish focal points of interest within an area of gradually changing geochemistry over the Basement gneisses as a whole, and (b) to recognized significant anomalies indicating mineralization in areas of strongly contrasting geology, as in the schist belts where the background geochemical patterns are extremely complex. The applications of trend surface, rolling mean and factor/vector analysis to these problems are examined below.

A. Trend Surface Analysis

Polynomial trend surface analysis is a procedure whereby systematic regional variations may be separated from the local variations and errors. The precise form of the calculated surface is that for which the sums of squares of the residuals has a minimum value.

Most applications of the technique in the geological sciences have been in the fields of geophysics and petrology (Grant, 1957; Krumbein, 1959; Whitten, 1959), however, the technique has been used to aid in interpreting data obtained in a geochemical soil survey in Utah by Connor and Meisch (1964).

The computations involved in determining trend surfaces are not feasible without the aid of an electronic digital computer. In the present study the programme published by Whitten (1963), was used on the Imperial College I.B.M. 7090/1401 computer.

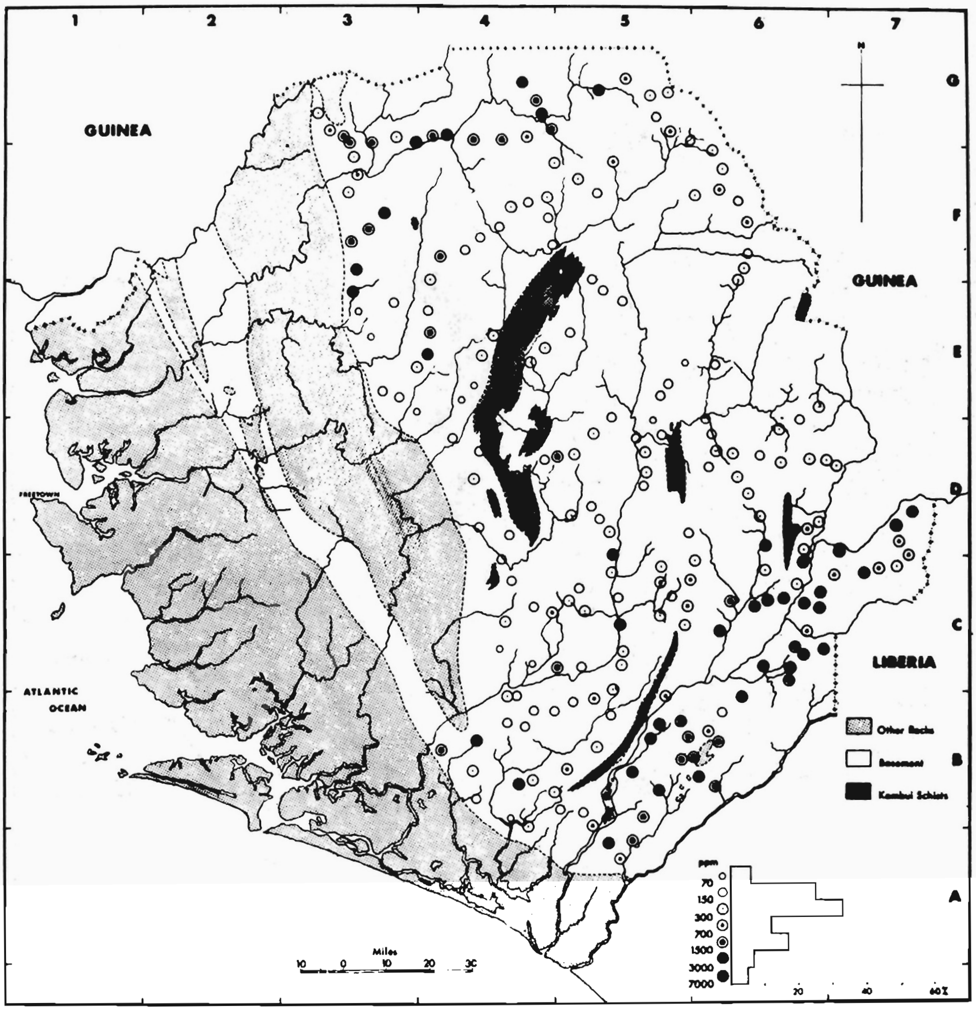


Figure 6. Mn contents, ppm, in -80 mesh fractions, of stream sediment over Basement Complex.

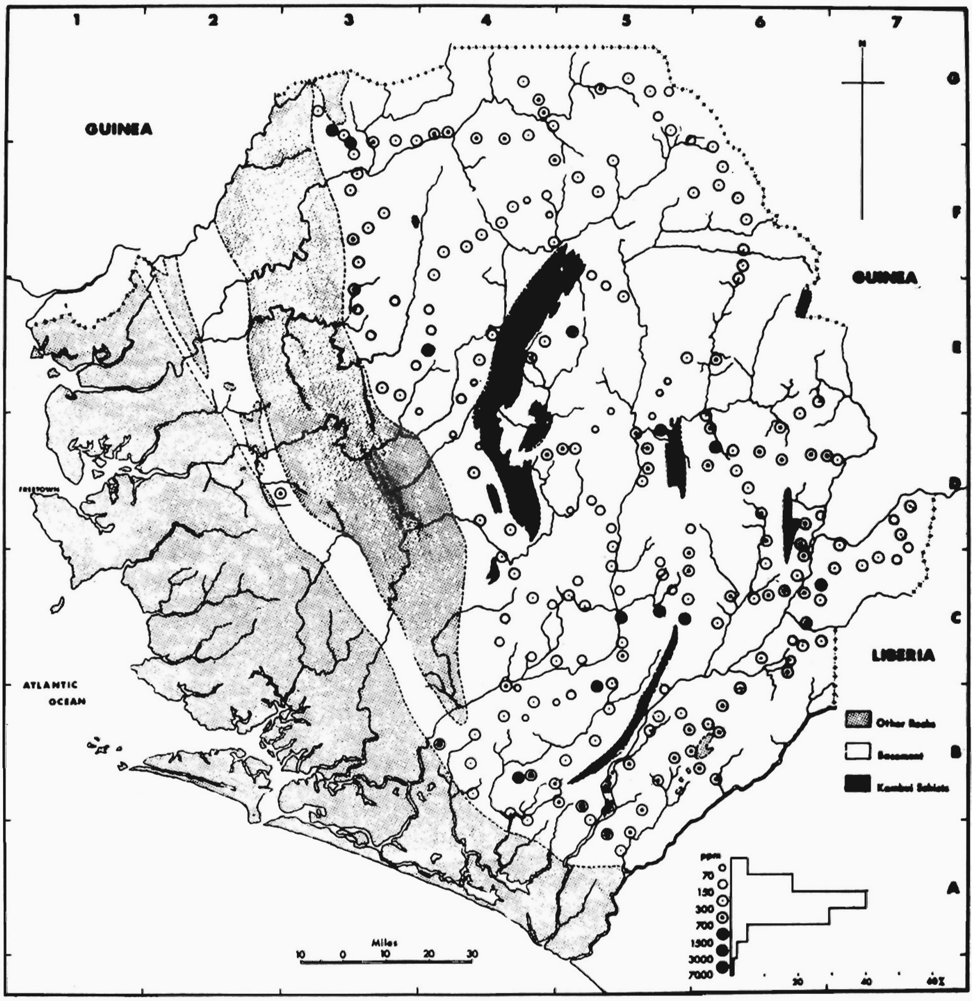


Figure 7. Ni content, ppm, in -80 mesh fractions, of stream sediment over Basement Complex.

Computation was carried out on the logarithmic transform of the data. The cubic trend surface computed for nickel (Figure 8), with a fit of 22%, displays more clearly the regional features in the metal distribution than is apparent from a visual inspection of the data.

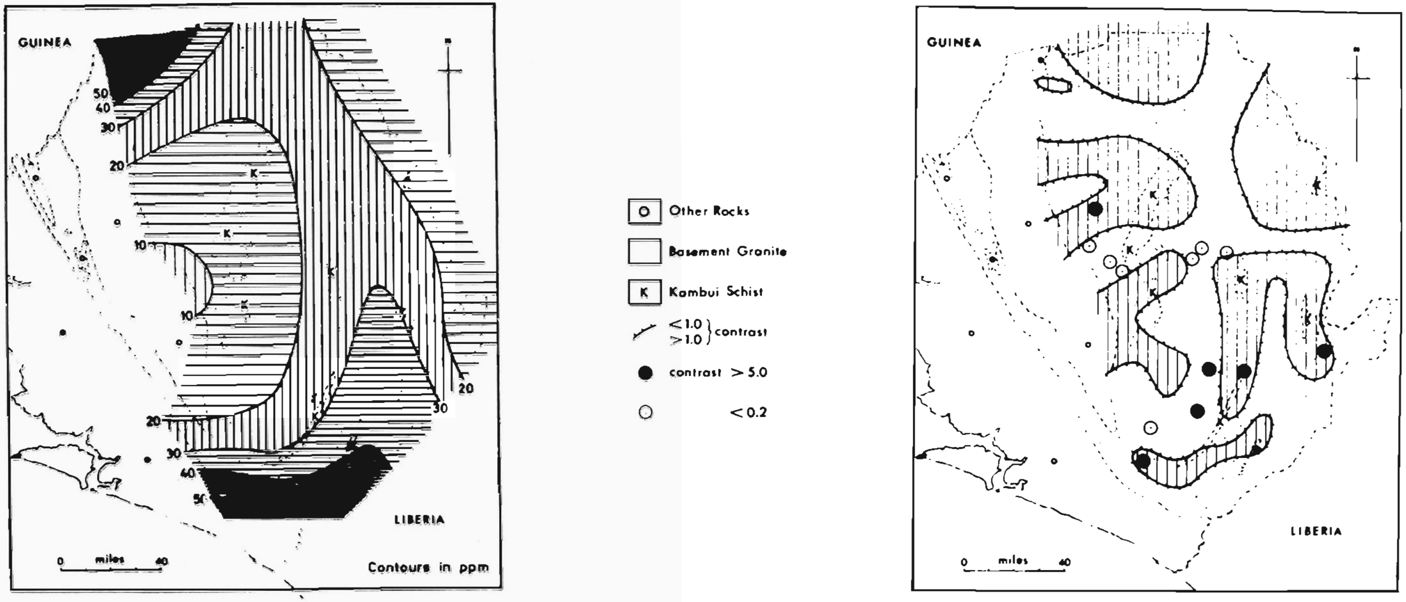
To attempt a meaningful interpretation of the residuals it is necessary to quantise the errors incurred in sampling and analysis and allow for them accordingly. The combined errors were estimated as the mean variance of the triplicate samples collected at each of the 200 or so sample sites. The associated standard deviation was then used to establish threshold levels arbitrarily placed at the ±2 sigma levels about the trend surface. By this method it has been possible to identify local areas where the data differs significantly from the regional trend.

Trend surface analysis has two main disadvantages in the present context. Firstly, the model of the regional trend if formed using a polynomial function assumes a priori that the areal distribution of the data follows a polynomial pattern. Secondly, the surface generated is prone to distortions around the edge of the area as it is the nature of the surfaces to increase their gradient towards the boundaries.

B. Rolling Mean Analysis

The advantage of rolling mean analysis over polynominal trend surface analysis lies in the fact that it does not assume an a priori shape for the surface. The first applications of rolling means to geological problems were the field of sedimentary petrology (Pelletier, 1958; Potter, 1955; and Schlee, 1957), where the technique was used successfully in elucidating trends in palaeocurrent data. The application of rolling means has been much extended by Krige and Ueckermann, 1963, in their work on determining trends in the distribution of gold assay data from the Witwatersrand. Connor and Meisch, 1964, used the technique to obtain some preliminary "smoothing" in some of their studies of copper distribution in alluvial soils, where it was found useful in reducing effects due to sampling errors and minor local fluctuations.

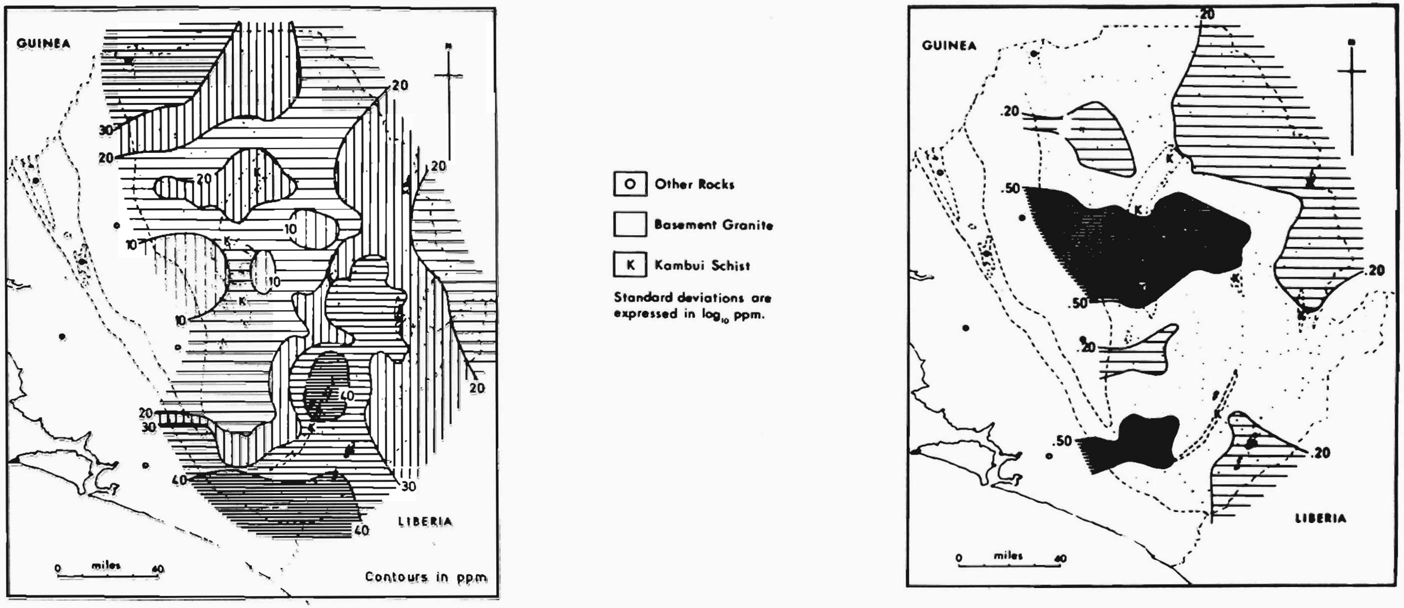
The calculation of rolling mean values is a long and tedious task, and for this reason a computer programme has been written to carry out the computation. The programme written in Fortran IV moves a search area across a 'map' of the data stored in the computer, calculating the geometric mean and standard deviation of the values within each search area. The new co-ordinates of the means are the arithmetic mean of the co-ordinates of the samples within the search areas. The use of rolling mean analysis does not allow residuals to be computed as in trend surface analysis, because the surface generated has no simple mathematical expression. Areas of high residuals, if they are erratic rather than a minor trend, will cause the standard deviation of the rolling means to increase. In this way areas



Cubic Trend Surface

Residuals

Figure 8. Cubic trend surface and residuals of nickel contents ppm, in -80 mesh fractions of stream sediments over Basement Complex.



Rolling Means

Standard Deviations

Figure 9. Rolling mean and variance of nickel contents ppm in -80 mesh fraction of stream sediments over Basement Complex.

of high geochemical relief related to complex geology, mineralisation or secondary environment will be reflected by high standard deviation. According to the degree of smoothing required, the overlap of search areas is adjusted. In the present exercise an overlap of 80% was selected.

The shape of the smoothed surfaces provided by the rolling means with a fit of 28% is in general agreement with those of the corresponding trend surface (Figure 9). Variations that do exist in detail are due to the limited adjustment permitted by the technique of polynomial surface fitting which fits a relatively simple surface to the entire data, whereas rolling mean analysis smooths the data in small increments of area across the map.

C. Factor Analysis

The techniques described up to this point have only dealt with the problem of interpretation of data related to a single element. A common requirement of the geochemist in the interpretation of data is to treat in his mind several elements simultaneously. In an attempt to remove the subjective element from interpretation of problems of this nature the application of factor/vector analysis has been investigated.

In the schist belts of Sierra Leone, the geology is complex and has considerable variation in composition, from ultrabasic through basic to acid igneous varieties and various metasediments including almost pure quartzites. The patterns in the associated stream sediments are correspondingly complex, although sediments derived from specific rock types do have characteristic trace metal compositions. In a complex environment such as this it may be exceedingly difficult to establish the provenance of the trace metal pattern of any particular sample.

Factor analysis sets out to determine the underlying causal factors effecting the distribution of a set of data. It is possible to determine the number of end members needed to account for the compositional variation observed, to identify the end members and to calculate in each sample the proportio attributable to each end member.

However, the composition of all the samples cannot be expressed completely in terms of these end members. The extent to which the fit succeeds is known as the communality, which may vary from zero to unity, unity being a perfect fit. The factors will be related to the dominant end members contributing to the formation of the data. From a mineral exploration viewpoint, it is the communality map that holds the important information in that it quantises the extent to which the composition of individual samples deviates from the various background populations.

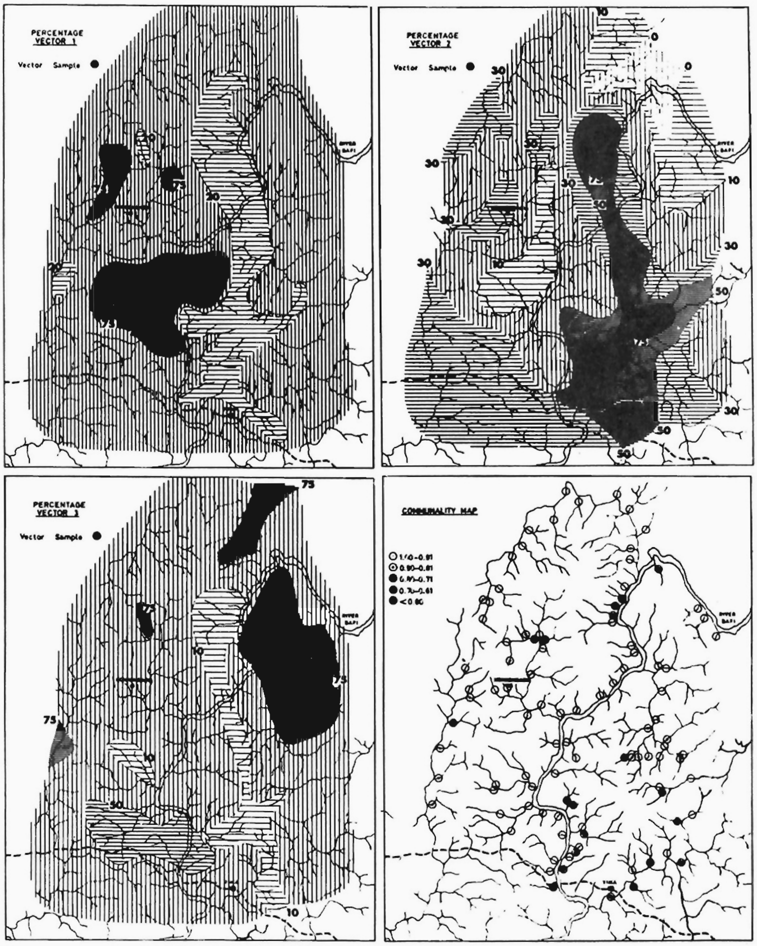
The concept of factor analysis was introduced by Spearman (1904) as a tool in psychometric research. The first published use of factor analysis in geology was by Krumbein (1957), followed by Imbrie and Purdy (1962), who used the method to investigate the classification of recent Bahamian carbonate sediments. Krumbein and Imbrie (1963), and Harbaugh and Demirmen (1964), demonstrated the role factor analysis can play with reference to the interpretation and the clarification of simple relations in complex data of Permian stratigraphy in Kansas. The most significant application of the technique to date in the geological sciences was a heavy mineral provenance study in the Gulf of California and on the Orinoco-Guayana shelf by Imbrie and Van Andel, 1964. The study demonstrated the existence of apparently simple relations in complex data corresponding to zones of littoral transport.

In the present study the technique was applied to an area of some 30 sq. mi. in one of the schist belts underlain by ultrabasic schists and metasediments surrounded by granitic gneisses. Thirteen variables were used (As, Co, Cr, Cu, Ga, Mn, Mo, Ni, Pb, Sn, Ti, V and Zn) for the computation which was performed in Q mode using the computer programme published by Manson and Imbrie, 1964. The data was logarithmically transformed and reexpressed as a percentage of the highest and lowest values for each variable prior to computation, which employs the Varimax method of factor selection and is followed by oblique rotation. As the factors are purely mathematical and have no geological reality the results have been expressed in terms of a number of vector samples. The samples are those which are the closest in nature to the axes of the oblique factor matrix.

It was found that 89% of the variability could be explained in terms of three end members or factors (Figure 10). From a study of these factors and their associated vectors, it appears that the first factor which accounts for 76% of the variability is related to the granite gneisses surrounding the schist belt. The second factor accounts for a further 8% of the variability and is related to the ultrabasic rocks, whilst the third factor accounts for a further 5% and may be associated with a particular facies of the granite. In addition the communality was plotted as an aid to interpretation. The samples with the lowest communality are of the greatest interest, as it is these that cannot be explained in terms of the chosen and known factors. The samples in question therefore contain information derived from other causal factors complicating the simple model evolved. From a prospecting point of view it would be hoped that at least one of these complicating factors is related to mineralization.

CONCLUSIONS

1. Handling and plotting of multi-element regional geochemical data can be carried out more efficiently by the use of computer techniques, linked with automatic plotting using a Stromberg-Carlson 4020.



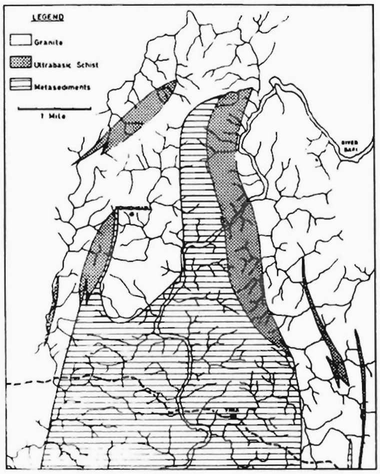


Figure 10.
Factor-vector and communality map of stream sediments in part of Nimini Hills, Sierra Leone.

2. In areas of simple geochemistry, exemplified by the basement granite area of Sierra Leone, trend surface analysis enabled the representation of the major regional trends as the trend surface and the local or minor features superimposed upon these trends as the residuals.

3. Due to limitations of trend surface techniques imposed by the particular mathematical properties of the fitted surface, rolling means were investigated as an alternative means of assessing the regional trends in data. The surface computed by the rolling mean method is more realistic, in terms of the original data, than the corresponding trend surface. Areas of high geochemical relief possibly related to areas including mineralization are identified on the standard deviation map.

4. In areas of complex geology, the applicability of factor-vector analysis has been demonstrated as a means of identifying and quantising the various causal factors contributing to a set of data. In this way it has proved possible to isolate areas of interest unrelated to the statistically dominant controls, the source of which in some cases may be mineralization.

Acknowledgments

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GEOCHEMICAL INVESTIGATIONS OF THE THUNDER BAY SILVER AREA

R.V. Oja*

INTRODUCTION

Two important belts of silver mineralization exist in the Thunder Bay area of Northwestern Ontario. One belt includes a string of diabasic islands in Lake Superior extending from Victoria and Spar Islands near the International Boundary at Pigeon River northeastward for 50 miles beyond once-famous Silver Islet. The other belt is roughly two miles wide and lies on the mainland 20 miles northwest of the island belt, and extends from the area northeast of the city of Port Arthur, Ontario, some 80 miles southwestward to the vicinity of Whitefish and Arrow Lakes (Fig. 1). After a short visit to these silver belts in 1911, Bowen referred to the mainland belt as the "black slates belt" and the island belt as the "gray argillites belt".

Although silver was first discovered on Spar Island in 1846, the area was not prospected actively until the Thunder Bay and Shuniah deposits were discovered in 1866 and 1867 respectively, followed by the discovery of the fabulous Silver Islet deposit in 1886. These finds, of course, precipitated a rush of prospecting and exploration resulting in the development of hundreds of prospects mostly on the more accessible mainland black slates belt, culminating in the development of nine producing mines (Table 1).

TABLE 1

SILVER MINES OF THE THUNDER BAY AREA

MINE	VALUE OF ORE PRODUCED
Silver Islet	$3,250,000
Beaver	550,000
Silver Mountain	500,000
Badger and Porcupine	300,000
Rabbit Mountain	50,000
Shuniah	50,000
Jarvis Mining Co.	40,000
Thunder Bay	20,000
3A and Beck	10,000
	$4,770,000

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* Wendigo Geophysics Limited, Port Arthur, Ontario.

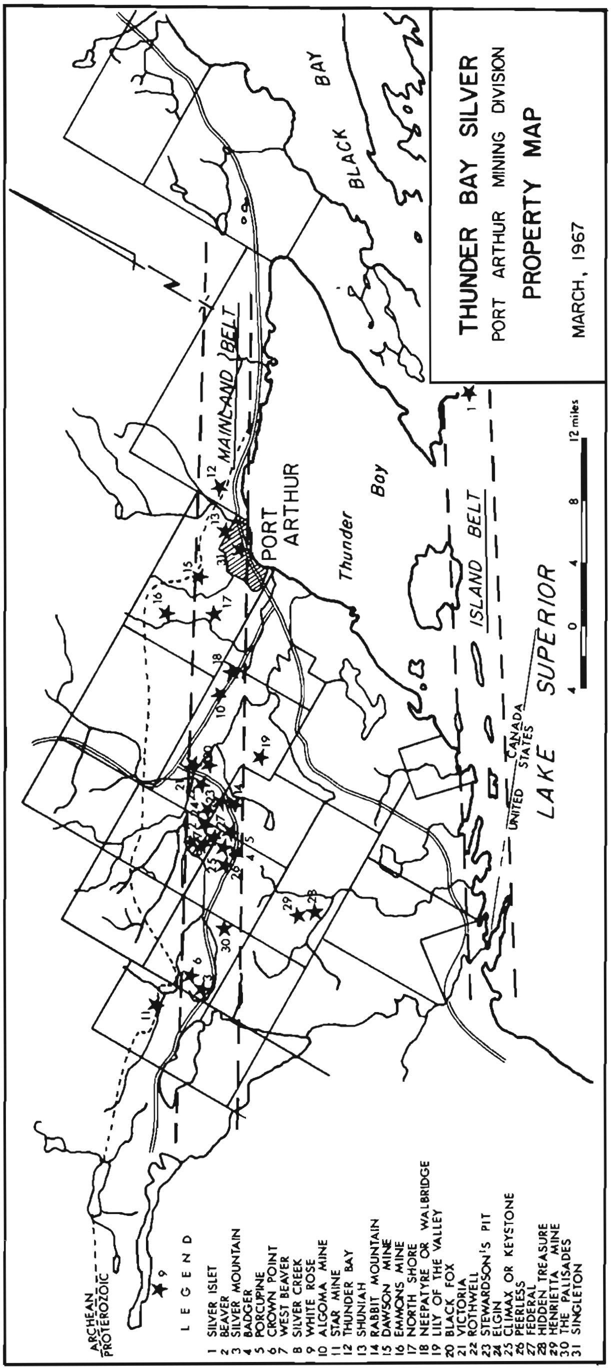
THUNDER BAY SILVER
PORT ARTHUR MINING DIVISION
PROPERTY MAP
MARCH, 1967
BLACK BAY
MAINLAND BELT
PORT ARTHUR
Thunder Bay
ISLAND BELT
LAKE SUPERIOR
CANADA
UNITED STATES
4 0 4 8 12 miles
ARCHEAN
PROTEROZOIC
LEGEND
1 SILVER ISLET
2 BEAVER
3 SILVER MOUNTAIN
4 BADGER
5 PORCUPINE
6 CROWN POINT
7 WEST BEAVER
8 SILVER CREEK
9 WHITE ROSE
10 ALGOMA MINE
11 STAR MINE
12 THUNDER BAY
13 SHUNIAH
14 RABBIT MOUNTAIN
15 DAWSON MINE
16 EMMONS MINE
17 NORTH SHORE
18 NEEPATYRE OR WALBRIDGE
19 LILY OF THE VALLEY
20 BLACK FOX
21 VICTORIA
22 ROTHWELL
23 STEWARDSON'S PIT
24 ELGIN
25 CLIMAX OR KEYSTONE
26 PEERLESS
27 FEDERAL
28 HIDDEN TREASURE
29 HENRIETTA MINE
30 THE PALISADES
31 SINGLETON

TABLE OF FORMATIONS

PRECAMBRIAN	
	Diabase sills and dikes
KEWEENAWAN	intrusive contact
	Sibley Formation (sediments)
Unconformity	
	Rove Formation 1000'±
ANIMIKIE	Unconformity
	Gunflint Formation 500'±
Unconformity	
ALGOMAN	Granite, granite gneiss, migmatite, granodiorite, pegmatite and related rocks
Intrusive Contact	
KEEWATIN	Metamorphosed volcanic and sediment assemblages

Production in the area ceased with the decline of the price of silver in 1892, and despite sporadic attempts, the area was never again actively revitalized. Following the numerous high-grade discoveries at Cobalt, Ontario, very little consideration has been accorded the Thunder Bay area. Over the past few years, however, interest in the mainland belt has been rekindled by several mining groups, and a limited amount of investigation and development has been conducted. This paper deals primarily with the mainland belt where, because of its relative ease of access, most of the investigation described herein has been concentrated.

GENERAL GEOLOGY

All the consolidated rocks in the area are Precambrian in age. The early Precambrian formations, some 2,400 million years in age (Lowden, et al, 1963), contain the usual assemblages of volcanic and sedimentary gneisses, schists, migmatites and granitic and related intrusives. Unconformably overlying these are the Gunflint and Rove Formations of the Animikie Series which are overlain in turn, apparently unconformably (Mooehouse, 1960 p. 18), by the Sibley sediments of the Keweenawan Series. All these formations were invaded by Keweenawan diabase in the form of sills and dikes. Strontium-rubidum analyses of the Rove argillites and Keweenawan diabase indicate an age of about 1,000 million years. Pleistocene and Recent deposits of till, gravel, sand, clay and talus cover most of the area except, of course, the numerous precipitous slopes of the diabase sills.

The contact of the early Precambrian formations against the gently southeast dipping Animikie series lies approximately five miles north of, and parallels the strike of the mainland silver belt. Both the Rove and underlying Gunflint Formations wedge out northwestward and thicken southeastward to estimated thicknesses of 2000 and 500 feet respectively. While the Gunflint formation includes a large number of thin carbonate, argillite, and conglomerate members and thick taconite members, the Rove is composed almost entirely of thin-bedded, fissile, black argillite. The argillites contain sporadic pyrite or marcasite clusters ranging to three inches in diameter as well as carbonaceous concretions, or "witches' caldrons", ranging to several feet in diameter.

The most important topographic features are the numerous buttes, mesas and cuestas capped by highly resistant diabase ranging to 200 feet in thickness. Only one major sill is known to exist despite the fact that diabase occurs at all elevations ranging from lake level (602' A.S.L.) to an elevation of 1,200 feet above sea level. This variation in elevation is the result of predominantly vertical movement along numerous steeply dipping, normal faults striking generally about N 70° E. A complimentary set of faults strikes roughly at right angles to the main set of faults, but movement along these faults was generally in the order of some tens of feet of lateral or vertical displacement resulting in only small variations in topographic relief.

It is within the two sets of fault zones that the important silver-bearing veins occur in the Thunder Bay area. Some veins, however, undoubtedly occur in tension or shear fractures parallel to either set of faults and, therefore, will not display any displacement or consequent topographic features.

The Silver Veins

The vein mineralization consists of an assemblage of gangue minerals which include white, amethystine, and smokey quartz, calcite, barite, and green and purple fluorite. The ore minerals include pyrite, pyrrhotite, galena, chalcopyrite, abundant sphalerite, argentite and probably some native silver. While silver values are confined, for the most part, to quartz-carbonate veins, important values also occur in minute, hairline fractures in wall rocks as well as in the fine bedding planes in the fissile argillite adjacent to the veins. In both the mainland and island belts, the silver mineralization is generally confined to rich ore shoots and lenses within the fault zones. On the mainland belt, both sets of faults appear to have been equally hospitable to vein formation. Insufficient detail information is available from any of the properties to indicate zoning or preferential distribution of silver values within the ore deposits of either belt. Although most of the mines are less than 1400 feet deep, and are, on the whole, confined to the Rove argillites, there is little evidence to prove that the silver is necessarily confined to veins occurring only in the Rove. On the contrary, several argentiferous veins are known to occur in the Gunflint formation, and indeed, in the lower portions of the Shuniah mine veins extended into the underlying Keewatin basement complex. Very little silver, however, appears to have been deposited in the generally narrow portions of veins extending into the overlying diabase capping.

There remains a possibility in the mainland belt, however, that the graphitic argillites offered a more hospitible environment, either chemically or structurally, for the deposition of silver than the basement complex, the Gunflint formations or the diabase sills.

GEOCHEMICAL INVESTIGATION

An appraisal of the results of all reasonably simple and cheap geophysical techniques indicated their inability to detect silver mineralization, and lead to the consideration of geochemical investigation. It was assumed that silver occurring in the near-surface portions of a fault zone should be present also in detectable amounts in the overburden. A survey of field and laboratory techniques for silver analysis proved them to be lengthy, rather complicated, and consequently expensive. Because zinc has been noted in association with silver in every deposit, and because of the simple techniques involved in its detection, both in the field and in the laboratory, trial tests for zinc were made on both humus and soil from known and suspect deposits. These tests were very rewarding, and full-scale geochemical surveys were conducted on two adjacent properties covering an area of 20 claims or approximately 800 acres.

The bulk of the analyses were made with a field kit produced by McPhar Geophysics Limited. Each sample is treated in a small disposable shaking bottle. A predetermined quantity, i.e. one, two or three millilitres of dithizone is added to each sample along with solvent and buffer and the resulting colour, within the range from green to red, indicates the quantity of heavy metals present. The McPhar kit is designed for work in the range from nil to 1200 parts per million heavy metals.

Another kit employing larger shaking bottles in which the sample is titrated to a grey or incipient green end-point was also tried. This titration method is preferred by some technicians because it is easier and quicker to place the sample in

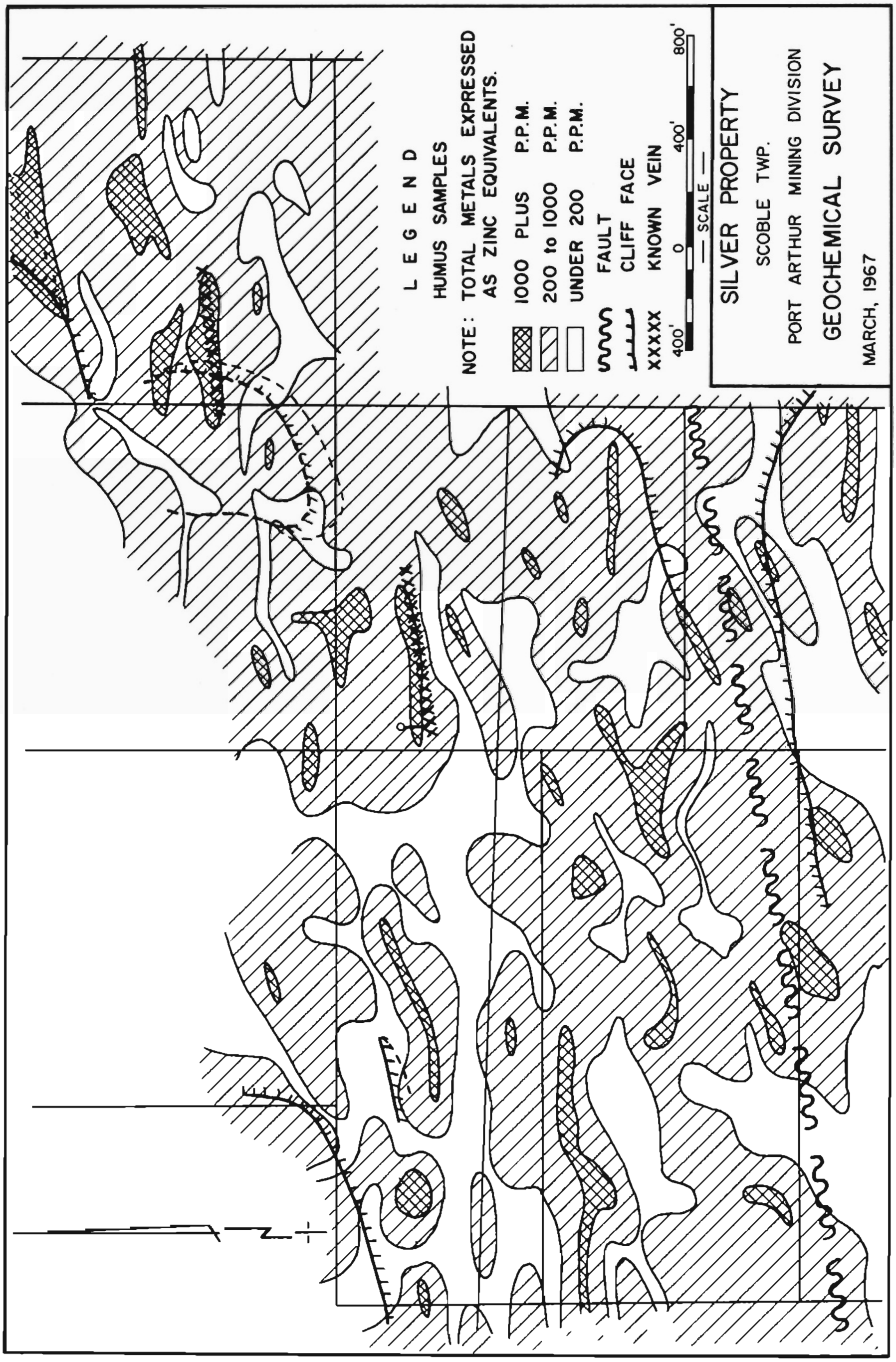

Figure 2. Geochemical Survey, Silver Property, Scoble Township, Port Arthur Mining Division. Total metals expressed as zinc equivalents in humus samples.

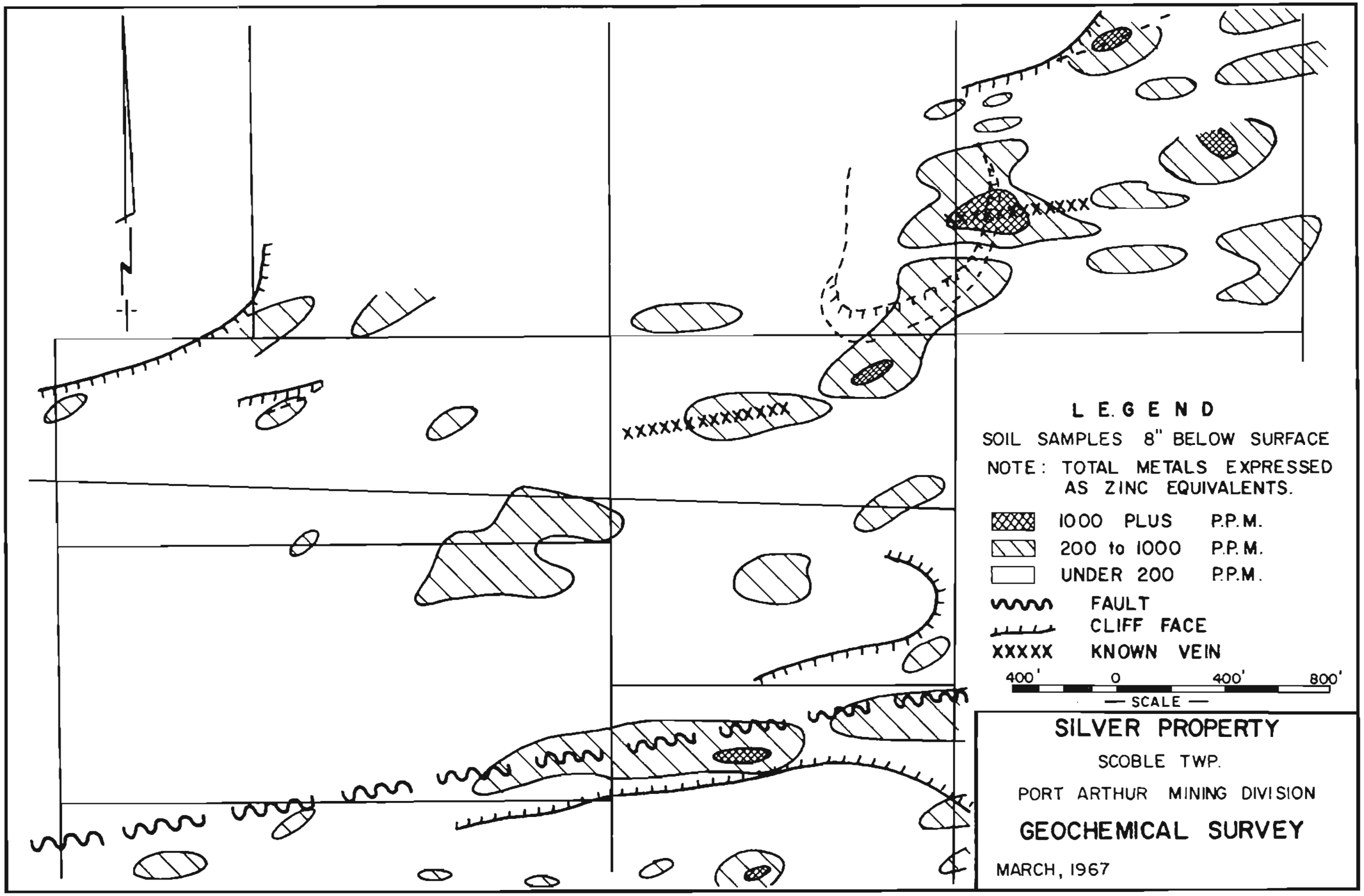

Figure 3. Geochemical Survey, Silver Property, Scoble Township, Port Arthur Mining Division. Total metals expressed as zinc equivalents in soil samples.

the shaking tube and produces more accurate results than the McPhar kit. Colourimetric and titration techniques were employed both in the field and in the laboratory.

Once reconnaissance field testing outlines an anomalous area, it is more efficient to analyse samples from a gridded survey area in a field or permanent laboratory. Two men can collect and label about 100 samples per day, while a two-man lab crew can analyse the same number per day.

The first complete survey work was performed on the Silver Property along lines previously used for self potential and electromagnetic surveys. Both the humus and soil samples reflected known mineralization unerringly (Figures 2 and 3). A comparison of the humus and soil maps shows that humus sampling is more sensitive for total metals detection than is soil sampling. In fact, about twice as many anomalies were obtained through humus sampling than from soil sampling. Because humus represents decayed vegetable matter, a single humus sample represents the heavy metal content of pre-existing vegetation growing in the area surrounding the sample site. Through the ability of vegetation to collect and concentrate heavy metals from the entire area probed by the root system, a single humus sample, therefore, represents the intregated heavy metal content of an area possibly up to fifty feet in diameter, and a depth equal to that to which the plant roots may penetrate. The sampling of humus is recommended, therefore, for reconnaissance work because of the ease of collecting samples and because of its higher heavy metal content over mineral occurrences.

It is assumed that soil sampling is more accurate for pin-pointing mineralization than humus sampling, because generally, the area of the soil anaomaly was found to be smaller than that of the corresponding humus anaomaly. Following additional development of the surveyed properties, more knowledge will be gained of the relative importance of the humus versus soil sampling. It will be interesting to learn also if a geochemical anomaly occurs over a fault or vein where the mineralization occurs at some depth below the rock surface. As most vein materials have been stressed and fractured, one might assume that heavy metal-bearing solutions from deep ore shoots may permeate through the veins and may reflect their presence in soil and humus samples.

A limited amount of stream sediment sampling has been attempted in the area around Beaver and Rabbit Mountains. Although positive results were obtained, little effort was made to complete a geochemical survey of available streams.

Special Investigation

During the development program of the Rabbit Mountain Property, a number of soil and humus samples were checked in commercial laboratories for zinc content by hot extraction and spectrographically for silver content. The hot extractions for

TABLE 2

METAL CONTENT, RABBIT MOUNTAIN PROPERTY SURFACE SAMPLES

Sample No.	Soil (ppm) Hot Zinc Extraction	Soil (ppm) Cold Zinc Extraction	Soil (ppm) Ag. Spec.	Humus (ppm) Hot Zinc Extraction	Humus (ppm) Cold Zinc Extraction	Humus (ppm) Ag. Spec.
2S-13E	650	1200	8.0	600	1100	0.3
2S-12E	450	1200	1.0	800	1200	3.0
4S-5E	600	1200	10.0	700	1200	10.0
4S-7E	650	1000	8.0	700	1000	10.0
4S-10E	300	300	0.3	370	1200	0.3
6S-8E	500	300	3.0	800	1200	1.0
6S-9E	650	1000	1.0	550	1200	0.3
8S-2E	300	50	8.0	350	1000	1.0
8S-3E	250	600	0.3	300	1000	0.3
8S-5E	700	1200	5.0	650	1200	1.0

zinc from both soil and humus samples returned values which were about 30 to 60 percent of those obtained by the McPhar cold extraction kit (Table 2). Silver values in the centres of the anomalies average from 2 to 5 ppm, but scattered values ranged to a high of 50 ppm. While each technique resulted in a different set of values, all techniques resulted in similarly shaped, superimposed anomalies.

CONCLUSIONS

It is evident from the foregoing that considerable research of the mainland belt alone is required to unravel some of the structural and geochemical problems relating to the deposition of silver. Whether silver mineralization is confined primarily to the Rove argillites is not known nor are the structural and geochemical requirements for silver deposition known with any degree of certainty. Geophysical techniques tested to date appear to be inadequate to detect the silver-bearing veins in the mainland area of highly conductive, flatlying argillaceous sediments. Magnetic surveys, no matter how sensitive, do not reveal fault zones any better than visual investigation of aerial photographs. The only hope of ore detection, at present, lies in the field of geochemistry, but the results to date indicate the necessity of a cautious approach to the final analysis of geochemical surveys. Geochemistry, however, has proved to be most positive and definitive technique in the search for additional ore deposits on the mainland belt of the Thunder bay silver area and will, no doubt, eventually lead to the development of ore deposits in debris-filled fault valleys and overburden-covered flatlands where a negligible amount of exploration has been conducted in the past.

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A TRACE ELEMENT STUDY OF PODZOL SOILS, BATHURST DISTRICT, NEW BRUNSWICK

E.W. Presant*

INTRODUCTION

The study described in this paper was part of an extensive geological and geochemical survey of the Bathurst-Newcastle area by the Geological Survey of Canada. Field work for the trace element study was completed in 1961.

Special thanks are due to Dr. R.W. Boyle who initiated the study, supervised the field work, and provided much helpful advice during the project. The advice and assistance of Dr. W. Tupper, Carleton University, is also gratefully acknowledged.

The large number of chemical and mineralogical analyses done on these soils would have been impossible without the assistance of personnel from laboratories of the Geological Survey, Mines Branch and Carleton University. Their assistance is gratefully acknowledged.

GEOLOGY AND SOILS OF THE BATHURST DISTRICT

Good descriptions of the general geology of the district are given by Skinner (1953), Smith (1957) and Boyle and Davies (1964).

The central part of the area is underlain by highly folded Ordovician volcanic and sedimentary rocks that are intruded by gabbro and diorite sills and dikes, and by granitic stocks and masses. These rocks are host to the massive lead-zinc-copper sulphide bodies that occur in the Bathurst district. North of the Ordovician rocks is a Silurian-Devonian belt of volcanic and sedimentary rocks intruded locally by dikes, sills and stocks of gabbro, diorite, quartz-feldspar porphyry and aplite. A number of small lead-zinc-copper sulphide lenses and veins occur in these rocks. South of the Ordovician folded belt the surface bedrock consists of flat-lying red Pennsylvanian conglomerates and sandstones.

Descriptions of the surficial geology and glaciation of the region are given by Chalmers (1886) and Alcock (1941). Glaciation is presumed to have been of limited extent, because most till stones have moved very little distance from their source areas. Most of the region has only thin ground moraine materials over bedrock.

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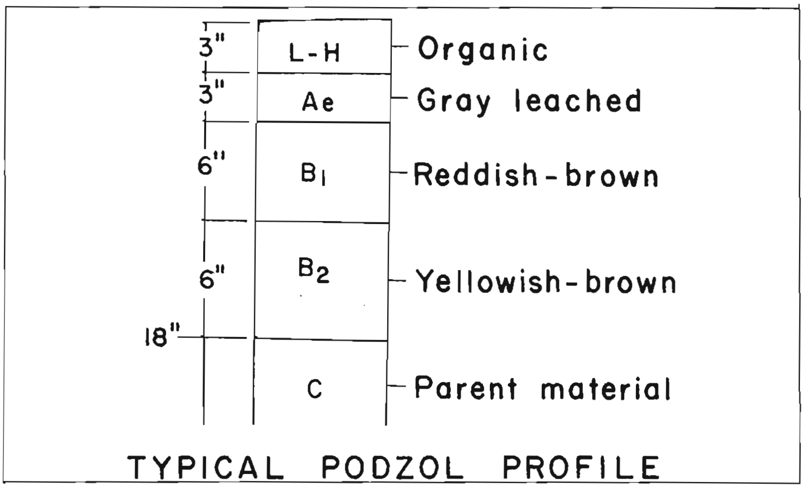

Figure 1. Schematic drawing of typical Podzol soil profile, Bathurst area.

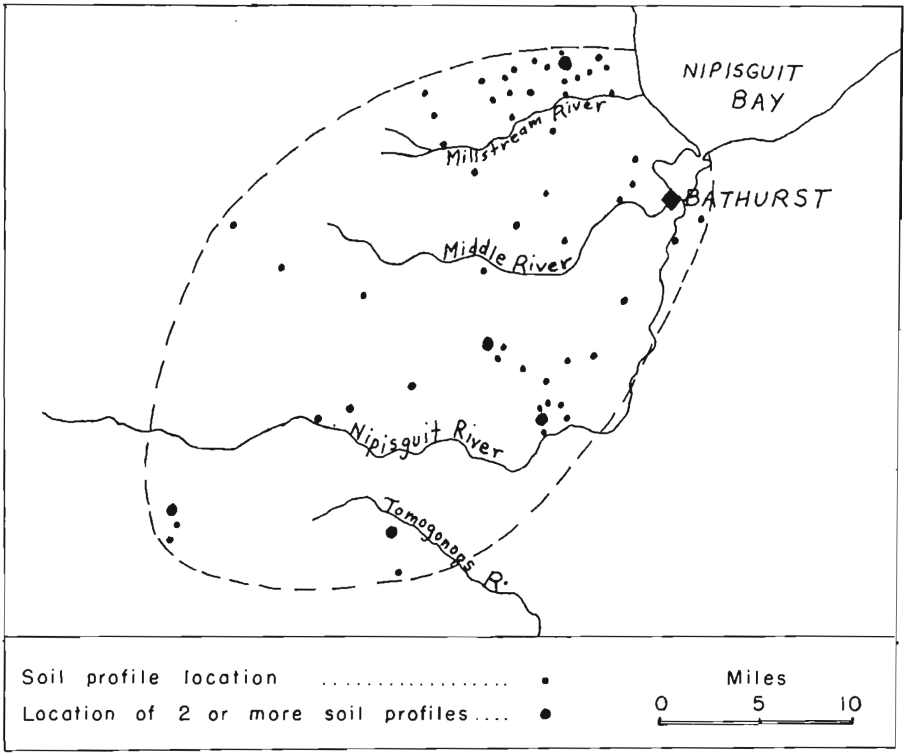

Figure 2. Sketch map showing soil profile locations, Bathurst district, New Brunswick.

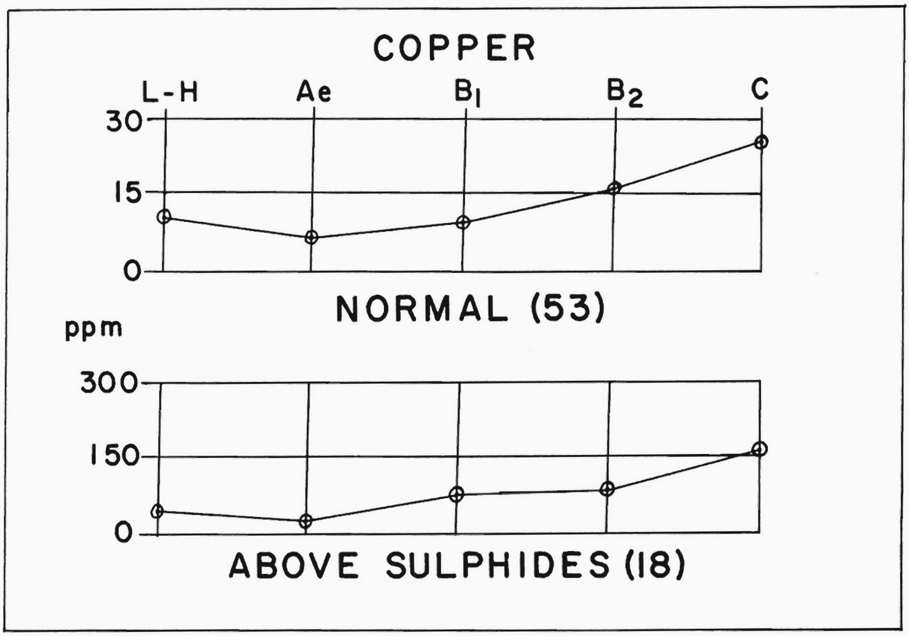

Figure 3. Mean copper distribution.

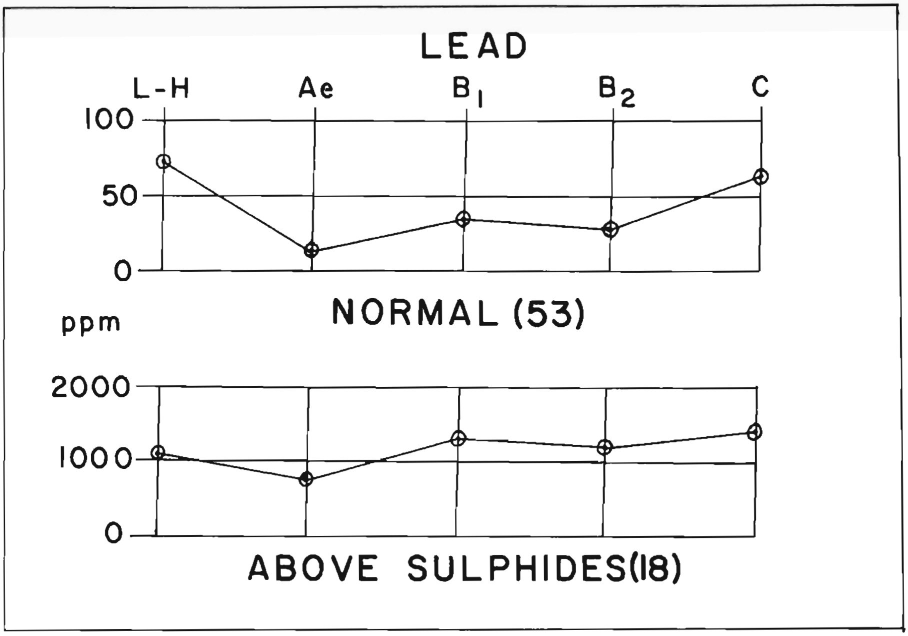

Figure 4. Mean lead distribution.

The well-drained soils in the Bathurst district belong to the Podzol Great Group. A schematic diagram of a typical Podzol soil in the district is shown in Figure 1.

FIELD AND LABORATORY WORK

Figure 2 shows the location of the soil profile sites in the Bathurst district. Only results from well-drained sites are discussed in this paper. Altogether, there were 71 well-drained sites, 18 of which lie above sulphide deposits.

All soil profile horizons were analyzed for pH and total lead, zinc and copper. Horizons of 20 profiles were analyzed for total iron, manganese, arsenic, antimony, silver and tin. Organic carbon was determined in 9 profiles.

Additional studies were done on the soil horizons from 6 sites to attempt to determine the association of the trace elements with various soil fractions. The fractions that were studied were the water-soluble, dilute HCl-soluble, organic matter, free iron oxide, coarse silt and sand fractions.

Detailed descriptions of the soil profiles and of the procedures used for chemical and physical determinations are given by Presant (in press).

RESULTS OF THE INVESTIGATIONS

The mean values for the different trace elements in well-drained soil profiles above "normal" non-mineralized rock, and above sulphide deposits are compared graphically in Figures 3 to 12. The number of profiles involved in each graph is bracketed under the graph.

Mean copper values for the Ae horizons are slightly lower than those of adjacent horizons in both graphs (Figure 3). Otherwise, a relatively gradual increase in copper content with depth is indicated. Detailed studies showed that copper was associated with organic matter in some L-H horizons, and with the free iron oxides in some B horizons. Results of these detailed studies are discussed more fully by Presant (in press).

Lead accumulations seem to have occurred in the L-H, B, and C horizons (Figure 4). These accumulations are most marked in the L-H horizons of "normal" profiles, whereas above sulphide deposits, the highest values are in the B and C horizons.

Detailed studies indicated that lead was definitely bound with the organic matter fraction in the L-H horizons. In some horizons it was associated with the free iron oxides of the B horizons; in the B horizons above the Brunswick No. 6 deposit, it was identified in beudantite ($PbFe_3\ (AsO_4)\ (SO_4)\ (OH)_6$).

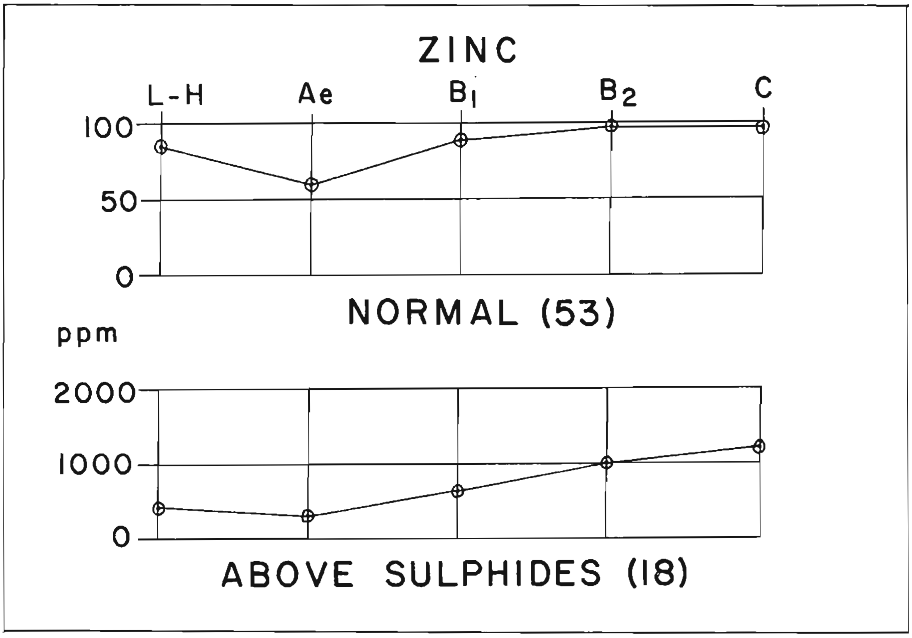

Figure 5. Mean zinc distribution.

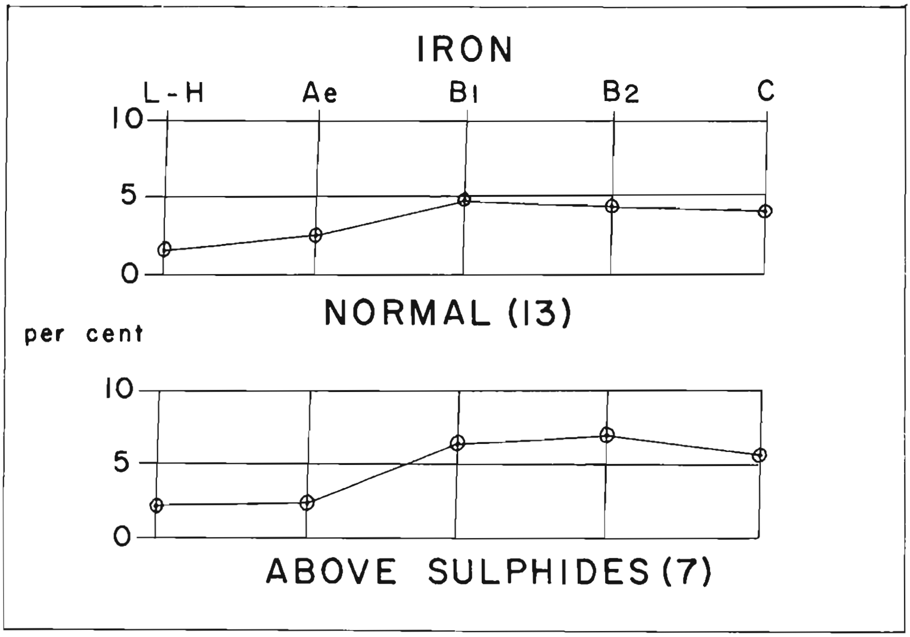

Figure 6. Mean iron distribution.

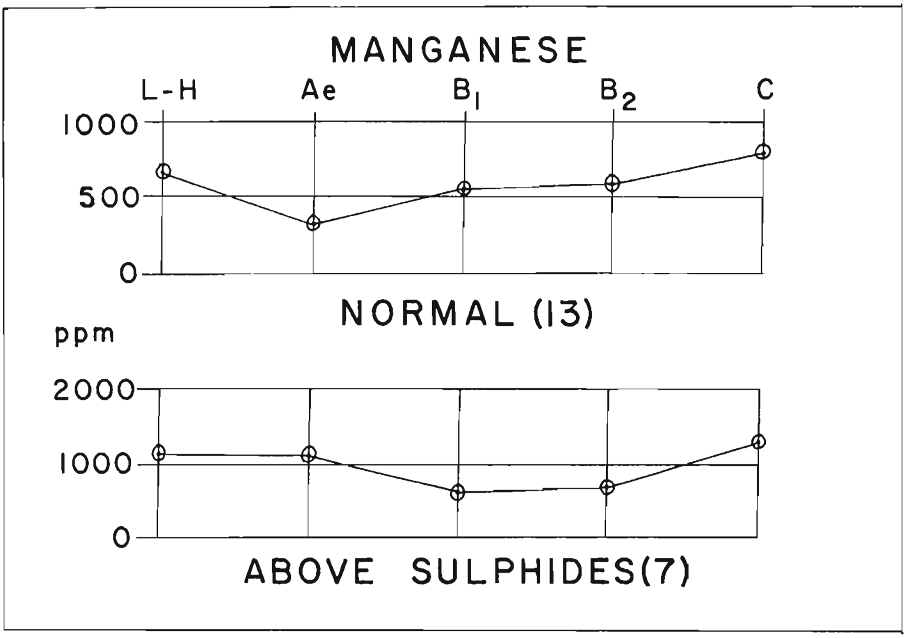

Figure 7. Mean manganese distribution.

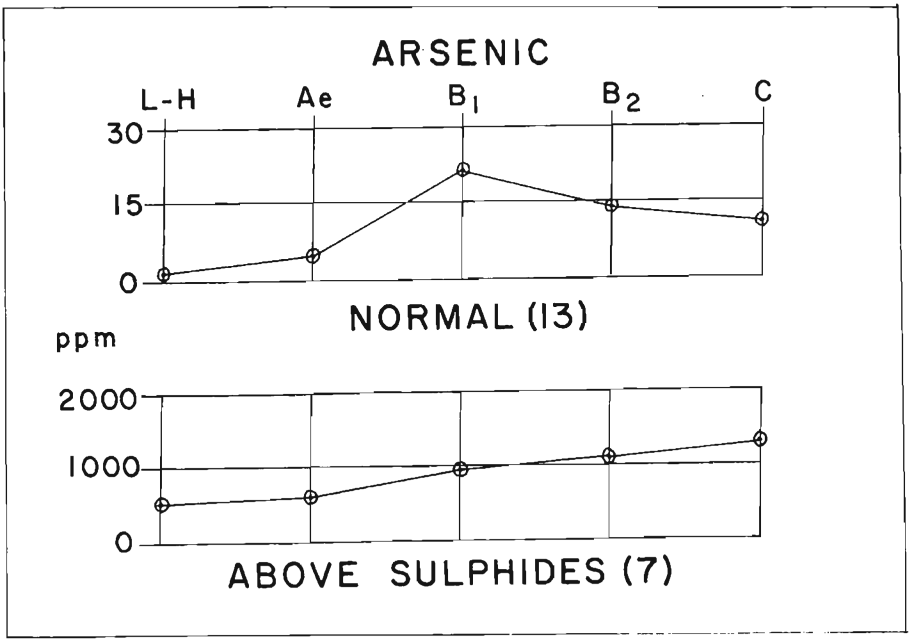

Figure 8. Mean arsenic distribution.

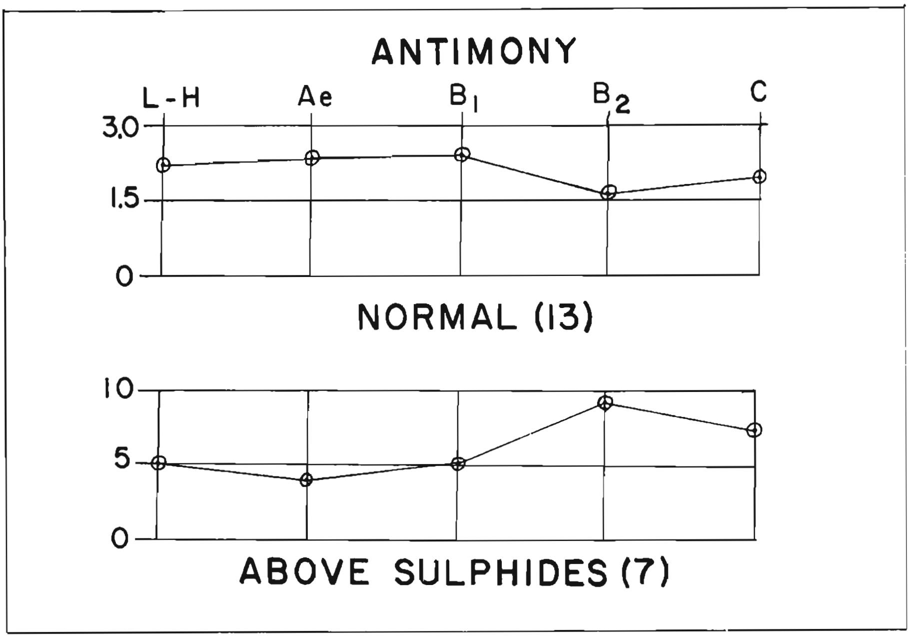

Figure 9. Mean antimony distribution.

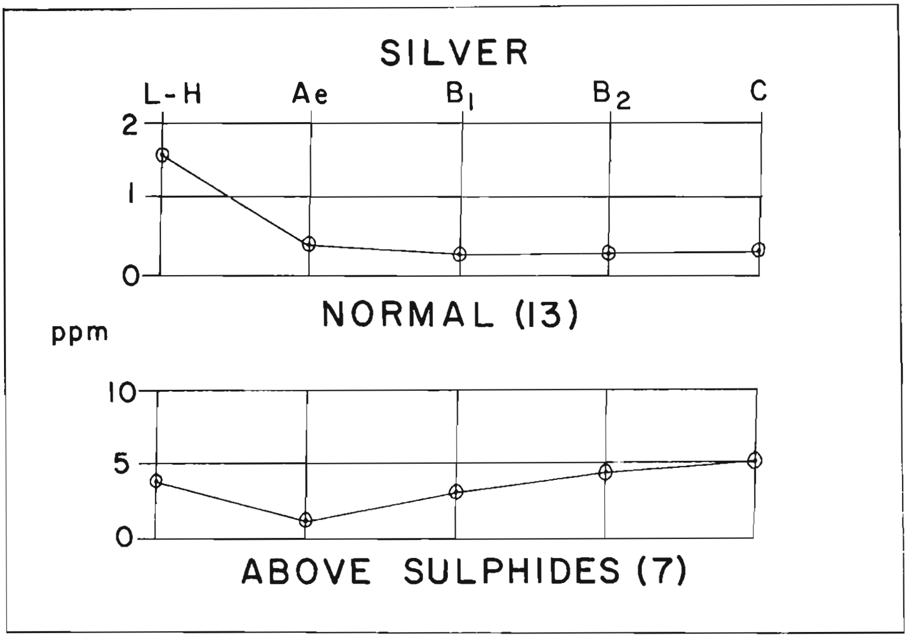

Figure 10. Mean silver distribution.

Considerable water-soluble lead was also present in all soil horizons over this deposit.

The distribution pattern of zinc in these soils resembles that of copper, except that there seems to be a greater tendency for zinc to accumulate in the L-H horizons (Figure 5). In the detailed studies, zinc was readily leached from the L-H horizons by dilute HCl. It was also removed in many of the organic matter and free iron fractions. Water-soluble zinc was dissolved from all soil horizons above the Brunswick No. 6 deposit. Above this and other sulphide deposits, zinc was present in the silt and sand fractions of the lower horizons, in sulphide form.

The distribution pattern and mean contents of iron are almost identical in both graphs (Figure 6). The only difference is a slightly higher mean iron content in the B horizons of soils above sulphides. The low mean iron value of the A horizons of these soils may be an indication of the amount of leaching that has occurred. Detailed studies indicated that up to 1.5% of the total iron in the B horizons was present in free iron oxide form. Some of this free iron may have originated in the A horizons.

Mean values for manganese are relatively high in the L-H horizons of all profiles, and in the Ae horizons of the profiles above sulphide deposits (Figure 7). Much of this manganese may be bound to organic matter in chelated form. The relatively low mean manganese values in the B horizons above sulphide deposits, may reflect the high mobility of this element under more acidic conditions.

The mean arsenic distribution above "normal" rocks differs from that over sulphide deposits in having relatively lower A horizon values, and concentrations of arsenic in the B_1 horizons (Figure 8). Detailed studies indicated that arsenic was bound to free iron oxides of the B horizons in all profiles, and of the C horizons in profiles above sulphide deposits. X-ray studies showed that arsenic was present as the sulphate-arsenate, beudantite, in the B horizon above the Brunswick No. 6 deposit.

Mean antimony values are similar in all horizons over "normal" rocks (Figure 9). Above sulphides, there is a sharp jump in the mean antimony contents of the lower horizons. Detailed studies indicated that antimony was bound to the free iron oxides of the B horizons.

Silver values are high in L-H horizons, especially in soils from non-mineralized areas (Figure 10). It is probably bound chiefly to the humus in chelated form in these surface horizons. The higher mean contents of silver in the lower horizons of soils over sulphide deposits reflect the contribution of this element by the underlying bedrock sulphides.

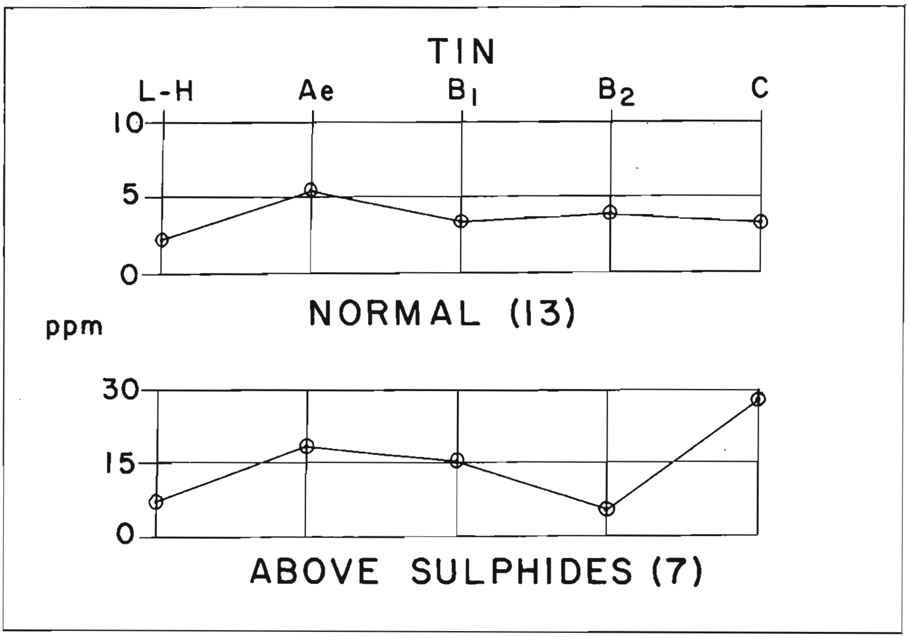

Figure 11. Mean tin distribution.

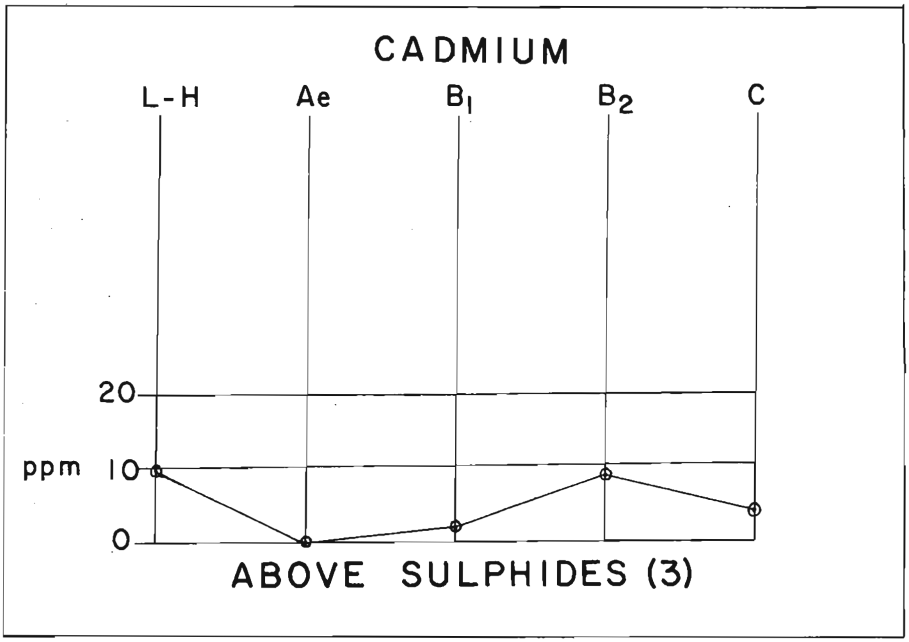

Figure 12. Mean cadmium distribution.

Concentrations of tin occur in the Ae horizons of all profiles (Figure 11). The element may occur here in resistant oxide form. The relatively sharp mean tin increase in C horizons above sulphides is probably due to its occurrence in sulphides and oxides.

Only 3 soil profiles showed measurable amounts of cadmium by the spectographic analysis method that was used (Figure 12). These profiles were all above the Nigadoo deposit.

SUMMARY AND CONCLUSIONS

Trace element contents are up to 100 times higher in soils above sulphide deposits than in soils above non-mineralized rocks. Arsenic, copper and zinc are the elements most enriched above sulphides; iron and manganese show the least enrichment.

Major concentrations of lead and silver occur in the L-H horizons of most profiles; minor concentrations of manganese, zinc and copper are present in many L-H horizons. Lead, zinc and copper are bound to the organic matter fractions in all horizons, probably as chelate complexes.

Higher tin content occurs in the Ae horizons and may be due to its concentration in resistant oxide form. The lowest profile values for most elements are in the Ae horizons, where acid, leaching conditions have presumably caused mineral breakdown and leaching of elements.

Trace element contents of B horizons above sulphide deposits are usually intermediate between those of the A and C horizons. Antimony, iron and manganese are exceptions to this trend. Antimony and iron contents are highest, and manganese contents lowest, in the B horizons above sulphides.

In B_1 horizons above "normal" rocks, arsenic, iron, antimony and lead are enriched. Detailed studies indicated that these elements, as well as copper and zinc, were bound to the free iron oxides in profiles above both sulphide deposits and "normal" rocks.

In C horizons over sulphide deposits, all the elements studied attain maximum values except for iron and antimony. This is because the soil materials of the C horizons contain mineral fragments and ions derived from the underlying sulphide bodies.

In the soils over non-mineralized rock, only zinc, copper and manganese attain peak profile values in the C horizons. This is probably because none of these elements is markedly associated with the humus or free iron oxide fractions, hence they are more mobile and more easily leached from the A and B horizons where active weathering is greatest.

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GEOCHEMICAL DISPERSION PATTERNS IN SOILS

at

MOUNT PLEASANT MINES, CHARLOTTE COUNTY, NEW BRUNSWICK

J.E. Riddell*

INTRODUCTION

This paper has been prepared from data collected over a period of 12 years, by several sampling and analytical groups. The basic data reflects slight differences in analytical procedure and also differences in sampling techniques. This factor renders it difficult to make fine interpretations of the distribution of metals in soils. Another complication lies in the widespread distribution of metallization in the bedrock which has resulted from the permeation of the mountain mass by mineralizing agents moving along multiple fracture and joint systems in successive waves of mineralizing activity. These repeated mineralizations have produced zonal and interlocking patterns in the country rock both in the development of alteration and in the distribution of the metals.

Compounding the problem of interpretation is the geomorphic history of the area which has resulted in the development of alluvial and colluvial soils from glacially disturbed soils which had previously been subject to the normal processes of mass wasting in pre-glacial time. Although the valley floor at Hatch Brook is covered to depths of up to 50 feet by glacial till containing large erratics of Devonian granite and Carboniferous conglomerates that have been transported from terranes which lie to the northwest of the area, the upper slopes of the mountain have only a thin, very uniform soil cover, which appears to be largely residual in character although an occasional erratic is found.

Mount Pleasant is a ridge trending magnetic north, which rises to 1175' above sea level. The local relief above the valley of Hatch Brook is between 600' and 850'. The west flank of the mountain is steep, with an abrupt decrease in slope where it merges into the valley bottom of Hatch Brook.

The western flank of the mountain has a well developed dendritic micro-drainage pattern which has formed with its main elements down the 'fall-line' of the mountain slope. The drainage pattern of the northern and eastern flanks is assymetrical with the main elements of the drainage being skew to the general slope. This skewness has apparently developed because of pre-existing bedrock controlling structures, etched out by pre-glacial streams, which have survived the masking effects of glaciation.

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The streams entering Hatch Brook on the west side of Mount Pleasant show the characteristics of barbed tributaries. This suggests that immediately following glaciation, during the period of marine submergence of the Macdougall Lake area which lies about five miles southeast of the mountain, Hatch Brook flowed towards the southeast. With the re-elevation of the coastal areas of New Brunswick the flow in Hatch Brook first ceased and then reversed to flow northwest to the Piskehegan, which was the direction of pre-glacial drainage.

Because of this reversal of drainage, the trend of the lower parts of the tributaries to Hatch Brook and their related metal dispersion trains sweep towards the south rather than northward in the present direction of flow of the main creek.

BEDROCK GEOLOGY

Mount Pleasant is underlain by altered volcanics and acidic intrusives of mid-Carboniferous age. Hatch Brook Valley is underlain by strongly folded greywackes and carbonaceous pelites which were regionally metamorphosed in Early Paleozoic time. The valley east of Mount Pleasant is underlain by red feldspar-quartz porphyritic rhyolites and pyroclastics. The main structural trends of faults and fracture zones are northwesterly and northeasterly. The volcanic formations of the mountain have a complex structure and have been strongly fractured and intensely metasomatized by the processes of silicification, chloritization, fluoritization and epidotitization. Locally topaz greisen is developed.

Tin mineralization is widespread and usually, although not invariably, associated with zinc and other base metals. Arsenic is a common associated metal. Molybdenum and tungsten accompany the tin mineralization but are most strongly concentrated in zones where tin values are low.

SAMPLING

The area surveyed is approximately two square miles in extent. B horizon soils were collected at intervals of 100 feet on east-west lines spaced 400 feet apart. In the central section of the area additional samples were collected at 100 foot intervals along north-south lines spaced 400 feet apart.

A total of over 2,500 samples has been collected and most of these have been analyzed for tin, molybdenum, copper, lead and zinc. Tungsten values were not determined. Standard methods of semi-quantitative colorimetric analyses were used throughout.

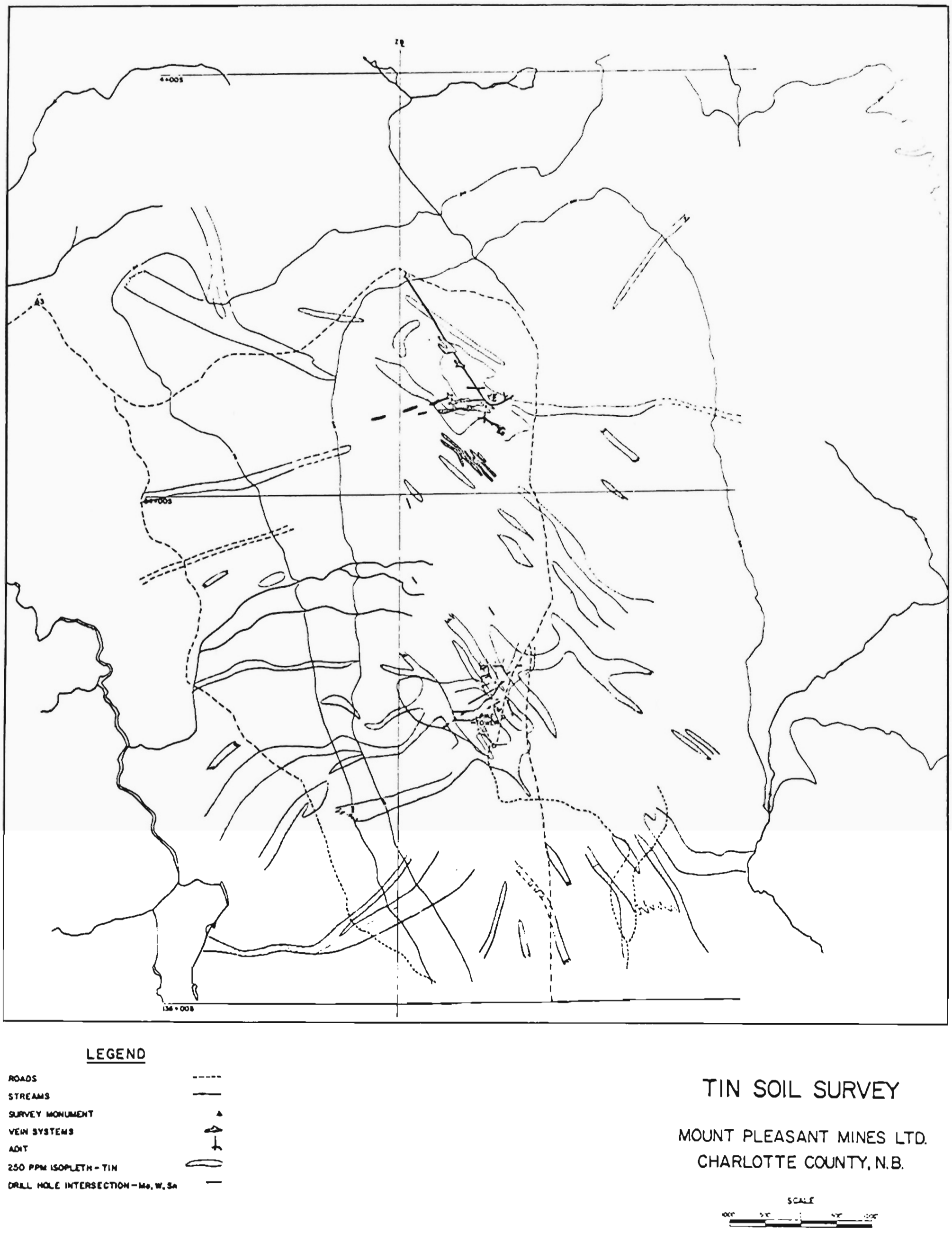

Figure 1. Distribution of tin in soil, Mount Pleasant Mines Ltd., Charlotte County, N. B.

INTERPRETATION OF THE SOIL SURVEY DATA

As an introductory comment I would like to point out that the soils over the major part of the area covered by the survey must be considered as containing anomalous amounts of metal when compared with the known regional backgrounds in southwestern New Brunswick. Because of this I have arbitrarily selected fairly high values of metal in the soils to define the areas which must be given primary consideration when using the metal patterns from an exploration view-point. I shall deal with the five metals individually for they each show distinctive patterns in which different controlling factors have been dominant.

TIN (Figure 1)

Soils containing anomalous amounts of tin (i.e more than 250 ppm) are distributed along the full length of the crest of the mountain with two areas of major concentration, one in the North area where the present underground workings have been opened and one in the Fire Tower area where stripping and limited drilling have defined strong tin bearing structures. Between these two areas are local zones of tin concentration which are elongated in the direction of glaciation, i.e. from northwest to southeast.

On the western flank of the mountain the tin anomalies are elongated at right angles to the contours and field examination of these areas shows that most of them are coincident with intermittent drainage channels or low ground which could have been occupied by drainageways in former times. Despite this coincidence of tin highs and drainages the major tributary streams to Hatch Brook (shown in Figure 1), do not contain the major anomalies although the streams head in close proximity to known tin lodes.

On the east flank of the mountain, and also on the south flank, most of the elongate tin anomalies lie parallel to the direction of glacial movement and to the direction of the drainage channels. These channels angle across the contours and appear to be controlled by strong structural trends in the bedrock although glaciation may have played some part in developing the present pattern.

In the northwestern quadrant of the map there is a west-northwesterly striking anomaly which at the southeast end is controlled by topography and drainage channels but at the northwest end, which lies on the crest of a small hill with shallow overburden, is certainly not related to drainage. The geology of this northwestern area is favourable for tin mineralization but no prospecting has been carried out up to the present time and therefore the source of tin has not been located.

Interpretation

In interpreting distribution of tin in soils, the most important consideration has been that 95% of the tin at Mount Pleasant is in the form of cassiterite, almost all of which lies in a size range of -72 mesh to +200 mesh. Cassiterite is a resistate mineral and therefore cassiterite dispersion has been controlled by physical factors. The geochemical test used for analysis does not distinguish between total tin and cold extractable tin hence any tin which has dispersed in solution from the breakdown of stannite or other complex tin sulphides was not identified.

In pre-glacial time residual soils were developed over the area, and eluvial placers formed over the outcrops of tin mineralization. Downslope movement from the eluvial concentrations resulted in the formation of colluvial placers on slopes and alluvial deposits in drainage channels. From the main zones of tin mineralization in the North area and the Fire Tower area, the main dispersion was to the northwest.

During glaciation, ice movement was from northwest to southeast and this resulted in movement of the pre-glacial dispersed tin concentrations back towards the bedrock source. The result of pre-glacial and glacial migration of tin was to form the present pattern of tin anomalies along the crest of the Mountain with the main concentrations very close to original source of bedrock mineralization. These anomalies are still strong and coherent partly because of the absence of any large amount of admixed till in the soils although far-travelled erratics are present at the highest elevations.

In post-glacial time bedrock weathering has been slight, with the exception that ice-wedging and frost-heaving have contributed large amounts of angular float to the thin soils of the upper slopes. During this period a well-developed micro-drainage pattern has formed and tin has dispersed down-slope and down drainage to form the flanking anomalies.

In a number of areas containing tin lodes the soils contain less than 250 ppm tin. This is probably due to the fact that these intersections are on single tin bearing structures, whereas the main lodes of the North area and Fire Tower area are in strongly fractured zones in porphyries and pyroclastics which contain widespread tin mineralization. Therefore, the pre-glacial placers developed in the North and Fire Tower areas were larger and stronger than those developed on isolated structures.

ZINC (Figure 2)

I have shown the distribution of zinc in soils using a value of 500 ppm as the lower limit of locally anomalous values. Zinc is closely associated with much of the bedrock tin mineral-

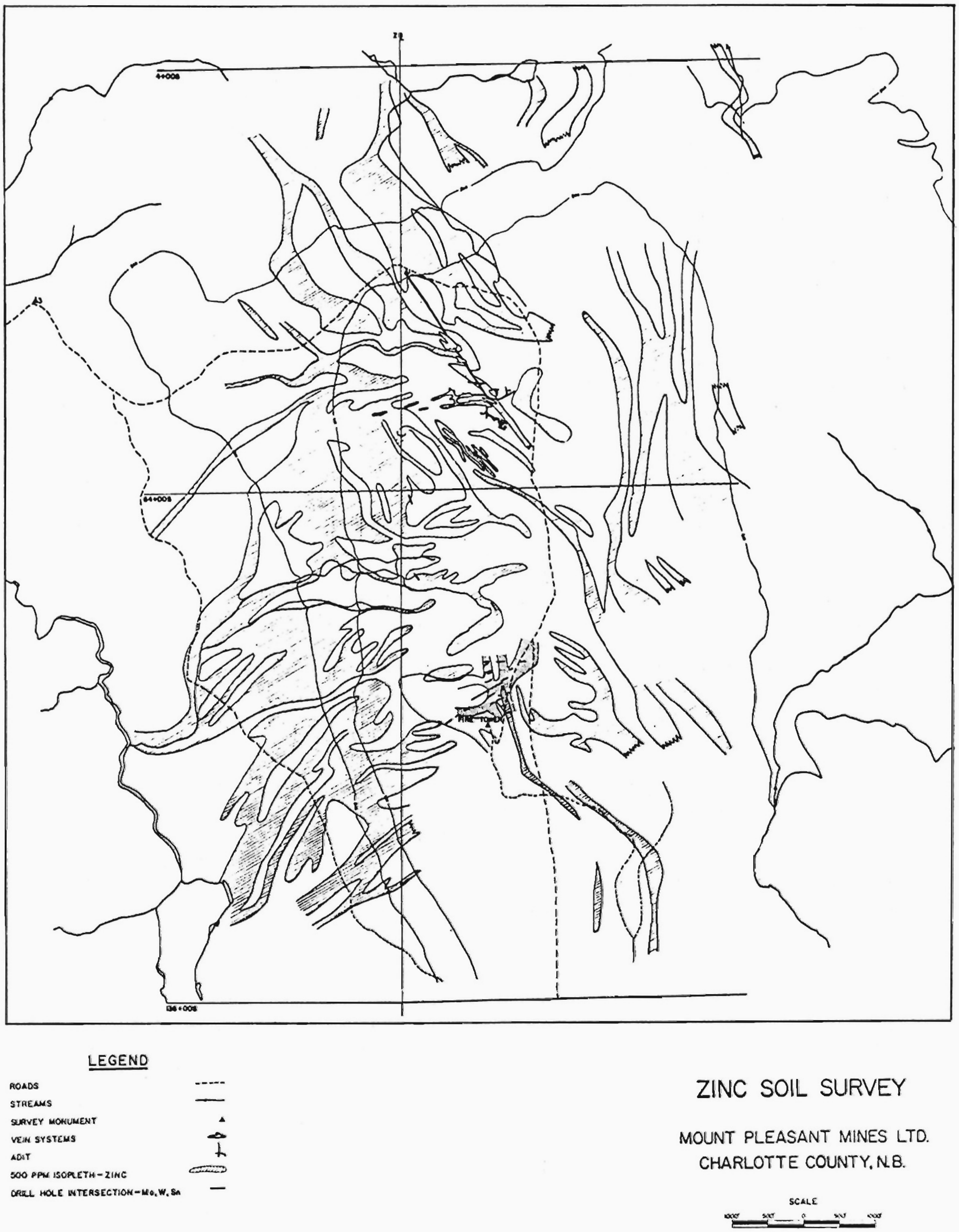

Figure 2. Distribution of zinc in soil, Mount Pleasant Mines Ltd., Charlotte County, N. B.

ization and is the most abundant heavy metal present in the mineralized zones apart from iron and arsenic.

In the exogenic geochemical cycle, zinc is chemically mobile. This is in strong contrast to tin and lead which show a marked lack of chemical mobility under conditions of weathering in the temperate zones.

The pattern of zinc distribution in soils in Figure 2 illustrates this mobility clearly. The soils along the crest of the mountain are generally low in zinc, and in the vicinity of the Fire Tower zinc is virtually absent, despite the widespread distribution of zinc in rock in the vicinity of the Fire Tower proper, where drill holes have cut zinc-rich zones averaging several per cent over hundreds of feet. Indium and cadmium accompany the zinc in the iron-rich sphalerite.

On both blanks of the mountain there are large areas of zinc-rich soils which show not only the effects of Zn dispersion by surficial drainage but also by underground waters emerging from springs and seeps at the base of the western slope along the main contact of Carboniferous volcanics of the mountain with the Ordovician meta-sediments which lie to the west. A similar pattern is evident along the northeast side of the mountain although the bedrock structure controlling the spring line has not been identified.

The general distribution of zinc in soil along the flanks of the mountain suggests that there is somewhat more zinc weathering from the bedrock of the North area than there is in the Fire Tower area. This is also suggested by the rather weak zinc dispersion pattern developed on the south slope of the mountain.

Interpretation

My interpretation of the zinc pattern is that it has developed in and on glacial soils during post-glacial time. There is little evidence of a pre-glacial or glacial dispersion pattern. Practically the sole control of the present zinc distribution in superficial materials is the movement of underground and surface waters. Because Mount Pleasant is a topographic high with strongly and deeply fractured bedrock, most of the drainage from the upper slopes of the mountain is underground apart from periods of spring run-off and heavy rain, therefore the strongest zinc anomalies are related to springs and seeps.

COPPER (Figure 3)

The distribution of copper values in the soils strongly suggests that the main source of copper in bedrock lies in the southern half of the mountain mass. In order to accentuate this distribution I have shown the 200 ppm isopleth as the lower limit of anomalous copper.

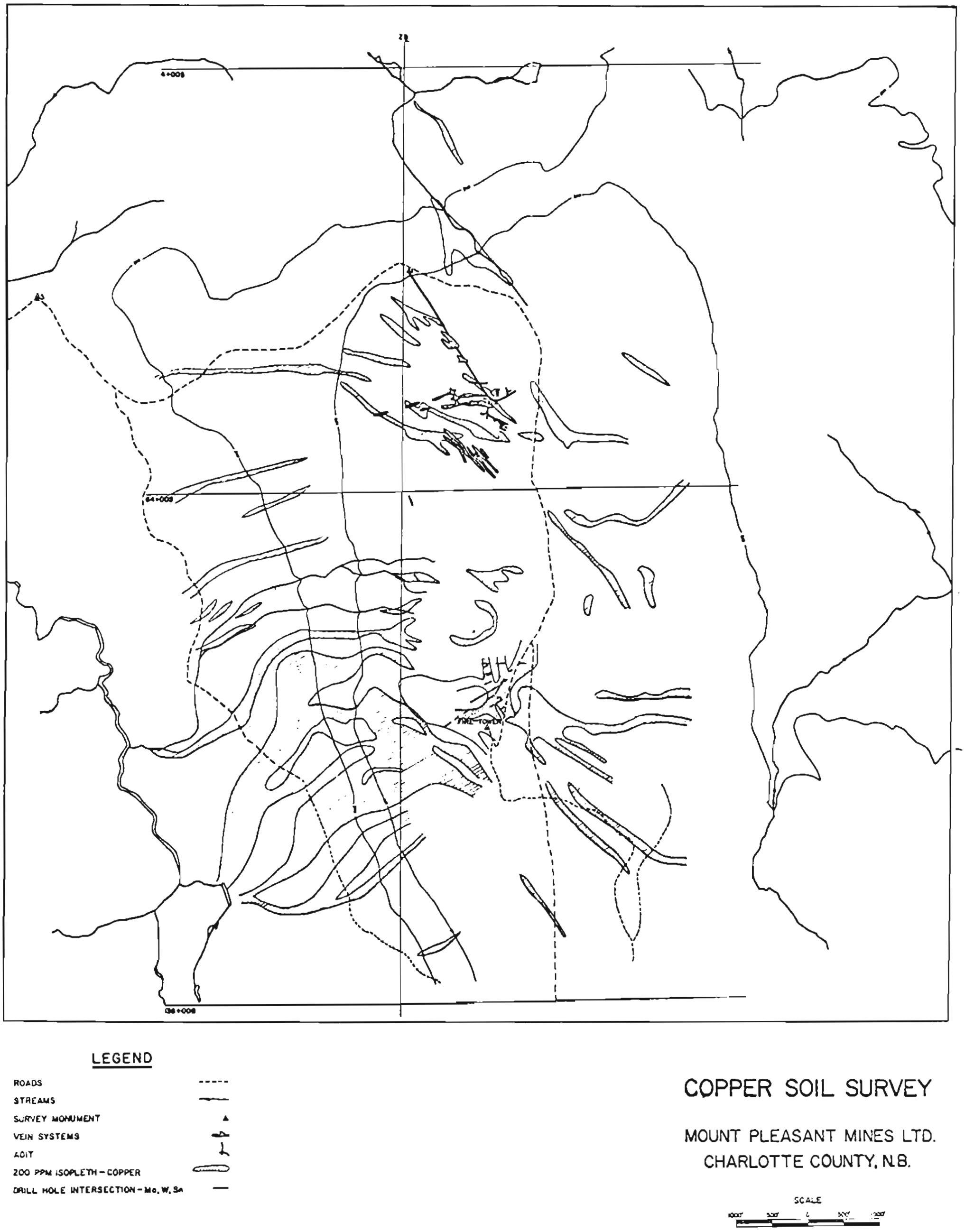

Figure 3. Distribution of copper in soil, Mount Pleasant Mines Ltd., Charlotte County, N. B.

Here again as in the case of zinc, there is a strong control of the copper distribution by the present surface and underground drainage pattern. The main area of concentration of copper values lies along the spring line on the southwest flank of the mountain. There is a strong continuation of this anomalous area in the up-slope direction. This up-slope prolongation is not so clearly shown by zinc.

The copper distribution in the soils of the North area appears to be partly controlled by drainage, but along the crest of the mountain the soil values reflect the presence of nearby bedrock mineralization.

However, in the area north of the Fire Tower, where copper mineralization grades are three to four times as high as in the North area, there is no corresponding geochemical high although drainage anomalies point directly to this bedrock source.

Copper values in bedrock in the North area appear to be closely related to the higher grade portions of the tin-rich zones. For the most part copper values are in the order of ¼ to ½ per cent. In one ore shoot however, copper values are better than 3 per cent.

Interpretation

My interpretation of the copper pattern is that the gross control of copper in soils is the distribution of copper in bedrock but that in detail the control is largely one of recent drainage dispersion from the mineralized areas. There is a possibility that the effect of glaciation is a factor but this point is not established. More information will be available on the effect of glaciation when the area immediately southwest of the Fire Tower is prospected for the source of the large amount of soil copper on the southwestern slope and along the lower spring line.

MOLYBDENUM (Figure 4)

The distribution of molybdenum in the soils forms an interesting pattern. For the purpose of this paper I have selected the 20 ppm molybdenum isopleth as the lower limit of the anomalous areas. Most of the background soils in the area of the survey run from 5 ppm to 15 ppm, and the data available on regional sampling suggests a regional background of between 0 - 10 ppm. Within the anomalous areas most of the values are in the order of 50 - 150 ppm, the highest values, with one exception, being 400 ppm. The one exception is a seep sample in the North Area of 3000 ppm.

It is obvious from Figure 4 that the main source of molybdenum lies near the crest of the mountain from a line about 1000 feet south of the Fire Tower to a line about 3000 feet north of the Fire Tower. The molybdenum anomalies are distributed in

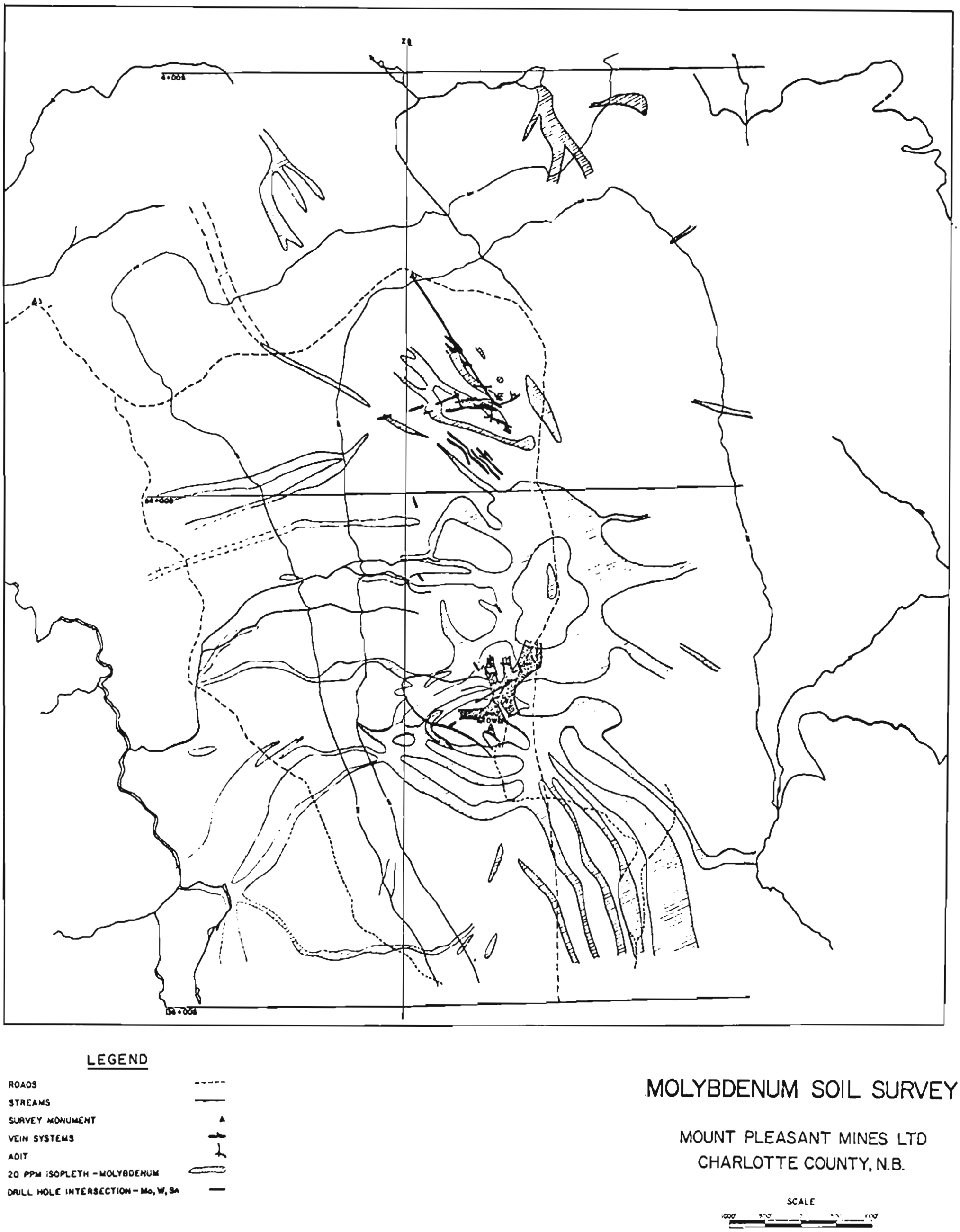

Figure 4. Distribution of molybdenum in soil, Mount Pleasant Mines Ltd., Charlotte County, N. B.

ring patterns about the highest ground with lateral distributary patterns from the flanks in the direction of the present drainage and towards the southeast in the down-glaciation direction.

In so far as the drainage anomalies are concerned, several of these show an interrupted pattern with high values near the upper section of the channel and in the low ground, but with lower values in the central section.

The strong concentration of zinc and copper along the spring line of the western side of the mountain is not present in the molybdenum pattern. Yet the source of the molybdenum is in the same general area as the copper and zinc, and it is certainly dispersed in most of the surface drainage channels.

In the Fire Tower area the central portion of the anomalous soil pattern is coincident with an extensive zone of silicification and fluoritization. Drilling in this area has yielded long intersections of low-grade molybdenite-wolframite-cassiterite-sphalerite mineralization in which the relative concentrations of these minerals show zoning with respect to each other and also with respect to the bedrock alteration pattern and structures. The strongest molybdenite concentrations are associated with the zones of silicification where they are most intensely fractured. The main tin values are in transgressive, northerly trending, fracture zones with the best tin and base metal values lying outside the area of strongest silicification. The wolframite-cassiterite ratio varies laterally and to depth with more wolframite in the peripheral area, at least on the southwest and southeast sides.

The general distribution of the silicified zone, shown in Fig. 4 as the stippled area, has been established by surface stripping, trenching, and drilling. Towards the west there is a large lobe of silicification, extending down the western side of the mountain, which is fairly well defined by scattered outcrops. Northeastward from the edge of the stippled area, where there is apparently a large source of molybdenum, outcrop is sparse but there are scattered showings of both silicified and chloritized bedrock.

Observations of bedrock in the exposed parts of the silicified zone show that the molybdenite is weathering with the formation of molybdic ochre. This ochre however does not appear to be widely distributed in the chloritic rocks which lie adjacent to, and down-hill from, the silicified zones.

Interpretation

For any full interpretation of the molybdenum pattern in soils more information about the distribution of molybdenum in bedrock is required. However, one can recognize certain obvious elements such as the strong down-glaciation pattern developed south of the Fire Tower, the very definite correlation of molyb-

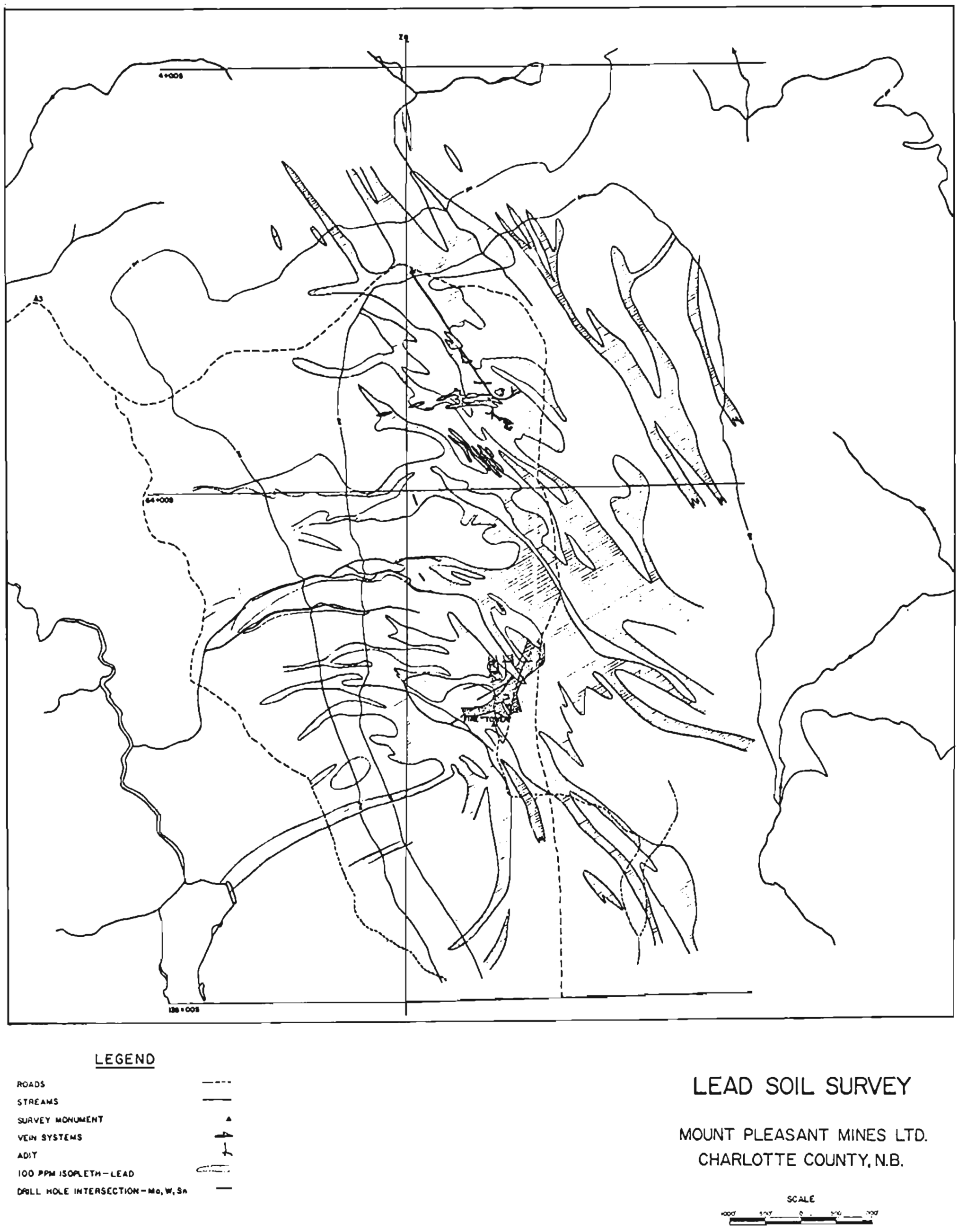

Figure 5. Distribution of lead in soil, Mount Pleasant Mines Ltd., Charlotte County, N. B.

denum in the soils of the upper part of the mountain with strong zones of alteration and bedrock molybdenite mineralization, and the peculiar encirclement of the higher portions of the terrain by molybdenum soil anomalies. Another important point is the absence of strong molybdenum concentrations along the spring line.

Taking these factors into consideration and with due regard for the patterns of the other metals in the soils I now consider that the molybdenum pattern developed as follows:

During pre-glacial weathering a strong dispersion pattern developed as a dispersion halo, on and below the outcrops of mineralization. The soils from this aureole were dispersed in the down-drainage direction but without any reconcentration as was the case with the heavy resistate tin mineral. During glaciation these residual and derived soils were smeared out in the down-glaciation direction towards the southeast.

In post-glacial time active weathering of the molybdenite has taken place with the formation of new dispersion aureoles in the near vicinity of the mineralized outcrops. However, very little molybdenum is moving down drainage in chemical solution at the present time, almost all movement taking place in the form of physical suspensions of fine particles. This movement only occurs during periods of active surface flow, with the probability that the bulk of this finely divided material is carried down over the steeper slopes to be deposited on the flood plains of the lower reaches of the creeks as the velocity of the waters decreases. This interpretation would explain the absence of molybdenum concentrations at the spring line and the interrupted pattern evident in some of the creeks.

There are other explanations such as changed eH-pH conditions which may equally well explain this type of distribution.

LEAD (Figure 5)

The dispersion pattern of lead, as defined by the 100 ppm lead isopleth, shows a dominant north-northwesterly trend that aligns closely with the trend of late-stage shatter zones in the bedrock. On the north and east slopes of the mountain these zones are in topographic lows which may or may not contain surficial drainage channels. The most southwesterly of these zones passes through a saddle in the north trending crestal ridge north of the Fire Tower. South of the Fire Tower the lead pattern coincides closely with the molybdenum pattern showing the characteristic strong anomaly at the southern limit of the surveyed area.

On the west flank of the mountain strong lead anomalies extend down slope along drainage channels. However these anomalies tend to die out where the streams enter the valley bottom. There is no spring line anomaly along the southwest flank such as is present in the case of zinc and copper. On the northeast slope there is an elongate anomaly in the near vicinity of the assumed zinc spring line anomaly but not coincident with it, nor parallel with it. The lead anomaly closely parallels a topographic low.

The central lead anomaly parallels the North adit and has an overall length of better than 8000' with widths of up to 750'. Almost all the underground workings lie within this zone and ore reserve calculations indicate that the various shoots grade about 0.14% - 0.20% lead. There is much finely disseminated galena along the length of the adit.

In the Fire Tower area the tin bearing ore shoots of the No. 7 lode system grade about 0.7% lead with local concentrations of 10% or more. These lodes lie within the limits of a very broad anomaly centred northeast of the Fire Tower.

Most of the exploration drilling shows broad zones of disseminated lead values however these are only one tenth as high as the values in zinc.

Interpretation

The lead distribution in the soils reflects mineralized structures lying more or less parallel to the direction of the glaciation. These structures have controlled the orientation of topographic lows and some of the drainage channels both surface and underground. During glaciation lead-rich residual and alluvial soils were moved in the down glaciation direction but this movement is difficult to define because of the parallelism of structure and ice-movement.

In post-glacial time galena has continued to weather and lead dispersion is acitvely taking place from the bedrock centres of mineralization into the overlying soils. Lead migration from these areas appears to be controlled primarily by the physical movement of contaminated particles down slope and down drainage. The absence of lead from the spring-line area of the south-western flank suggests that lead has limited chemical mobility under the existing weathering regime.

CONCLUSION

In conclusion I suggest that the data presented in this paper point up the necessity of evaluating the geomorphic and geological history of an area before attempting a unique interpretation of the relationship of soil anomalies to bedrock mineralization. Of particular importance in glaciated areas of moderate topographic relief is the matter of distinguishing between pre-glacial, glacial and post-glacial dispersion both chemical and physical. Working with this particular type of mineralization, where the concentrations of various economic metals in bedrock are not coincident, in an area where both physical dispersion and chemical dispersion are active, leads me to believe that it is essential, after outlining the general areas of interest by routine soil and drainage surveys, to follow and outline geochemical patterns in the field with micro-drainage maps in one hand and appropriate soil sampling and test kit in the other. It is not possible to produce satisfactory interpretations in the office without detailed reference to local field conditions.

Figure 1.
A bird's-eye view looking southwesterly across the prospect area. The small canyon hidden in the shadow is Big Pine Creek, a tributary to the South Fork of the Payette River which flows westerly through the main canyon. The prospect area is elongate northeasterly and is cut by both drainages but is centred on the sharp ridge between them.

Figure 2. A photo taken from the south side of the river looking northeasterly along the axis of the dike swarm. It shows the characteristics of the slopes and an indication of the attitude of the dikes.

GEOCHEMICAL CASE HISTORY AT THE LITTLE FALLS MOLYBDENITE PROSPECT, BOISE COUNTY, IDAHO

O.H. Rostad*

The Little Falls molbdenite prospect is along the South Fork of the Payette River about 40 airline miles northeast of Boise, Idaho. The nearest locality that is shown on most maps is Lowman, 11 miles to the east.

Altitude at the prospect ranges from 3400 ft. to 4200 ft. above sea level. Slopes are steep with many over 35°. The south-facing slopes are naturally dry and most markedly so where steep slopes at lower altitudes are underlain by batholithic rocks. Soil is thin and has a poorly developed profile. Vegetation is limited to grass, sagebrush and a few scattered pine trees.

The mineralization is contained in a swarm of Tertiary dikes which trends about N30E. These dykes range in composition from olivine diabase to rhyolite. They cut the Idaho batholith and generally dip about 70° to the southeast. No sedimentary or metamorphic rocks are present. About two miles to the southwest, the dike swarm enters the Boise Basin, an area noted for its production of gold from placers in the 1800s.

The prospect area is within a pyritized zone about 3,000 ft. to 4,000 ft. wide by 22,000 ft. long. The most intense pyritization is confined to a zone about 2,000 ft. wide by 10,000 ft. long. Oxidation of the pyrite has produced sufficient iron oxides to give the area a noticeable color anomaly. Molybdenite has been noted over an area 1,000 ft. wide by 3,000 ft. long within the most highly pyritized zone.

Molybdenite mineralization is present in quartz monzonite of the Idaho batholith, early lamprophyre dikes and two types of rhyolite dikes but it preferentially occurs in hair-line fractures in fine-grained rhyolite dikes of porcelaneous appearance. Some molybdenite is associated with narrow veinlets of quartz, hair-line to 1/4 in. wide. Minor fluorite and traces of chalcopyrite also occur.

The prospect was discovered in 1961 by Congdon and Carey, a Denver-based syndicate which specializes in exploration for minerals. After Congdon and Carey secured their land position by staking, and prior to their drilling, American Metal Climax ran a geochemical soil survey over the anomalous zone, sampled the road cuts and took stream sediment and water samples from the drainages.

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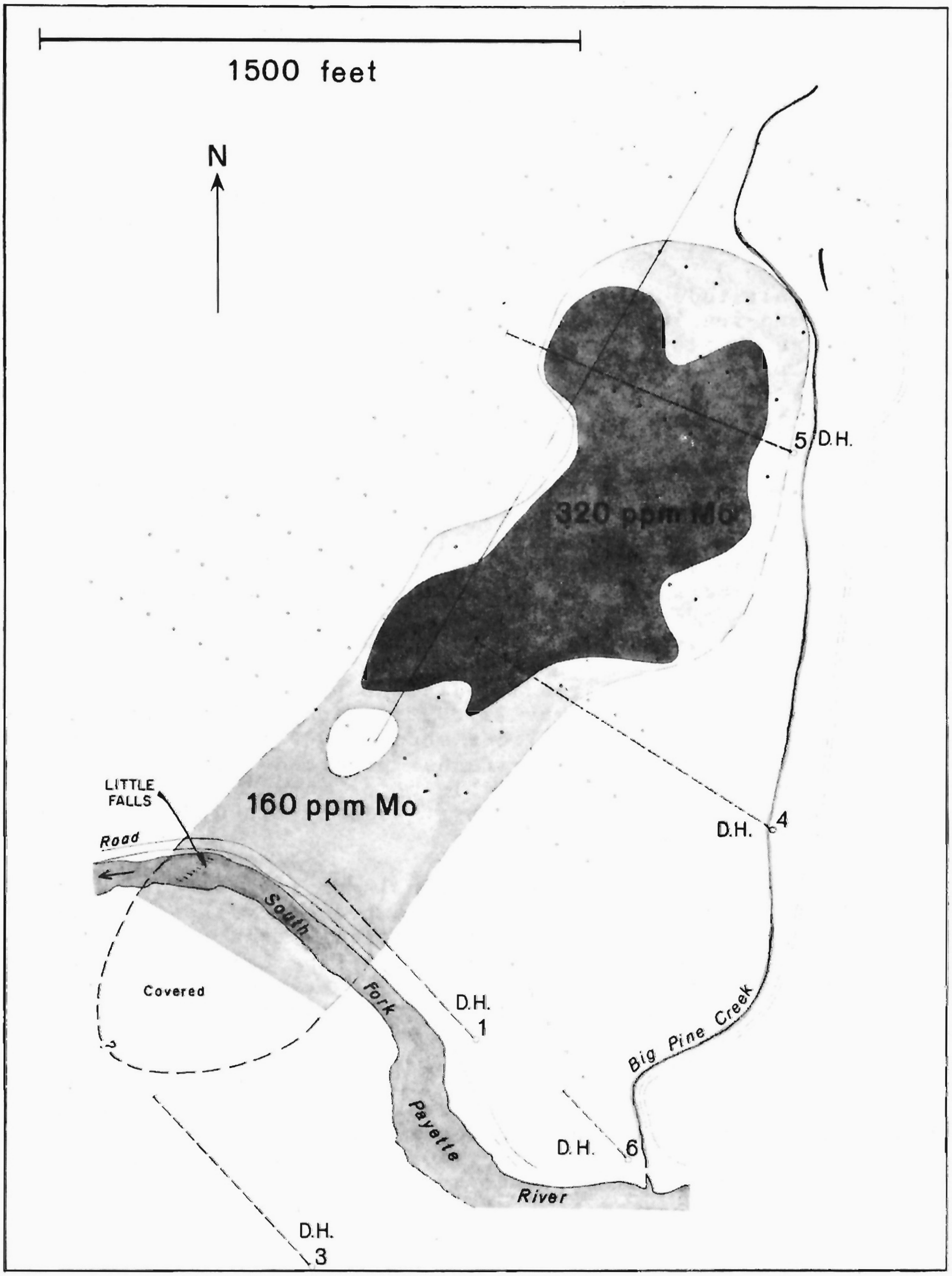

Figure 3. Little Falls molybdenite prospect, Boise County, Idaho.

Soil samples were taken at 100-ft slope distances along cross lines spaced 200 ft. apart. The samples were collected from the B horizon at a depth of 6 to 12 in. and sieved through a 35-mesh screen. The -35 mesh fractions were analyzed for molybdenum and copper by thiocyanate and biquinoline colorimetric methods respectively, using fusion extractions. Some of the plus 35 mesh fractions from the soil samples and all of the surface rock samples were also run by the same method.

Figure 3 shows the molybdenum soil anomaly. Soil samples from the light shaded area contain 160 to 320 parts per million molybedenum, whereas samples from the dark shaded area contain over 320 ppm molybdenum. Individual samples in the central area ran as high as 1400 ppm molybdenum. Background for soil samples in the prospect area is 20 parts per million for both molybdenum and copper. Regional background for molybdenum is much lower. The pH of the soil is between 5.1 and 7.5 and averages 6.6.

Soil samples in the central area contain on an average about 2.5 times as much molybdenum as is present in the immediately underlying bedrock. Drill core from the sulfide zone in holes 4 and 5, which undercut the highest parts of the soil anomaly, contain only about half as much molybdenum as the surface bedrock samples.

One of the reasons for the greater molybdenum content of the soil samples is that determinations were made on the -35 mesh fraction and not on the whole soil samples. The +35 mesh fractions from slightly more than 10% of the soil samples were analyzed for comparison. It was found that the -35 mesh fractions contain on an average 2.8 times as much molybdenum as the corresponding +35 mesh fractions. The molybdenite preferentially occurs in hair-line fractures; thus, as the rock breaks apart, molybdenum minerals are easily liberated to the fine fractions of the soil.

Another reason for the higher molybdenum content in soil versus rock may be tied in with the character of iron oxides present; however, AMAX has not investigated this aspect.

Stream sediment and water samples have been taken repeatedly from three stations in Big Pine Creek and two stations in the South Fork of the Payette. The pH of the water ranges from 6.7 to 8.1 and averages 7.4. Most of these samples failed to show any molybdenum values. In 1965 a series of samples was taken from late spring to fall to obtain information on seasonal variations. Four sets of water samples taken from Big Pine Creek in this series gave results which might be considered anomalous; one was obtained early in the season while spring runoff was still in progress and the other three were collected after some heavy rains.

Some molybdenum is being moved by water as samples of the water discharging from the collar of drill hole 6 averages 250 ppb Mo, excluding one determination which was 2500 ppb. In addition, ilsemannite has been noted several times in one small spot along the main road cut. The ilsemannite was only noted after approximately two weeks of dry weather. No ilsemannite is present after a rainfall which suggests that it is carried away in solution.

A possible explanation for the general absence of molybdenum in the water samples may be that the only time water percolates through the fractured molybdenum-bearing rock on the ridge is during the spring thaw or after a heavy rain.

The South Fork of the Payette evidentally carries so much water that any contribution to it from this prospect is not generally detected by ordinary procedures.

The stream sediment samples were uniformly nil in molybdenum. This seems reasonable because there does not appear to be any material moving off the prospect slopes to Big Pine Creek and any material being eroded from the mineralized rock where it is cut by the river is probably so little as to be lost in the mass of sediment from unmineralized areas.

The writer gratefully acknowledges permission from Congdon and Carey and American Metal Climax, Inc. to publish the above information.

SOME PROBLEMS IN APPLIED GEOCHEMISTRY

Harry V. Warren, Robert E. Delavault and
Christine H. Cross*

INTRODUCTION

To those who were involved some twenty years ago in the introduction of geochemistry, the general acceptance at the present time of this relatively new addition to the science of mine finding is highly gratifying.

Unfortunately, because of the seemingly obvious simplicity of some of the general ideas associated with geochemistry, many persons become involved in investigations before acquiring a sufficient background of essential data, without which the chances of fulfilling a successful program are considerably lessened.

It should be remembered that some of the best known workers in the field of applied geochemistry developed their techniques for use in the U.S.A., the U.S.S.R., Africa, and Australia. These techniques, although excellent for the purposes for which they were developed, are not always equally applicable elsewhere. By way of example, there are many soil sampling techniques that are particularly useful in areas where soils are residual and mature. It just happens that many Canadian soils are transported and most are, geologically speaking, young, often even where they may be morphologically mature. Again, some of the highly rewarding geobotanical studies reported from several countries are not likely to prove equally rewarding in Canada. Botanical colleagues inform us that we have not had time to develop soils with a distinctive plant ecology.

Fortunately it has been our experience that most techniques can be used profitably if their limitations are appreciated and taken into account. Unfortunately, from time to time one hears of geochemical surveys that are termed failures. Failures are discouraging to all concerned; some are doubtless unavoidable, but many could be averted. It is with the hope that some unnecessary failures can be avoided in the future that we propose to discuss briefly a few illustrative examples involving some geochemical problems we have ourselves encountered.

In the midst of so much talent and originality, we trust that the points we raise will at least stir up some controversy; on this occasion we make no pretence of introducing any new or radical ideas.

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SOIL SAMPLING - PEDOGEOCHEMISTRY

In any soil sampling program it is well to remember that the organic and clay components of a soil can greatly affect its metal content. Furthermore, in so far as the organic and clay fractions of a soil vary from horizon to horizon, it is essential to pay close attention to the soil horizon or horizons to be sampled.

Ideally it would be helpful to sample all horizons of the soil profile at each sample site. Manifestly, considerations of time and cost rule out such a procedure. Many soil samplers screen their samples, and this certainly may assist the operation: it is a moot point as to whether screening produces data worth the extra cost.

In the examples that follow, all results are reported in ppm. of sulphuric acid extractable metal. No particular horizon is being touted, the authors merely wishing to emphasize how variations of as little as one inch in the selection of the horizon to sample can, in an extreme case, make the difference between success and failure in the spotting of an anomaly.

A. Soil associated with Lead Zinc Mineralization, West Kootenay, B.C.

In this particular example the A horizon was about one foot thick and the B horizon approximately eight inches.

	Cu	Zn	Pb
A horizon	24	2100	560
B horizon	12	240	12

B. Soils associated with Lead Zinc Mineralization, East Kootenay, B.C.

In this example a great fault related to, but not itself containing the ore body, had been mapped for thousands of feet. Over this fault the soil profile consists of three inches of dark fluffy humus - the L-H horizon, two inches of brown loam-like material - the A_h horizon - and more than ten inches of light brown loamy material - a B horizon.

	Cu	Zn	Pb
L-H horizon	160	7900	2000
A_h horizon	32	2800	2400
B horizon	20	1400	1400

Obviously one would have little difficulty in suspecting the presence of nearby lead zinc mineralization.

However, less than one hundred feet away - at right angles to the fault - and for a further distance of at least several hundred feet, no such soil profile could be found.

Indeed, less than one hundred feet from the fault the soil had an entirely different profile. At the top was one inch of black material with some leaf litter - L-H and A_h ? - , then one inch of light ash grey loamy material - the A_e horizon, and lastly about eight inches of light brown loamlike soil - the B horizon.

	Cu	Zn	Pb
L-H A_h horizon	6	74	500
A_e horizon	6	450	Trace
B horizon	6	400	2

In this instance, had a sampler taken material from the B horizon he might have been excused for not becoming overly enthusiastic; he could never have been forgiven had he passed on, because the mineralization involved was that of the Sullivan Mine.

Incidentally, at this second site the biogeochemical results clearly pointed to lead-zinc mineralization, but this, as the story-teller would say, is another story.

The point we wish to make is that a mere hundred feet from the fault it is possible to take a sample after removing the forest litter, a normal procedure, and have this sample report lead, a trace! Surely this shows how a soil sampling program that is carried out in routine fashion, and without geological co-ordination, may well prove to be less than satisfactory.

The above examples dealt with soils formed in a relatively dry climate with a rainfall of less than 30 inches. Let us now turn to an example taken from Vancouver Island in a district with more than 80 inches of rain per year. Here we have Western Mines with a lead-zinc ore that also carries a little copper. Above, and close to mineralization, a soil profile was examined and found to consist of three inches of L-H, then one foot of an A_e , followed by one foot of B horizon.

	Cu	Zn	Pb
L-H horizon	20	370	72
A_e horizon	32	320	140
B horizon	40	410	180

Some three hundred feet away from the above profile, and in a position believed to be similarly related to ore, the profile is decidedly different. Here there are two inches of L-H, followed by four inches of A_h , then two feet of A_e , and then three inches of B material.

	Cu	Zn	Pb
L-H horizon	96	520	19
A_h horizon	8	500	56
A_e horizon	3	260	10
B horizon	24	290	Not detected

Obviously some care will be required in setting up a soil sampling program in this area if the results are to be meaningful. Unfortunately, we did not determine the soil fractions in the above two instances. However, it would appear that an abundance of clay minerals may be responsible for retaining quantities of heavy minerals adequate to indicate buried mineralization. The ability of organic material to hold metal is also shown in the above profiles.

It would be possible to give many more illustrations and doubtless most readers could provide others from their own experiences. However, all that must be emphasized is that it is wise to have soil sampling programs carried out under the direction of a geologist, and also to make a series of orientation profiles before embarking on a wholesale sampling program which must, of necessity, deal with one particular soil horizon, whichever one may prove most efficacious under the particular circumstances involved.

When discussing this problem we cannot help remembering an instance when a post mortem was being held after drilling a barren hole as a result of following up an apparently potent geochemical soil anomaly. It eventually transpired that the soil sampler had unwittingly passed from a series of A_e horizon samples to one involving largely humus: he had followed orders and had taken his samples at uniform depths below the surface but, unfortunately for all concerned, the depth of the A_h horizon had varied significantly throughout the traverse!

It probably is not necessary to make determinations on organic matter in all samples, but it is well to keep in mind that organic matter can accumulate large amounts of some metals where conditions are suitable.

WATER SAMPLING - HYDROGEOCHEMISTRY

In discussing water samples with experts, it is not necessary to point out that a one, two, or even three litre sample can, only under very special circumstances, be considered as representative of the run-off from any appreciably sized area.

There are many ways by which it is practical to determine the trace metal content of water. It is possible to report with a reasonable degree of confidence on water with a content in the range of from one to five parts per thousand million of such elements as copper, zinc, lead, molybdenum, and uranium.

As far as generally available knowledge is concerned, comparatively little attention has been paid to the problems involved in obtaining even relatively representative samples of metals present in run-off water from specific drainage areas.

The trace element content of water is of concern not only to exploration geologists, but also to epidemiologists. Unfortunately, many epidemiologists have sampled water supplies and not found useful correlations between trace elements and disease patterns. As far as can be told from reading some of these papers, many water samples are taken without a full appreciation of the problems involved in obtaining representative material. We suspect that a few geologists also underestimate the difficulties inherent in water sampling.

In northern latitudes, with which we have been primarily concerned, our climate provides seasonal variations in temperature and rainfall. These fluctuations result in water tables that change position greatly throughout the year. The water in any stream, at any given time, consists of a meld of surface run off, usually relatively pure, and of ground water. Ground water, when it has been involved in those interactions that take place when the zone of oxidation and the water table are suitably related to one another, can become highly charged with metal ions! Eh and pH are primary controls in holding or releasing chelated and/or adsorbed metals from the zone of oxidation. In general, it is safe to say that ground waters are more apt to be highly charged with metal ions at those times when the water table is passing up or down through the zone of oxidation than they are when the water table is well above or well below the zone of oxidation.

It is possible in British Columbia to sample a creek for weeks on end and obtain analyses of less than one part per thousand million, and then one day find the same creek reporting five, ten, or even many more parts per million. We well remember reporting negative results from a fair sized creek, and returning to it many months later to find it turning our dithizone purple. Purple Creek, as it was named, led to the discovery of interesting and heretofore unsuspected mineralization which, alas, has not as yet proved to be economically rewarding.

Until an effective and efficient method of sampling over adequate periods of time can be devised, we are of the opinion that water sampling cannot be considered an unconditionally reliable tool. Were the problems of sampling to be effectively solved, we suggest that water testing might be found to be an effective prospecting tool, particularly when used in conjunction with stream sediments.

VEGETATION SAMPLING - BIOGEOCHEMISTRY

We have, over the years, extolled the dangers and the virtues of biogeochemistry: we have no wish to repeat our statements. However, "brush" sampling as it is referred to by some, requires some knowledge and experience.

We have one relatively new discovery to report, namely that Douglas Fir seems to have the ability to concentrate arsenic to a remarkable extent. This ability to collect arsenic may be used in the search for base metal or gold bearing ores which contain as little as one per cent arsenic, and possibly even less. In an area of known gold-arsenopyrite mineralization we established that the soil carried from 8 to 38 ppm., depending on its proximity to the ore and the soil horizon that was sampled. The ash of all but two of the ten species of trees growing on this soil ran less than 4 ppm. of arsenic: the ash of fresh Douglas Fir growth ran 560 ppm. A great deal of work has been done since that discovery. We now know that Douglas Fir is quite capable of reporting strongly anomalous amounts of arsenic at distances of from three to four hundred feet down hill from a buried outcrop that contains as little as one per cent of arsenic.

Most elements report particularly well in a few species of trees or lesser plants. Fireweed, alder, soopolallie, and lupin are especially useful for reporting molybdenum. In the fullness of time we hope that it will be possible to specify particular species of trees and lesser plants peculiarly suited for finding anomalies of each element.

In 1965, while establishing background values in an area for which we had limited knowledge, we determined the copper, zinc, lead, and molybdenum content of the ash of twelve species of lesser plants that were growing profusely. The results we obtained serve to illustrate how different species of plants pick up varying amounts of each element.

Table 1

The Copper, Zinc, Lead, and Molybdenum
Content of the Ash of Young Growth.
Some Lesser Plants in the Watson Bar
Area of B.C.
(in ppm.)

Common Name	Scientific Name	Cu.	Zn.	Pb.	Mo.
Rosy Pussytoes	Antennaria rosea	100	610	16	49
Indian Paintbrush	Castilleja rhexifolia	81	260	10	63
Blue Jacob's Ladder	Polemonium pulchemium	85	310	28	71
Locoweed	Oxytropis monticola	74	200	15	150
Mountain Phacelia	Phacelia sericea	39	150	10	24
Lupin	Lupinus latifolium	100	220	11	86
Hair Leaved Sandwort	Arenaria capillaris	79	780	37	63
Spotted Saxifrage	Saxifraga bronchialis	150	200	48	92
Stonecrop	Sedum lanceolatum	110	71	4	54
Yarrow	Achillea millefolium var. lanulosa	100	260	46	76
Globe anemone	Anemone multifida	120	500	18	120
Field chickweed	Cerastium arvense	78	400	20	120

It can be seen that there are wide variations in the selectivity of these species for different elements.

Before lesser plants such as the above can be used effectively in biogeochemical studies, similar collections from many different areas will have to be analyzed and the results compared. In the above collection we were most interested to note that Locoweed picked up more molybdenum than Lupin, which we had heretofore considered one of the most potent gatherers of this element. Countless other questions are raised by a set of results like that above. What is the cause, or reason, for Hair Leaved Sandwort picking up eleven times as much zinc as Stonecrop?

In previous publications we have warned that in comparing the metal content of different organs of various trees, it is also necessary to remember that the metal content of plant material varies from season to season, and from year to year. Recently, we encountered a text book illustration of just such variations. Some of this data has already been published (Warren, Delavault, and Cross, 1966), but it is worth repeating, because it may not have been read by all who should be interested. The mine was Copper Mountain, and the collection of trees came from the vicinity of known mineralization on a claim called "Helen Gardner". The results are given in Table 2.

Table 2

The Copper Content of the Ash of Organs of Varied Age
in Trees at Copper Mountain, B.C.
(in ppm.)

	Most Recent Growth		Previous Year's Growth	
	Tips		Stems	Needles
Douglas Fir (Pseudotsuga menziesii)	180		670	240
Lodgepole Pine (Pinus contorta)	220		570	300
White Spruce (Picea glauca)	260		1000	100
	Stems	Leaves		
Willow (Salix sp.)	370	180	680	
Alder (Alnus sitchensis)	350	300	500	

In the examples given above it can readily be seen that second year stems point to a clear cut copper anomaly. The second year needles, and the most recent growth, at this time and place, would have been of much less help. Incidentally, the lesser plants provided little assistance in pointing to any copper anomaly.

MEN AGAINST MACHINES

The Twentieth Century has seen some remarkable changes in the art and science of mine finding if viewed through the eyes of geological engineers and geologists. In the earlier decades of the century it was common to find that many were willing to assume the mantle of mine geologist. Mine examinations and prospect evaluations were frequently made by mining engineers and "practical operators". Times changed, and a division of labour became accepted practice; the geologist and geological engineer assumed the responsibility for finding ore, and the mining engineer for removing it from the earth's crust. Ideally the miners and geologists co-operated, but, unfortunately, there were some who did not, and we had some regrettable examples of mining engineers attempting to control geological work, leading in some cases to inefficiencies only matched by those admittedly more rare instances where geologists usurped the role of mining engineers.

But while, in their own eyes at least, the geological engineers and geologists were coming into their own, their difficulties also were increasing; greater and greater demands were being made for the discovery of new ore bodies. These demands necessitated the use of new tools and in retrospect it seems inevitable that geology would turn for help to her sister sciences, to physics, to chemistry, to biology, and also to mathematics and every phase of engineering. By the middle of the century geophysics, geochemistry, and biology had all been accepted and become integral parts of most large and integrated mining companies. Unfortunately, the complexity of all this new assemblage of knowledge brought its own set of problems. No one man, even the best of geologists, could hope to master all the basic disciplines involved. Obviously, co-operation was indicated. However, was the geophysical survey, or the geochemical survey, to be carried out by men who were geologists primarily but with special training in physics and chemistry, or by physicists and chemists with some knowledge of geology? It would be our opinion that the best results have been achieved where there has been harmonious co-operation between teams of specialists, each of whom was able to evaluate competently the special knowledge and problems of his associates.

This brings us to the point where we would like to express our belief that geology, and not chemistry, should be in control of geochemistry, and the geochemical exploration should be looked upon as an aid to geological exploration and not the dominant or controlling motivation. Let us turn now to geochemistry, with which this presentation is particularly concerned.

During the past few years many new tools, and new machines, have been placed in the hands of geochemists. First thoughts would be that nothing but good could result from these new weapons being made available to those whose aim is bringing to light new wealth. Nobody would wish to be so brash as to suggest that being able to detect one part of mercury in ten or in one hundred million parts of soil or dry plant is not a useful thing to be able to do; moreover, it is doubly useful if results of this degree of sensitivity can be carried out by production line methods. Few would be willing to deny that new vistas are being opened up by its being possible to enlist the help of computers to store, process, and regurgitate a wealth of data in a way undreamed of only a short time ago.

Alas, however, we feel called upon to issue a note of warning, even at the risk of being labelled as conservative, old-fashioned, and reactionary.

Some years ago our attention was drawn to a slogan seen in a doctor's office. It ran as follows:- "Get your happiness out of your work or you won't know what real happiness is". It would be well for all engaged in mine finding to think about this slogan for a little while. Many of us chose geology and geochemistry because we felt that it would be fun to have a part in finding new mines. A few of us had the added idea that it might be financially profitable. We never anticipated that our chosen work could be made into an unmitigated bore, bereft of all the job of personal involvment and the thrill of discovery. Is it possible - we have no doubt that it is desirable - to make these new aids our servants, and not our masters?

We must ask ourselves if we would willingly choose to spend a precious summer collecting water or soil samples by the thousand, or snipping tree samples by the bushel, with the prospect of never knowing what our samples had been found to contain? Many companies, for reasons of efficiency or security, never divulge the results they obtain to those in the lower echelons. From the company's point of view, they feel that they cannot act differently. Most of us are not skilled poker players, and if we run a laboratory in the field, or actually test in the field, which of us could be counted on to hide our emotions from keen observers after encountering a significant anomaly? What field man amongst us cannot recall claim-staking based on the indiscretions of a cook, a packer, or a junior assistant? The packer may have disappeared, but the helicopter pilot and his assistant have replaced him. Actually we are passing through difficult times in this period of affluence; many will not accept a dull routine job when other more interesting, and sometimes better paying opportunities are available.

It is not only the possible boredom of the collector that presents a problem. The geochemist who is responsible for the assembling of samples seldom analyses, or has himself ever analyzed against time, a multitude of samples. Today, backed up by an efficient laboratory, the geochemist has a grave tendency to place his reliance on the number of results he can get on a map; he has analyses made with a premium on quantity rather than quality. This is not to suggest that most of the great analytical laboratories are not doing excellent work, most of them are. What we are suggesting is that, armed with analyses in quantities of which he could hardly have conceived a few years ago, the geochemist is apt to relegate geology to a position less than it deserves, and this, we feel, is dangerous.

Nor can we envy those who spend all their days in laboratories doing hundreds of routine determinations, having little or no conception of the significance of their work. Routine work is necessary, but we have found that, where practical, it makes life more rewarding if the worker feels that he or she is a part of some plan, and not an infinitesimally small component in a big machine.

We are sure that we do not know all the answers to the problems we have raised, but we are confident that no machines can produce results better than the data with which they are fed.

Perhaps what we are trying to say, and asking others to think about, is that, although we want to make use of every new tool available to us, we must, in some way, devise our programs of mineral exploration so that more of those engaged in these programs will find more human satisfaction, and not become mere robots measuring their satisfactions solely in terms of their emoluments.

For reasons that we have already discussed, we feel that by far the greater number of water samples taken in British Columbia have represented wasted effort. Likewise many of the soil samples have not fully justified their expenditure. We have been loath to set up arbitrary standards; too often these standards are accepted as gospel. Any good geochemical program depends on setting up a project and treating each case on its merits. Only by charging our machines with the best and most significant data capable of being produced by the ingenuity of man, can we achieve the results for which we are all so earnestly seeking.

At this juncture, there may be those who are asking themselves why these academically involved geochemists are discussing aspects of their work that might more naturally be considered to be in the realm of operating companies. Our justification, if any be needed, is that over the years we have seen the supply of geological engineers, and to some extent geologists, diminish to the point where the supply does not begin to meet the demand. As for geochemists, we have been unable even to make an award for the one modest but, by the University, eagerly accepted scholarship available to us. This is not the place to discuss the many reasons which we believe are responsible for this regrettable state of affairs, but one reason we must give. If geological and geochemical summer work cannot be made to provide a challenge, mental and physical, and a thrill in the sense that a man is pitted against the forces of nature, if geology, and here we include geochemistry, fails to attract those kinds of men and women that it has in the past, then the future for all of us is gloomy. We live in an affluent society, and there is a wide choice of opportunity open to young people today. We must put the better face of geology before the public, and the better face of geology is not boredom, monotony, and frustration.

Once again, to sum up, we say by all means make use of all that modern ingenuity and science have to offer us, but let us put our heads together and find ways and means to harness those basic qualities of man which, in the past, have done so much to aid in his development, his curiosity, his inventiveness, and his eagerness to wrestle with nature. Geology and Geochemistry have real drawing powers because they do afford a link between man and the earth on which he lives. If we remove all the human aspects and over-computerize our science, we do so at our peril.

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It must be clearly understood that the ideas expressed in this paper are those of the authors, and that they in no way represent the views of the many companies and organizations that have over the past twenty years supported our geochemical investigations.

Amongst those who have supported us are, the Geological Survey of Canada, the Defence Research Board of Canada (Grant 7510-16), the Geological Society of America, the Department of National Health and Welfare with the co-operation of the British Columbia Department of Health Service and Hospital Insurance, the Multiple Sclerosis Society of Canada, the National Research Council of Canada (Grant No. A.1805), Amex Exploration Inc., the Consolidated Mining and Smelting Co. of Canada Ltd., and most particular by Kennco Explorations (Western) Ltd. Many other companies and individuals, too numerous to record, have assisted us in many ways. To all the above we express our thanks.

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ABSTRACTS

STUDY OF HEAVY MINERALS IN GLACIAL SOILS

N.H. Brundin*

The distribution of heavy minerals in till near twelve Swedish ore deposits is under active investigation.

Pits were laid out "downstream" from the deposits, i.e. in the direction of glacial transport, and in profiles approximately perpendicular to this direction. The heavy minerals were concentrated on a shaking table and further investigated.

Some preliminary results regarding the occurrence of ore minerals in till have been obtained, and some general conclusions will be presented. The content of heavy minerals increases with depth even in apparently unsorted till deposits. The presence of ore in a number of the investigated cases is clearly indicated by the distribution of heavy minerals. As a specific example, the significance in prospecting of the occurrence of manganese minerals in till will be cited.

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HYDROUS MANGANESE-IRON OXIDE SCAVENGING: ITS EFFECT ON STREAM SEDIMENT SURVEYS

F.C. Canney*

Appraisal of a large body of data based on the analyses of several thousand active stream sediment samples from Maine has revealed a strong positive correlation between the cold-extractable heavy metal (cxHM) and manganese contents of stream sediments from unmineralized terrane. The relationship is exponential with the formula $\text{ppm cxHm} = a\ (\text{ppm Mn})^b$ where a and b are constants. This correlation reflects the preferential scavenging and accumulation of significant amounts of zinc by hydrous manganese-iron oxides, commonly occurring as coatings and crusts on bed material in many stream courses in glaciated areas. In such areas, calculation and use of a single threshold value in the conventional way will produce many anomalies unrelated to mineral deposits. Samples from streams draining mineralized areas, however, generally have ratios higher than predicted by the above equation, often considerably so. On this basis the HM-Mn ratio offers promise as a yardstick by which the significance of heavy-metal stream-sediment anomalies in glaciated terranes can be evaluated.

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GEOCHEMICAL PROSPECTING RESEARCH BY THE UNITED STATES GEOLOGICAL SURVEY

F.C. Canney and R.L. Erickson*

Geochemical prospecting research by the U.S. Geological Survey, both in field and laboratory programs, is devoted to the examination of principles of geochemistry that may have potential for mineral exploration. The program consists of applied research projects aimed at developing new methods, instruments, and techniques to help find concealed mineral resources, with considerable emphasis on development of analytical methods that can be taken to the field to directly guide geochemical sampling and make results immediately available. A few projects are geochemical reconnaissance surveys for ground favourable for the occurrence of minable ore. And still others (geochemistry of gold; geochemistry of mercury) have the objective of accumulating basic geochemical background data to provide a sound theoretical and experimental basis for the applied research programs.

The principal applied geochemical studies include,1) projects aimed at the difficult task of prospecting in the Basin and Range Province of the Western United States where much ground favourable for the occurrence of minerals is concealed by a relatively thin (less than 200 feet) cover of pediment gravels; 2) the development and study of techniques of geochemical reconnaissance in glaciated areas based on water and stream sediments where considerable emphasis is now being given to techniques of anomaly appraisal; 3) the determination of accessory-sulphide distribution patterns in relation to vein deposits in some intrusive rocks in the Front Range of Colorado; 4) studies on the distribution of minor elements in barren and productive stocks of the Western United States; and 5) research on the preparation and interpretation of geochemical maps based on analysis of stream-sediment samples.

Chemical research has recently yielded very sensitive wet methods for determining gold, silver, and mercury that can be performed relatively easily in mobile laboratories operating close to the field areas. Currently plans are well advanced to study the integration of atomic absorption instrumentation for collecting data in applied geochemical prospecting programs.

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GEOCHEMICAL PROSPECTING PROCEDURES, THEORY AND PRACTICE

D.R. Clews*

The dispersion patterns and mechanisms as well as the mode of occurrence of metals in the geochemical cycle are described. These include the clastic agencies of wind, rain, gravity, etc. as well as saline agencies. The solubility of metals in natural waters is considered as well as transport and precipitation in this medium. Dispersion patterns related to drainages and soils are described.

Geochemical prospecting methods and analytical techniques for regional appraisals as well as detailed investigations are listed.

Examples of the mechanism by which false anomalies are formed in soils are detailed. Some of the major types of false anomalies are listed and examples of the criteria used for differentiating between false and true anomalies are given.

Geochemical prospecting techniques in Canada are discussed. These include those designed for residual or partly residual soil covered areas as well as the totally transported soil covered Shield areas.

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STREAM SEDIMENT SAMPLING DURING TRAVERSE MAPPING*

E. Dimroth**

Stream sediments were sampled during traverse mapping on a scale of 1 inch equal ½ mile by most field parties of the Geological Exploration Service, Department of Natural Resources, Quebec. Sediment samples were taken from all streams intersected by traverses. In this way an irregular sampling grid with an average density between 1 and 2 samples per square mile was obtained. The samples were analyzed for Cu, Zn, Pb, Mo, and in certain cases, for Ni by the Laboratories Service.

The relatively small number of samples (between 150 and 350 per map-area) does not allow an exact analysis of the frequency distribution of the trace element contents. Background values can be interpreted as log-normally distributed. Anomalous

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* Published by permission of the Deputy Minister, Department of Natural Resources, Quebec.

** Geological Exploration Service, Department of Natural Resources, Quebec, Quebec.

populations can be interpreted as log-normally distributed and partly overlapping the background population. Anomalous values occur in certain cases in tectonically defined zones, coinciding with known or presumed zones of mineralization. Procedures and results are demonstrated by an example from the Labrador Trough.

GEOCHEMICAL PROSPECTING, CASE HISTORIES AND EXPLORATION ARCHITECTURE

J.A.C. Fortescue*

The application of geochemical prospecting methods in Canada has frequently been criticised because results obtained by a given method in one area are considerably more reliable than results obtained by the application of the same method in a second area. In this paper the role that case histories can play in recording the scope and limitations of geochemical methods in Canada is discussed. The need for a simple, but generally accepted, terminology for the description of geological, geophysical and geochemical components of an exploration program is stressed and one set of terminology for this purpose is described under the heading of "Exploration Architecture".

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MERCURY DISPERSION HALOES AS PROSPECTING INDICATORS AT THE BASE-METAL DEPOSITS, WEST SHASTA DISTRICT, CALIFORNIA

G.H. Friedrich* and H.E. Hawkes**

Geochemical work in the West Shasta district, California, has demonstrated that mercury anomalies occur in soils over blind but known orebodies of the Early Bird Mine, the Keystone Mine, and the Mammoth Mine. The lenticular and flat-lying orebodies, consisting of massive pyrite, smaller amounts of chalcopyrite and sphalerite, and minor amounts of galena, tetrahedrite, pyrrhotite, and magnetite, are overlain by unmineralized rhyolite and tuff horizons. The ore occurs at a depth of about 200 feet. The mercury content of the soil samples taken above the orebodies is far above the background value. They contain up to 340 ppb (parts per billion) mercury. The background range is from 20 to 60 ppb Hg.

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CODING SYSTEM AND FIELD CARD FOR GEOCHEMICAL SURVEYS OF STREAMS

C.F. Gleeson* and W.M. Tupper**

The card, consisting of two sheets separated by a thin carbon, was used to record data for four samples or stations. One copy is retained in the field, the other sent to the computer centre where the coded data are punched on IBM computer cards. The card, parts of which are colour toned for easy reference, was designed for an 80 digit system.

Some data, such as stream width and depth, sediment composition, pH, temperature and metal content is recorded on the card in its exact form. A mnemonic system (letters) is used for rock names. The remainder of the data are coded, using numbers; thus, the flow rate of water was coded as 0 = not flowing, 1 = slow, 2 = moderate, and 3 = fast.

Coding of the field data and the field cards offers several advantages; all data and observations are reduced to a "common denominator", no observations are omitted or forgotten, and note-taking time is considerably reduced over conventional methods. Greater advantages accrue when the coded data can be mechanically processed.

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GEOCHEMICAL PROSPECTING FOR MOLYBDENUM-A CASE HISTORY IN THE MOUNT STE-CECILE AREA, FRONTENAC COUNTY, QUEBEC

R.W. Kelly* and R. Assad**

Two zones of vein type molybdenum mineralization are known in the area.

Soil, vegetation, and stream sediment samples were analysed for molybdenum. This element is distributed in the samples as two near log-normal populations of which the one with the highest modal value is considered as anomalous.

One of the mineralized zones was not revealed by the stream sediment survey. The other zone gave anomalous results and would have been found with a greater sampling interval than

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the 500 foot spacing used. The soil and vegetation survey revealed the molybdenite-bearing veins, but a close spacing sampling pattern is required.

Humus rich samples collected in swamp areas were enriched in molybdenum. Winter sampling gave results similar to those obtained during the course of the summer sampling. Samples collected during periods of heavy rain did not show marked differences in their molybdenum content.

THE ANALYSIS OF LARGE NUMBERS OF GEOCHEMICAL SAMPLES

J. Mogensen*

The proper way of bagging, drying, and sieving the samples is discussed, showing two slides to describe the mechanics involved in the absorption of metal ions, as well as the cementation caused by the drying procedure.

The "cold" and "hot" results on the same sample are discussed, using one slide to illustrate the two types of digestion and their effect on the sample material.

Special equipment used in handling large numbers of samples per day (1,000) is shown on five slides. Its use is described, and instructions are given on how to make and where to buy the equipment.

The importance of certain minimum standards in the manufacture of geochemical solutions for field or laboratory use is demonstrated, using three slides.

Finally, a short summary of one of the most important geochemical field tests, the THM (total heavy metals) test, and the different ways it can be handled safely in the field, is given.

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FOUR GEOCHEMICAL EXPLORATION CASE-HISTORIES FROM EASTERN CANADA

H.C. Morris*

Four examples of restricted geochemical exploration programs from Eastern Canada are described: a reconnaissance stream sediment survey from the Lake Superior North Shore, a preliminary soil sampling program near Manitouwadge, Ontario, and two detailed soil geochemistry surveys from New Brunswick.

(1) Preliminary stream sediment reconnaissance along the Prairie River, Ontario, located anomalous drainage from 81 Creek. Zinc and copper contents in excess of 1000 p.p.m. in stream silts were encountered as the anomaly was traced to a source in a mineralized graphitic argillite horizon with low zinc and copper values. It is concluded from this and other local examples that stream geochemistry is a useful and valid technique in this portion of the pre-Cambrian shield.

(2) A preliminary soil survey was carried out on the Lun-Echo Property near Manitouwadge, Ontario, in 1962. Analysis of the Cx-Total Heavy Metal content of soils from the "C" horizon gave several anomalies in excess of 300 p.p.m. THM over a background of 10-50 p.p.m. The strongest anomaly coincided with a known ore zone and three others were correlated with minor mineralization. One rather vague anomalous area could not be explained.

The close spatial ties between THM anomalies and known and located mineralization suggest that geochemical soil sampling methods can be effectively used in glaciated areas of this type.

(3) Attention was drawn to the Tribag property in New Brunswick by an anomalous stream sediment. An ensuing Cx-THM survey outlined areas of anomalous metal in soils, but lacked enough precision to control drilling. A more detailed survey of total lead content in soil gave anomalies which were satisfactorily assigned to drilled lead-zinc mineralization, or to drainage controlled by cross-cutting jointing.

It was concluded that lead values provided the closest guide to bedrock mineralization in this area, although complications arose from surface run-off features.

(4) Soil geochemical surveys for Cx-THM, and total zinc copper and lead on the Stratmat property in New Brunswick have outlined the general location of thin sedimentary horizons which host the mineralization. Copper and lead anomalies are much more diagnostic than zinc or THM, but do not always separate ore zones from modest mineralization. Irregular swampy drainage along strike complicated the anomaly pattern.

*Cominco, Ltd., Box 2000, Kimberly, B.C.

Soil sampling provided a good guide to mineralization and was useful in appraising geophysical surveys in the Stratmat Area, although non-ore mineralization can also yield attractive anomalies.

The four surveys described represent technical successes in applied geochemistry. However, conclusions from them are only applicable to the general areas under consideration and wide extrapolation is unwise, as similar programs have been much less effective in other regions.

GEOCHEMICAL CONTROL OF COPPER DEPOSITION ON GRAND MANAN ISLAND, BAY OF FUNDY, NEW BRUNSWICK

G.E. Pajari and L.T. Trembath*

The west half of Grand Manan Island consists of a series of tholeiitic volcanics and related sills overlying flat red Triassic sandstones and siltstones. The maximum thickness of the igneous series is approximately 500 feet.

The sediments immediately underlying the volcanics contain a higher concentration of copper than the sediments lower in the section. A simple model of copper precipitation from groundwater moving from the volcanics into the sediments is proposed by the writers. The physicochemical conditions of this process are described and interpreted.

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GEOCHEMISTRY IN THE SELWAY-BITTERROOT WILDERNESS AREA, CENTRAL IDAHO

P.L. Siems*

A geological, geochemical, and geophysical survey of an area of 2,400 square miles within the Idaho batholith and surrounding metamorphic rocks was commenced in 1965. The primary objective of the 9-year program is to evaluate the mineral potential of the wilderness area.

Knowledge of geology and possible mineral deposits of the area is limited because of difficult accessibility. Deposits

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outside the wilderness, but still spatially related to the margins of the Idaho batholith, have collectively produced tungsten, cobalt, antimony, mercury, gold, and monazite.

Geochemical reconnaissance is based on stream sediment, soil, water, and rock sampling. Colorimetric analytical procedures for molybdenum, beryllium, cobalt, tungsten, and cold-extractable and total copper and zinc are planned.

Low background values of 0.5 ppm heavy metals by Bloom's citrate-extractable procedure, and less than 1 ppm cxCu by Canney and Hawkins' procedure, are indicated for active sediment collected from granite and schist terrains. Slightly higher background values of 1 ppm heavy metals and 2 ppm cxCu represent a quartzite, hornblendite, and metamorphosed calc-silicate rock terrane.

HEAVY MINERALS AS PROSPECTING GUIDES, GASPE, P.Q.

W.A. Sims*

During the summers of 1964 and 1965, the heavy minerals from Recent stream sediments were collected in the region of Gaspé Copper Mines, Gaspé, Quebec.

Chemical and mineralogical analyses of these samples may provide useful prospecting data for copper deposits associated with skarn.

This applied research project is being sponsored by the Ministère des Richesses Naturelles, of the Province of Quebec.

* Mount Allison University, Sackville, New Brunswick

DETECTION OF ANOMALOUS CONCENTRATIONS OF ORE METALS IN PRECAMBRIAN COUNTRY ROCK

J.R. Smith*

In numerous areas in which Precambrian country-rock in Saskatchewan has been sampled on a reconnaissance basis (4 to 20 specimens per square mile), concentrations of Ni, Cu, and Zn exceeding 200 parts per million are rare, ranging from less than one out of one hundred specimens to about one out of fifteen specimens in different areas. Although contouring of the metal concentrations in some cases reveals trends on which the high

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concentrations lie, their significance is not immediately apparent. The purpose of this paper is to illustrate the nature and possible significance of some anomalously high ore-metal concentrations found by reconnaissance sampling of bedrock.

From an area underlain by granodioritic intrusive complexes surrounded by Amisk-type basic volcanic rocks where 16 specimens per square mile were taken, 100 out of some 1,600 specimens (or one out of 16) contain more than 200 ppm of copper. In the basic volcanic rocks themselves, the ratio is one out of nine, and it is highest in units which are closest to the granodioritic intrusions. The highest ratio of all (one out of five specimens containing more than 200 ppm of copper) is in a relatively small unit which is the host of three known copper orebodies. The ratio is the same among 370 specimens per square mile collected near the Coronation mine, and the specimens with more than 200 ppm of copper are concentrated along a belt on strike with the orebody.

The same reconnaissance sampling detected many high concentrations of nickel in meta-gabbro sills, and suggested a zonal distribution of nickel in some of them. Detailed sampling of one sill disclosed a marked increase in nickel concentrations toward the contact with ultrabasic rocks, and chemical analyses demonstrate that the sill itself is ultrabasic gabbro.

Reconnaissance sampling (20 specimens per square mile) of a second area near Hanson Lake, Saskatchewan, suggested clustering of high concentrations of copper near the contact of a granitic body and of nickel and zinc in metasomatized volcanic and sedimentary rocks. Detailed mapping and sampling (400 specimens per square mile) disclosed many well-defined anomalies in the distributions of all three metals, the most marked of which surrounds the only known showing of copper-zinc sulphides in the area. Most of the few scattered high concentrations of nickel, copper, and zinc found by the reconnaissance sampling are neighboured by many specimens containing as much as several tenths of one per cent of the ore-metals. Preliminary mineralogical studies suggest that concentrations greater than 200 ppm of copper and zinc signify the presence of chalcopyrite and sphalerite in the specimens, but that much or all of the nickel may be in silicate minerals.

It is concluded that reconnaissance sampling of Precambrian country-rock for geochemical studies can reveal information of geologic and economic value, even though no well-defined "anomalies" are obvious. Detailed sampling of bedrock discloses many well-defined anomalies, some of which delineate zones of disseminated ore-sulphides which normally escape detection by detailed geological mapping and by geophysical surveys.

GRANITE STUDIES RELATED TO ORE FORMATION IN THE EASTERN TOWNSHIPS, QUEBEC

R. Van Ingen*

Three Devonian granite masses were mapped and samples collected by stratified random sampling methods.

No ore deposits are associated with the mesozonal Winslow granodiorite mass, outer portions of which are basified.

Molybdenite-quartz stockworks, occurring in hornfelsic siltstones of Silurian age, are spatially related to biotite leuco-quartz monzonite at both ends of the epizonal St. Cécile quartz-monzonite-granodiorite stock.

Stratabound Cu-Zn sulphide deposits, occurring in sheared Ordovician volcanics, are spatially related to muscovite-biotite leuco-quartz monzonite which crops out in a crescent shaped area that makes up the western part of the epizonal Weedon granodiorite.

Both the epizonal masses are characterized by bimodal distributions of SiO_2 values and significant differences in mineralogical compositions, probably related to differences in the composition of crustal rocks that were fused.

The molybdenum contents of all three granite masses is probably normal. For example, 55 samples of granite and 6 of dykes from St. Cécile contained from 1 to 3 ppm Mo, with a mean of 1.7 ppm Mo. Mo is inversely proportional to SiO_2.

The base metal contents of the granites are somewhat lower than comparable data from Sandell and Goldich, 1943.

* Kennco Explorations, (Canada) Limited, 25 King Street West, Room 1230, Toronto 1, Ontario.

SiO_2

	Mean	Median	Range	Std. Er. Mean	No. Specimens
Winslow	64.3	65.0	51.3-74.2	1.8	14
Weedon	71.9	73.8	66.7-75.0	0.8	17
St. Cécile	72.0	71.0	68.2-76.3		53
			Cu ppm		
Winslow	6.6	6	2-26	0.8	33
Weedon	6.4	3	1-28	1.0	41
St. Cécile	7.4	5	2-45		53
			Zn ppm		
Winslow	46.1	50	9-82	3.0	33
Weedon	38.5	33	9-63	2.8	41
St. Cécile	30.0	28	10-60		53
			Pb ppm		
Winslow	2.2	1	1- 8	0.3	33
Weedon	7.3	7	1-15	0.7	41
St. Cécile	8.7	6	2-25		53

The St. Cécile leuco-quartz monzonite phase has a mean Cu content of 5.9 ppm, excluding anomalous values of 170 and 190 ppm Cu, which is significantly higher than the 1.6 ppm Cu content of the leuco-quartz monzonite phase of the Weedon granite. However, anomalously high Cu and Zn values come from this phase where it has assimilated host rocks of the Weedon deposit which terminates at depth in granite.

If the ore deposits are cogenetic with the granite, as inferred from evidence that sulphides replace granite and contact metasomatic minerals, the deuteric alteration hypothesis postulated by Earl Ingerson may account for their origin. But both the Cu-Zn and Mo deposits are cut by dykes having compositions that can be correlated with those of the granite phases, and the Weedon deposit may be a "contact metamorphosed" deposit.

PRIMARY GEOCHEMICAL DISPERSION AND ITS APPLICATION TO EXPLORATION AND MINING PROGRAMS

J.L. Walker*

Primary geochemical dispersion involves the distribution of elements in igneous and metamorphic rocks at relatively high temperatures and pressures characteristic of deep-seated conditions. The resultant distribution patterns of elements permit an examination of the chemical variations in the rock which have resulted from primary dispersion processes. These patterns can be studied today in rocks below the zone of weathering and provide valuable additional data as to the geological history of the area. In particular, however, trace element distribution patterns can be an invaluable guide to mineral deposits.

In the U.S.S.R. primary dispersion studies have played an important role in exploration for blind orebodies of hydrothermal and/or metamorphic origin for some time. Research investigations have been undertaken in other parts of the world by both Universities and Mining Companies. Much of this research, however, has been confined to certain aspects of the overall concept. Nevertheless, these investigations have proved the applicability of "rock" geochemistry as an aid to geological mapping, and as an ancillary guide to mineral deposits. As a result of these investigations, primary dispersion studies are becoming an integral part of geological exploration and development programs.

Primary dispersion studies in certain forms have been fundamental to the study of geology. Initially, mineral assemblages and mineral distribution patterns were the only parameters used. As chemical analyses have advanced, the chemical composition of the major element constituents of rocks and minerals has become a common means of elucidating geological processes. In mineral exploration also, the chemical composition of major constituents is used in the assaying of rocks for their ore metal content.

By the examination of the trace element constituents of rocks and minerals, "rock" geochemistry has broadened the concept of primary dispersion in providing measurements of parameters which are submicroscopic. This has been possible with the development of geochemical analytical techniques, which have provided rapid and quantitative analyses of trace quantities of metals.

Four of the principal aspects of investigation in which primary dispersion studies have been undertaken are as follows:

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(a) delimiting geochemical provinces by comparing the abundance of trace elements in igneous rocks, and to a lesser extent in sedimentary rocks, in a particular area to their average concentration in the earth's crust as a whole;
(b) aiding geological mapping of folded strata by establishing marker horizons based on their characteristic trace element assemblages, ratios, and/or absolute values;
(c) discovering blind orebodies by detecting anomalous concentrations of metal in rocks overlying the deposit;
(d) determining hydrothermal and/or metamorphic patterns around orebodies by measuring the trace element content of rocks and minerals in order to establish chemical gradients in depth, along strike, and around the deposit, whereby prospect drilling and/or mine development can be directed towards the maximum concentration of ore metals.

Primary dispersion studies are proving to be a valuable ancillary guide to the discovery of ore deposits. The applicability of this approach to exploration in North America as well as in other parts of the world has already been proven. Just as in the surface environment, where geochemical techniques have provided additional and often primary data in the discovery of mineral deposits, so, in the prospect drilling and development stages of exploration, primary geochemical dispersion can provide invaluable and at times unique data concerning the nature of the mineralization and the direction in which to go in search of ore.

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