

GEOCHEMICAL DISPERSION IN MINERALIZED SOILS OF A PERMAFROST ENVIRONMENT

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ABSTRACT

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The Agricola Lake massive sulphide body occurs in metavolcanic rocks of Archean age in the northwestern Canadian Shield. The mineralization contains Zn, Cu, Pb, Ag and Au and, in addition, there are elevated contents of As and Hg. The area lies within the zone of continuous permafrost.

The distribution of elements in soils in the vicinity of the mineralization shows the influence of three independent dispersion processes — glacial, solifluction and hydromorphic — superimposed on the primary bedrock distribution. Oxidation of sulphides has been active in the past and continues to this day. In the absence of large amounts of carbonate minerals, this has produced an acidic weathering environment.

The most mobile of the elements studied — Zn — has been largely removed from the mineralized soils and dispersed a considerable distance down drainage. Au, Hg, Pb and Ag are relatively immobile and are retained in the soils overlying mineralization or in nearby, glacially dispersed detritus. Fe, Cu and As are of intermediate mobility and are deposited in the proximal portion of the drainage system. The estimated order of mobility is: Zn > Cu > Fe > As > Ag > Pb > Hg > Au. Glacial action dispersed oxidized detritus, already depleted in mobile elements. Material precipitated along the proximal portion of the drainage system shows an association of As and Cu with iron oxides and Ag and Hg with manganese oxides. In addition to the elements discussed above, Mg in soils indicates the alteration zone underlying the massive sulphide and Ca outlines the soils subject to acidic leaching.

INTRODUCTION

In 1972 a reconnaissance lake sediment survey was carried out over a 93,000 km² region of the northwest Canadian Shield. The survey data were published early in 1973 and showed a number of interesting anomalies (e.g. Allan et al., 1973; Allan and Cameron, 1973). At that time lake sediment surveys were in an early stage of development. In particular, there was little knowledge on which to judge the possible significance of anomalies and no experience of follow-up or classification. Therefore, a follow-up survey was

carried out in 1973 in that part of the reconnaissance area that lies in the eastern part of the Slave Province (Cameron and Durham, 1974a, b). This region contains a number of distinct anomalies for base metals and uranium. As the published geological maps showed the terrane to be a metasedimentary belt enclosed within granitic rocks, there was a possibility that the anomalies were spurious. This is because most base metal mineralization in the Canadian Shield is associated with volcanic rocks.

The follow-up studies located metavolcanic rocks along the margin of the metasedimentary belt. Most of the base metal anomalies are related to mineralization in these rocks. One anomaly was thought to be of particular interest, having possibly been derived from massive sulphide mineralization (Anomaly "Y", Cameron and Durham, 1974a, b). The lake sediments were notably anomalous in mobile base metals (i.e. Zn, Cu, Ni, Co) and As. A target was outlined 4 km up-drainage from the most anomalous lake sediments by the distribution of immobile metals in soils (e.g. Pb, Ag, Au), by favourable geology, and by chemical evidence of hydrothermal alteration in bedrock samples.

Subsequent to the publication of these results in preliminary form (Cameron and Durham, 1973), the ground was staked by the YAVA syndicate. Drilling in 1974 confirmed the presence of a Zn-Cu-Pb-Ag-Au-bearing massive sulphide body. Drilling and exploration was continued in 1975 and 1976, but no grade and tonnage values for the body have been published, beyond preliminary data from early drilling (Northern Miner, August 15, 1974).

In 1974 an integrated geological-geochemical-geophysical study of the area was carried out by the Geological Survey, both before and during company drilling (Boyd et al., 1975; Cameron, 1975a; Cameron and Durham, 1975; Cameron and Lynch, 1975; Horton and Lynch, 1975; Kornik, 1975; Pearce and Lefebvre 1975; Scott, 1975; Slaney, 1975; Williams, 1975). This was done mainly to investigate the most suitable methods for follow-up and interpretation of base metal anomalies. However, the scope of the work was broadened to allow a fairly complete "case history" examination of exploration methods in the permafrost environment of the northern Shield. The present paper describes one aspect of this investigation: the distribution of elements in the soils.

The lake from which the most anomalous lake sediment samples were collected in 1972 has been named Agricola Lake and the study area is referred to as the Agricola Lake prospect. The prospect area is shown in Fig.1. It is located 480 km northeast of the town of Yellowknife.

GEOLOGY

Preliminary descriptions of the geology of the area are given in a number of the papers referenced above. Recent mapping of the area has been reported by Padgham et al. (1974) and by Frith and Hill (1975). The massive sulphide

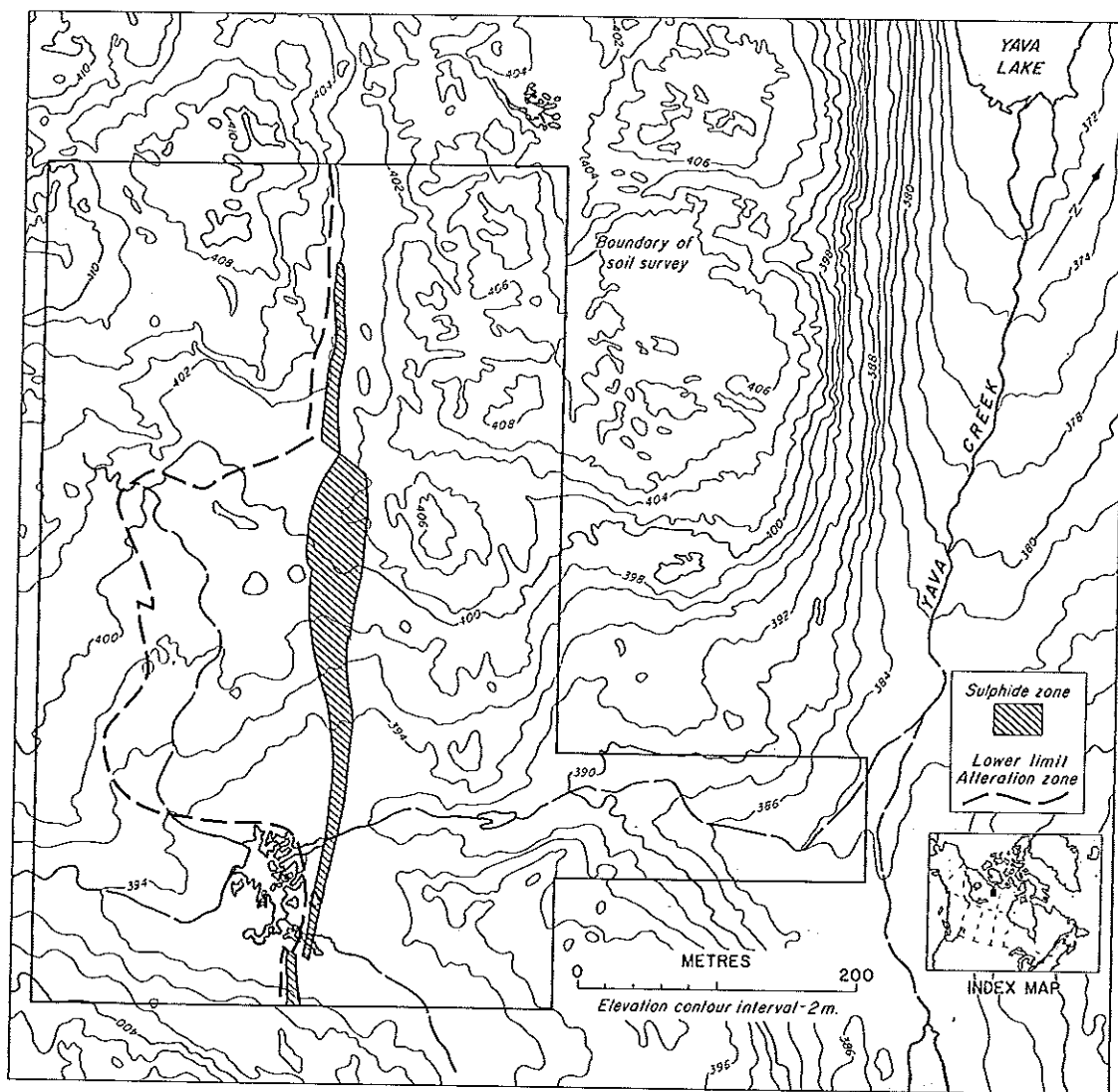


Fig.1. Location of soil survey area.

body occurs in the upper part of a steeply dipping sequence of mafic to felsic metavolcanic rocks. The geological map of the prospect (Fig.2) is based on detailed mapping by D. Lefebvre. It shows that the surface geology represents a cross-section through a typical massive sulphide. The main body of mineralization is stratigraphically controlled and is underlain by hydrothermally altered rocks of the feeder pipe. Of significance to the topics discussed in this paper is that carbonate-rich horizons are not intimately associated with the body; although they do occur within the volcanic sequence. Their absence has allowed the oxidation of sulphides to develop an acidic environment both at depth and at the surface. Oxidation is active at present, as evidenced by the high contents of base metals in groundwaters (Cameron and Lynch, 1975). Oxidation has removed all but trace amounts of base metal sulphides from surface outcrops and soils! Only pyrite is present in any quantity.

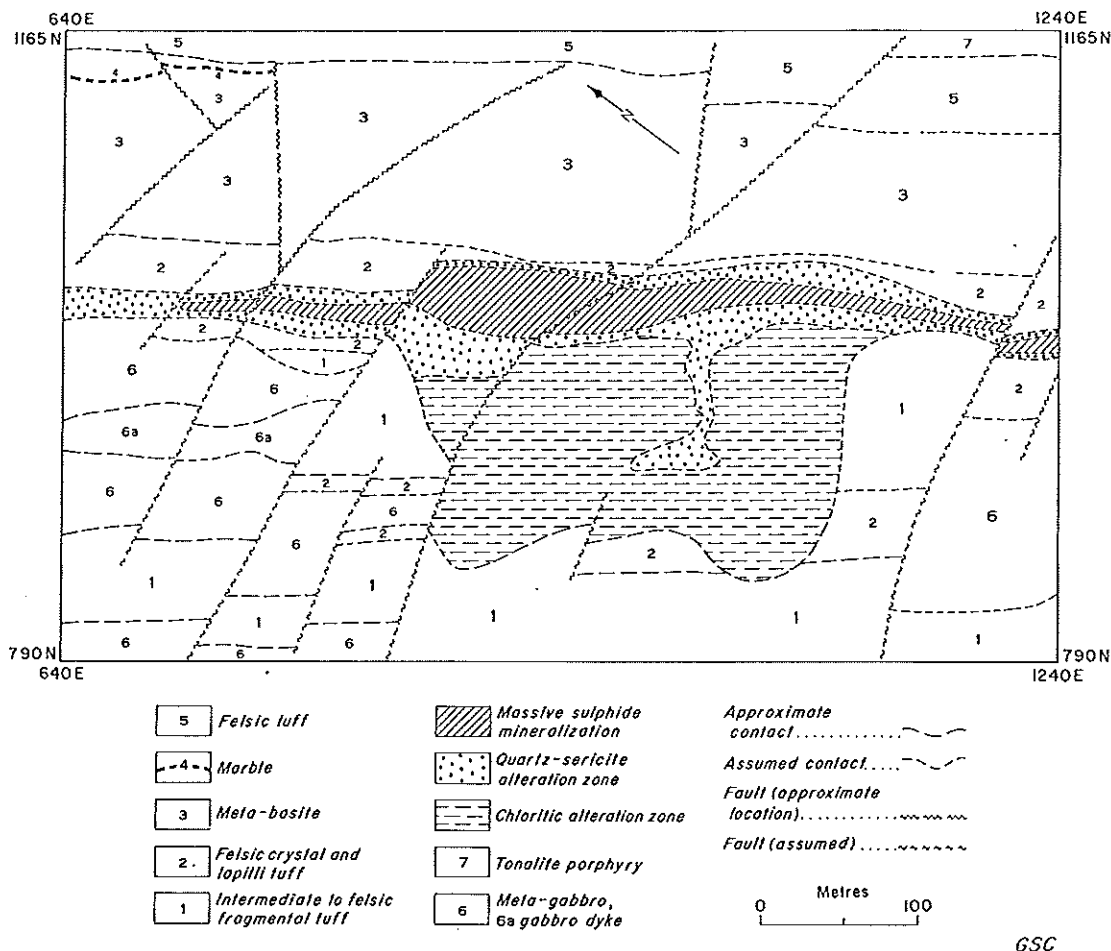


Fig.2. Geology of survey area.

The region has been glaciated, the direction of ice movement roughly parallel to the dominant north-northwest strike of the rocks. Glacial cover is thin to non-existent in the prospect area.

SURFACE FEATURES

The massive sulphide body and the associated alteration zone are less resistant than the enclosing volcanic rocks and occur in a topographic depression (Fig.1). This drains eastwards across strike and into a north-northwest-trending valley formed in soft slates that overlie the volcanics.

Soils are best developed within the central topographic depression and along drainage channels (Fig.3). Elsewhere, they are restricted to depressions in areas of outcrop or blockfield. Even in these areas, however, it was generally not difficult to obtain samples on a regular grid pattern.

Soils of the area are notably patterned. A variety of terms have been applied to the features of patterned ground: frost boils, mud boils, tundra craters, stone polygons, sorted circles are but a few. Some terms are synonyms,

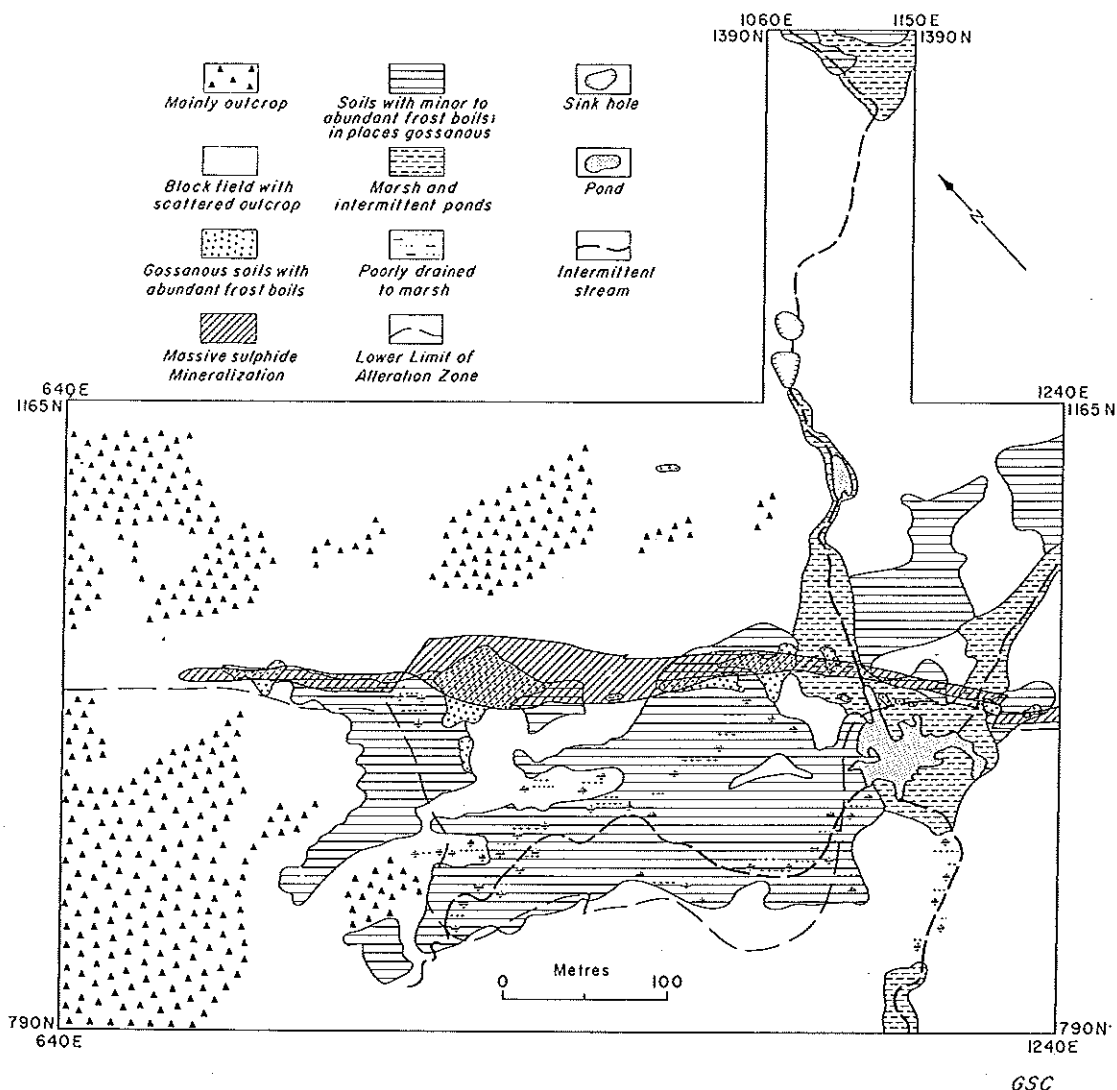


Fig.3. Surface features of survey area.

others describe variations in shape, texture or sorting. Theories of origin are as numerous as the terms (Washburn, 1956); currently diapiric origin (e.g. Butrym et al., 1964) is most generally accepted. The term "frost boil" will be used in this paper, since it does not denote any particular shape or texture.

The frost boils of the prospect are roughly circular or polygonal in shape. They are sorted and typically are comprised of rock fragments in a silty matrix at the centre and sorted rock fragments at the margin. The centre of the boils are free of vegetation and are often a less oxidized, grey colour than the buff to reddish margins. In size they range from 25 cm to 1 m or more in diameter. The largest occur over the most mineralized zones. This may be related to a possible thickening of the active (summer-thawed) layer over these zones, caused by the exothermic heat of sulphide oxidation. The soils vary from dark grey to red in colour. Those overlying the main sulphide body

are buff to red and are very sparsely vegetated. Frost churning has prevented the normal development of soil profiles.

Soils of the central depression are wet throughout the summer, the water being confined by the underlying permafrost. On slopes, solifluction is active. Thawed channels, or "taliks" are present in the permafrost since mineralized water discharge from the sulphide body, and the main stream draining the area disappears in a sink hole (Fig.3), emerging downslope in the north-northwest-trending valley.

pH OF SOILS AND WATERS

The pH of soils, pond and stream waters was measured in situ at a large number of locations within the study area. Soils were generally moist enough for direct determination of pH. For a few, better-drained locations, a slurry was made in the soil pit with distilled water.

Soils and waters associated with the main sulphide zone have the greatest acidity. Soils in the vicinity of 1000N, 910E had a pH of 2.4 and along this zone soil pH of 3–4 were most common. A highly mineralized spring water at 993N, 1035E had a pH of 3.4.

Over much of the ground underlain by the alteration zone, the pH of soils and of pond waters were most commonly in the range 4–5. There was excellent correlation between adjacent soil and pond measurements. Away from the main sulphide and alteration zones, soils were generally better drained with pH values in the range 5–6.

The highly mineralized and acidic waters coming from the sulphide zone mix with waters of pH approximately 4.6 in the main stream to produce waters of intermediate pH. For instance, waters in the pond at 1120N, 1135E (Fig.3), produced by mixing of these two sources, had a pH of 4.0.

SAMPLING AND ANALYSIS

Samples were collected on a 30 m (east) by 15 m (north) grid (Fig. 4). The main portion of the grid was extended from 1165N to 1390N to cover the main drainage channel. While this is intermittent, the stream running underground for much of the year, drainage is probably along the surface during spring run-off.

Where possible, the finer-grained, central portions of frost boils were sampled. Samples were taken from a depth of 15–20 cm.

After drying, the samples were sieved and the minus 80-mesh portion analysed by atomic absorption spectrometry, in a field laboratory, for Zn, Cu, Pb and Ag (Horton and Lynch, 1975). Extraction was by a mixture of 4M HNO₃ and 1M HCl at 90°C for 2 hours.

Subsequently, approximately one-half of the samples (on a 30 m × 30 m grid) were analysed in Ottawa for a variety of elements. Mn, Fe, Ni, Co were analysed by atomic absorption after total sample dissolution in a mixture of

HF, HNO₃, and HClO₄. Ca and Mg were measured on the same solution by a direct-reading spectrometer equipped with a rotating disc electrode. Hg was determined by cold vapour atomic absorption spectrometry, following extraction with a hot mixture of 3M HNO₃ and 0.1M HCl. The measurement of As was by flameless atomic absorption (Aslin, 1976) after aqua regia attack. Au was analysed by atomic absorption, after preconcentration by fire assay.

DISTRIBUTION OF ELEMENTS IN SOILS

For the 305 possible sites on the 30 m X 30 m grid, 284 samples have been analysed for Au, and 302 for all other elements. Statistical data for these samples are given in Table I. This table includes data for 1349 nearshore lake sediments from the eastern part of the Slave Province (Cameron and Durham, 1974b). These data are the best available estimate of geochemical abundances in surface materials of the region. The contrast between thresholds in the soils and the lake sediments decreases in the order: Pb > Ag > Hg > As > Cu > Zn > Mn > Fe > Mg > Ca > Ni (Table I, column 8). If comparative data were available for Au, this metal too would undoubtedly show as being highly anomalous in the soils. The above order is determined by two independent factors: the degree of enrichment in the primary mineralization and host rocks and the degree to which the elements have been removed in the drainage waters.

Factor analysis was carried out to identify interelement relationships. The Varimax matrix (Table II) was derived from the 284 samples for which data for all 12 elements are available and was computed by Program Geofact (Cameron, 1967). The element associations shown by the different factors will be discussed in turn.

Least mobile, sulphide-associated metals

The strongest loadings on Factor 1 are for Au, Ag, Pb and Hg, with weaker positive loadings for Cu, As and Fe. The distribution of metals most strongly associated with this factor is illustrated in Fig.4 (Pb), Fig.5 (Ag) and Fig.6 (Au). The distribution of these metals in the soils was determined by four principal processes. The first of these was primary dispersion which produced the high metal values that occur along the stratigraphic horizon of the massive sulphide body. Subsequently, glacial action has moved these metals in a direction slightly north of west, that is towards the lower left corner of Figs. 4-6. That this is not due to more recent solifluction movement is shown by the material having being moved upslope from the central topographic depression (Fig.1). A study of the composition of bedrock in the area (to be published) shows that in many places, glacially transported, metal-rich soil overlies barren bedrock. Because of the direction of glacial movement, the contribution of the hydrothermal alteration zone to the base metal content of the soils is obscured.

TABLE I

Statistical data for soils from the Agricola Lake prospect and for lake sediments from the eastern part of the Slave Province

| Element | Soils | | Lake sediments | | | | Ratio: column 5/column 7 | | |
|----------|---------------------------|--------------------------|---|--------------|-----------------------------------|--------------------------|-----------------------------|-----------------------------------|-------|
| | arithmetic mean (1) | geometric mean (2) | log standard deviation (s_m) (3) | range (4) | geometric mean + $2s_m$ (5) | geometric mean (6) | | geometric mean + $2s_m$ (7) | (8) |
| Mg (%) | 1.43 | 1.28 | 0.20 | 0.3- | 5.1 | 3.29 | 0.66 | 1.42 | 2.3 |
| Ca (%) | 0.81 | 0.69 | 0.28 | 0.1- | 2.1 | 2.53 | 1.22 | 1.84 | 1.4 |
| Mn (ppm) | 430 | 385 | 0.21 | 42 - | 1597.0 | 1027.0 | 89.0 | 266.0 | 3.9 |
| Fe (%) | 5.40 | 4.83 | 0.19 | 0.6- | 33.8 | 11.7 | 2.18 | 3.93 | 3.0 |
| Ni (ppm) | 28.5 | 22.9 | 0.31 | < 5 - | 310.0 | 97.0 | 23.3 | 78.0 | 1.2 |
| Cu (ppm) | 157.0 | 104.0 | 0.39 | 11 - | 1530.0 | 610.0 | 19.6 | 68.0 | 9.0 |
| Zn (ppm) | 159.0 | 121.0 | 0.30 | 15 - | 1520.0 | 486.0 | 31.8 | 106.0 | 4.6 |
| As (ppm) | 103.0 | 47.0 | 0.40 | 5 - | 6246.0 | 299.0 | 2.3 | 20.2 | 14.8 |
| Ag (ppm) | 6.5 | 2.6 | 0.60 | < 0.4- | 71.0 | 26.0 | 0.39 | 0.74 | 35.0 |
| Hg (ppb) | 206.0 | 39.0 | 0.70 | < 5 - | 9705.0 | 949.0 | 11.2 | 35.9 | 26.0 |
| Pb (ppm) | 511.0 | 108.0 | 0.77 | 3.0-13130.0 | 3770.0 | 3770.0 | 12.9 | 19.9 | 189.0 |
| Au (ppb) | 67.0 | 15.3 | 0.69 | 10 - | 2230.0 | 358.0 | - | - | - |

TABLE II

Varimax factor matrix of logarithmically transformed soil data. Matrix accounts for 90.2% of variance of 284 samples. Only loadings of 0.25 or greater shown

| | Factor | | | | | | |
|----------------|--------|------|-------|------|------|-------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Sum of squares | 3.6 | 1.2 | 1.4 | 1.2 | 1.2 | 0.9 | 1.3 |
| Mg | | 0.96 | | | | | |
| Ca | -0.25 | | -0.77 | | 0.40 | | |
| Mn | | 0.47 | -0.30 | 0.46 | | -0.31 | 0.50 |
| Fe | 0.35 | | | 0.83 | | 0.27 | |
| Ni | | 0.26 | | | | | 0.92 |
| Cu | 0.48 | | 0.63 | 0.29 | 0.36 | | |
| Zn | | | | | 0.92 | | |
| As | 0.45 | | | 0.29 | | 0.77 | |
| Ag | 0.85 | | 0.30 | 0.25 | | | |
| Hg | 0.83 | | | | | 0.33 | |
| Pb | 0.83 | | 0.37 | | | | |
| Au | 0.90 | | | | | | |

The two latest dispersion processes are solifluction and the migration of elements down the drainage channels. Because of the relatively low relief of the study area, the former process causes local movements only, generally no more than 10 m. Thus, while the effects of these movements can be discerned visually, they are too small to show on the geochemical soil maps. The more highly mineralized, gossanous soils appear to be more subject to solifluction.

Dispersion along the drainage channels is best shown in samples from lines 1120N and 1390N and, as will be discussed later, is believed to be mainly the result of hydromorphic dispersion. The elements most strongly associated with Factor 1 (Au, Ag, Pb and Hg) show very high values in soils directly over the massive sulphide body but are only weakly dispersed along the drainage channel. The true maximum values for Ag are not reflected in Table I because the analytical method is inappropriate to such high concentrations. Re-analysis of selected samples using an aqua regia attack gave a maximum value of 237 ppm Ag. A sample (742446) collected from a more detailed soil grid over the massive sulphide body at 885E, 1020N contains 15.2% Pb, 1000 ppm Ag, and 135 ppm Hg.

This factor is believed to relate to elements enriched in the sulphide mineralization that are relatively immobile in the surface environment. They are retained, to a greater or lesser extent, in the soils overlying mineralization or in similar, glacially transported detritus.

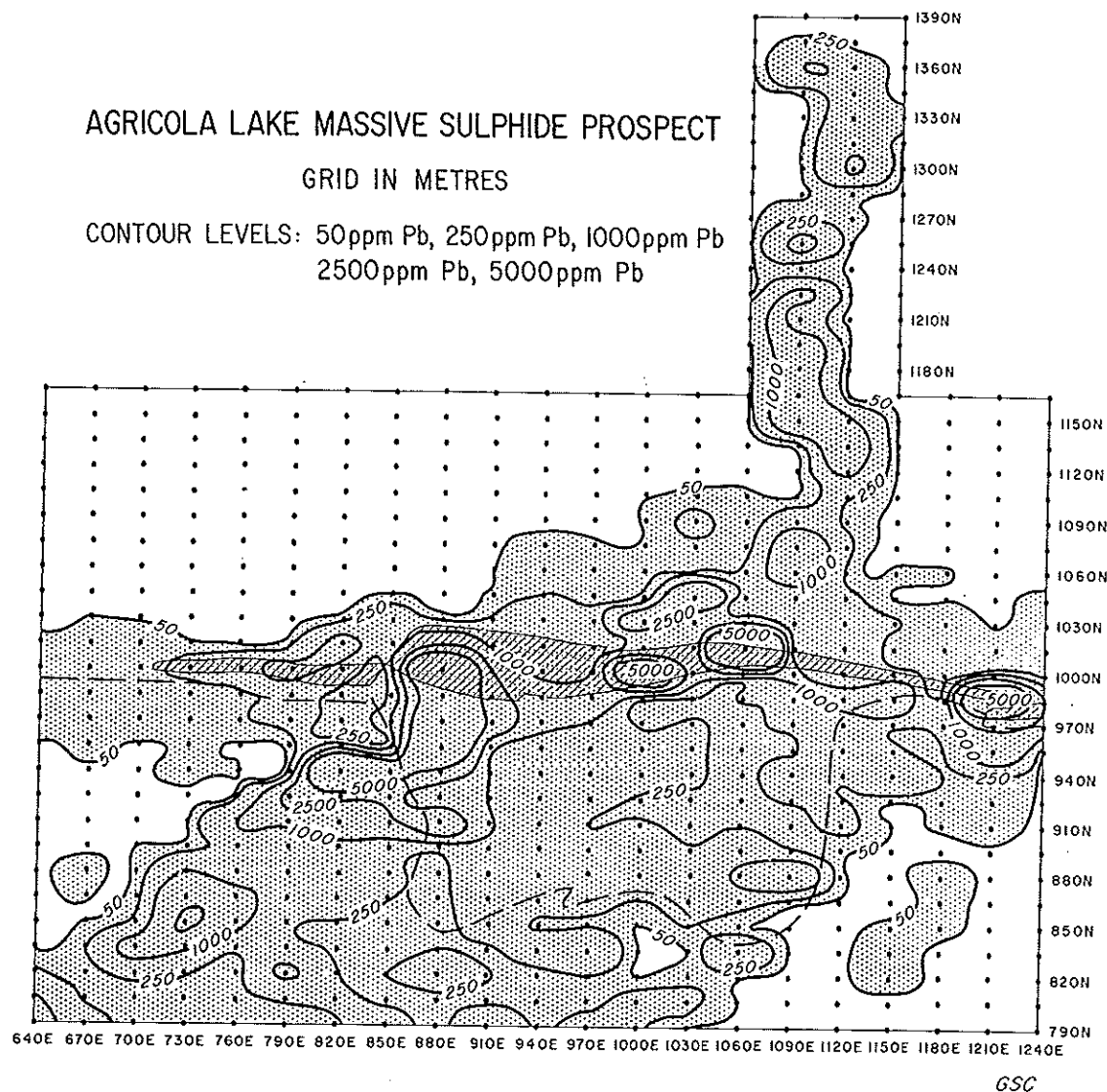


Fig.4. Distribution of lead in soils.

Elements of the alteration zone

Factor 2 (Table II) contains virtually the entire variance of Mg and lesser proportions of the variance of Mn and Ni. The map of Mg distribution (Fig.7) shows maximum values (to 5.1% Mg) in the soils overlying the alteration zone, with glacial smearing of high-Mg material to the west. Metasomatic enrichment of Mg in the feeder pipe below massive sulphide deposits is common and has been demonstrated for the rocks underlying this body (e.g. Cameron and Durham, 1974b). Low values for Mg in soils near the massive sulphide body (Fig.7) probably reflect underlying silicified volcanic rocks.

AGRICOLA LAKE MASSIVE SULPHIDE PROSPECT

GRID IN METRES

CONTOUR LEVELS: 2.5ppm Ag, 10ppm Ag, 25ppm Ag,
50ppm Ag

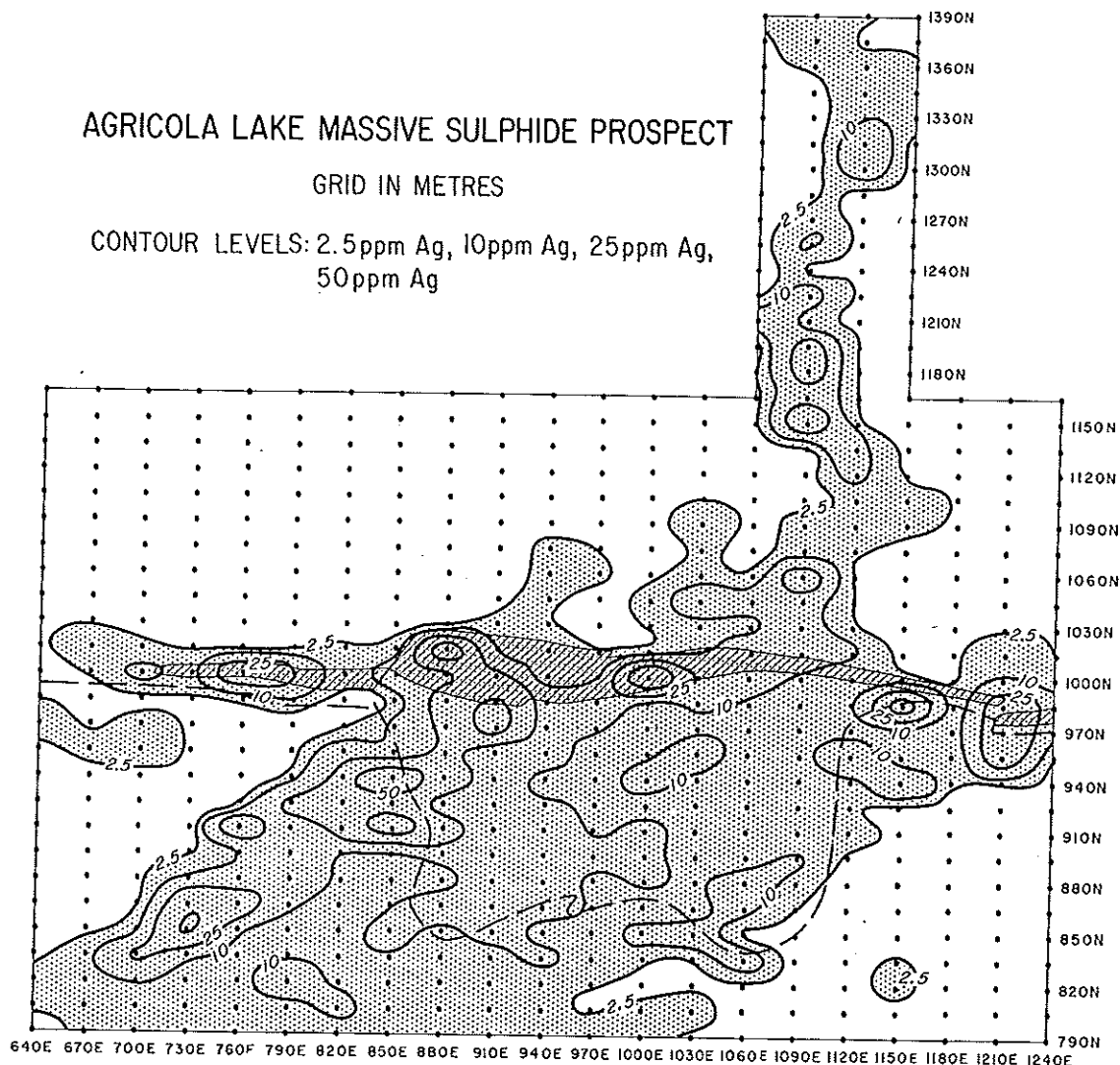


Fig.5. Distribution of silver in soils.

GSC

Elements of intermediate mobility

Factor 3 (Table II) is related to the transport of elements in solution and their subsequent precipitation. High scores (Cameron, 1967) for this factor are virtually confined to the area of stream, pond and marshy ground between 940E, 850N and 1090E, 1180N (Fig.3). The positive loadings for Cu, Ag and Pb are thought to represent portions of these elements which have been dissolved near the mineralized zones, then precipitated in an environment of higher pH, in the range 4.0–4.6, that is characteristic of this water-inundated area. Cu has the highest positive loading. The map of its distribution (Fig.8) shows higher concentrations along the drainage channel than in the soils directly over the mineralized body.

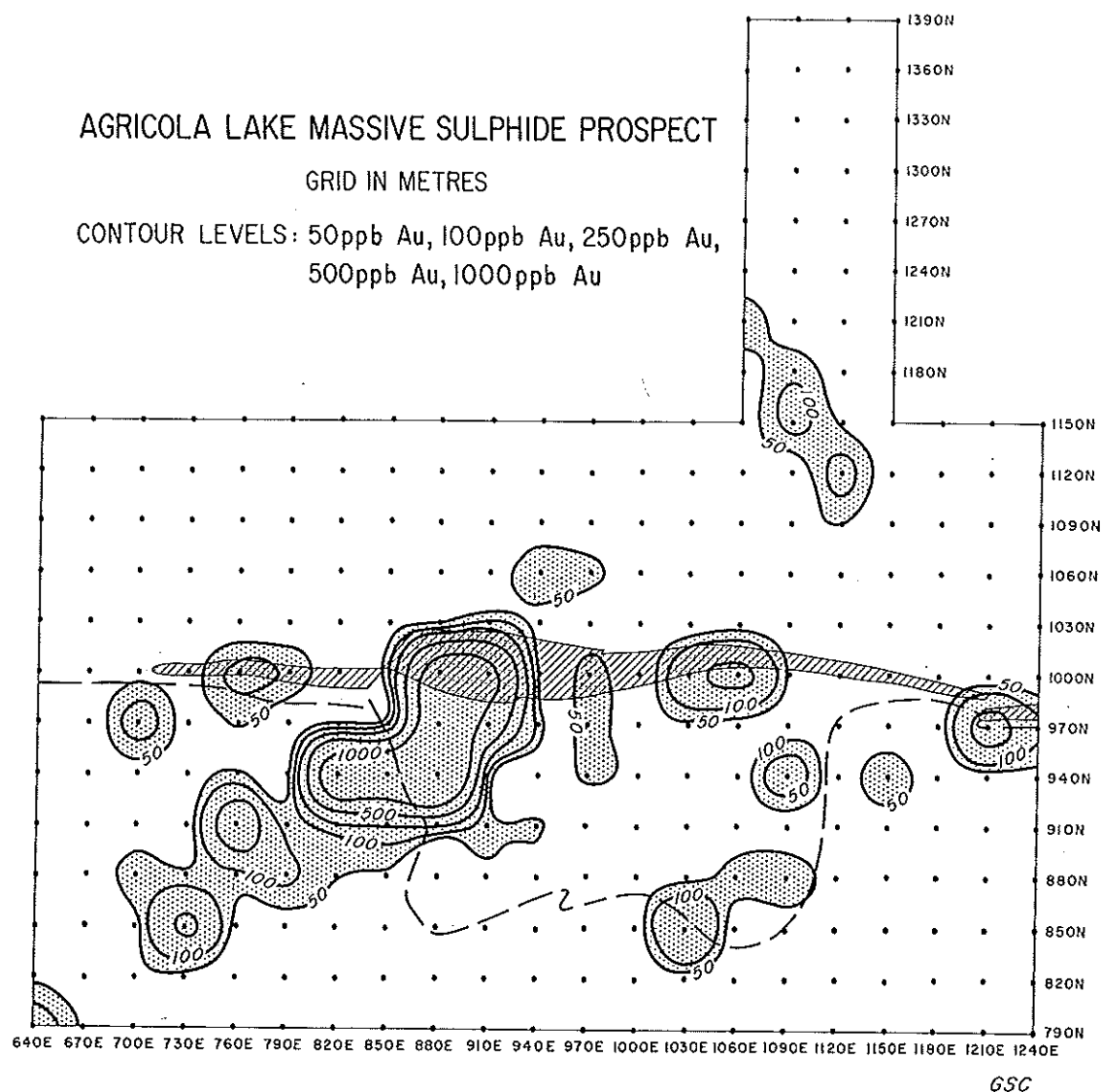


Fig.6. Distribution of gold in soils.

Like Cu, both Fe and As show significant concentrations along the drainage channel. Apart from this similarity, their distributions are not identical and thus the principal loadings for these three elements occur on three different factors (Table II). In the case of Fe (Fig.9), higher concentrations occur in the drainage channel than over the massive sulphide and vice versa for As.

Highly mobile elements

Cu is of intermediate mobility. While it has been largely removed from the low-pH soils directly overlying the mineralization, it has been reprecipitated, in part at least, in the drainage channel (Fig.8). The mobility of Zn is greater,

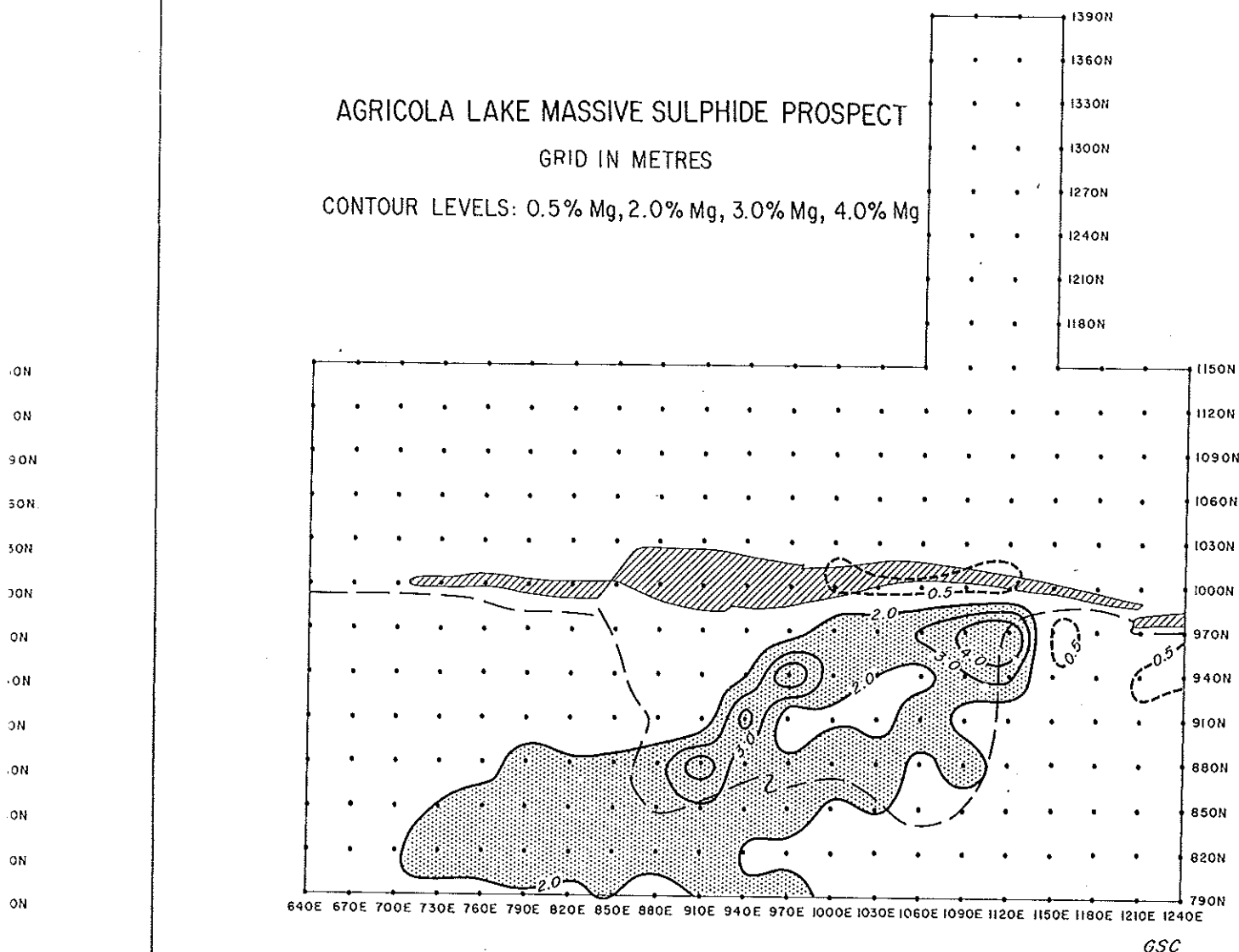


Fig. 7. Distribution of magnesium in soils.

for in addition to having been leached from the soils, no large quantity has been precipitated within the soil study area (Fig. 10). The loss of Zn is so complete that the central mineralized area shows as a "low" on the Zn map. This map is akin to a photograph, the centre of which has been washed out. The central "washed-out" area has pH in the range 2.0–4.5. The element has been retained in the surrounding, better drained and less mineralized soils with pH of 5 or greater. Features of interest in the Zn map include a prominent anomaly in the soils developed on the hanging wall volcanics that lie immediately above the thickest portion of the sulphide body. Also, in the lower left quadrants of Figs. 8 and 10, glacially derived trends similar to those for Pb, Ag, Au can be seen. However, the values for Cu and Zn in this well-drained area are relatively low. This suggests that the glacier moved oxidized, well-leached residue, rather than unweathered sulphides, for in the latter case

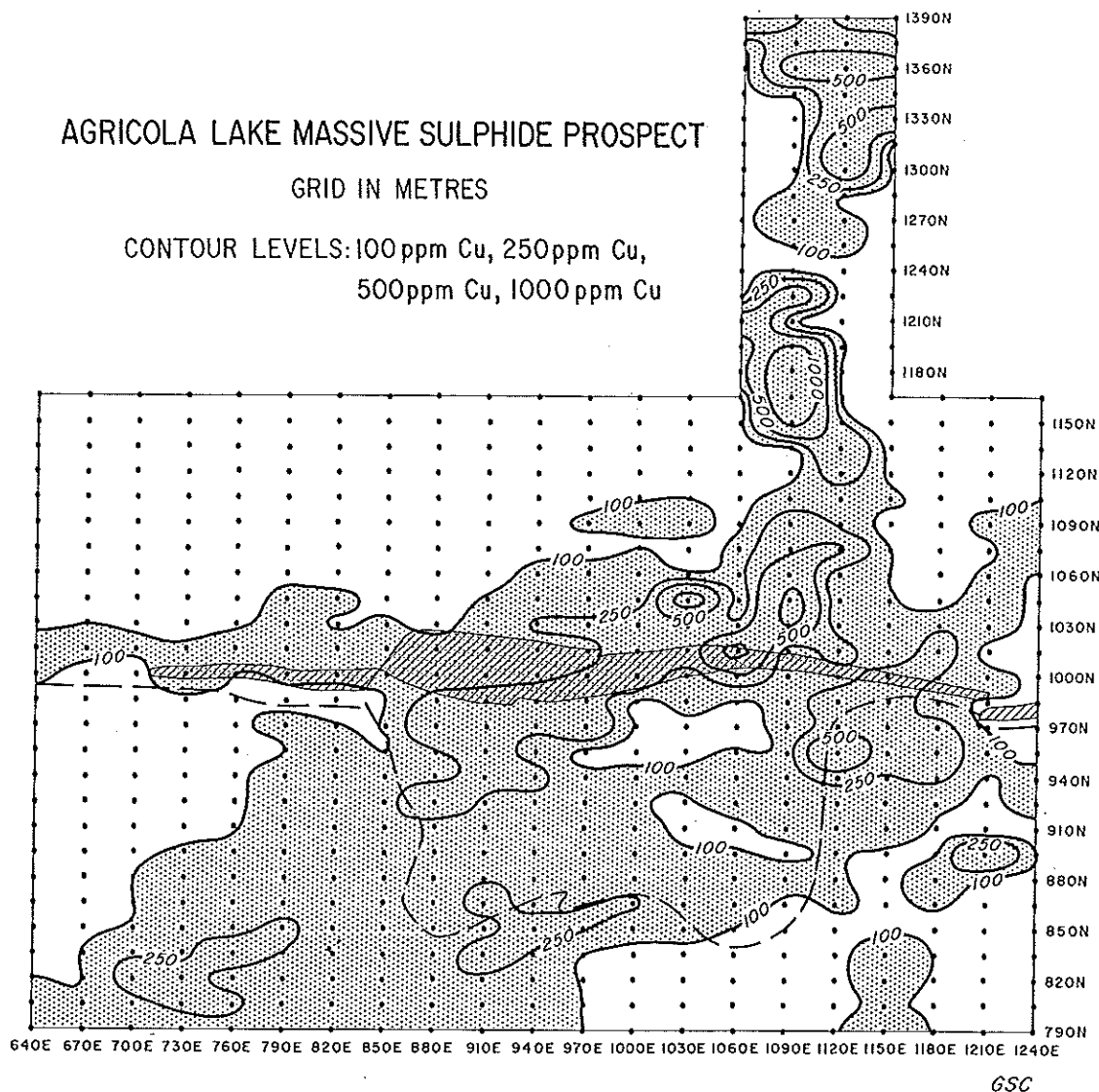


Fig.8. Distribution of copper in soils.

greater amounts of Zn and Cu would have been preserved.

Ca has a positive loading, along with Zn on Factor 5, and a *negative* loading, opposite to Cu, on Factor 3. These associations very well describe the removal of Ca from the soils on the central, mineralized area and also its removal from the drainage channel where much Cu and some Zn are precipitated. Ca may be considered to be the most mobile of the elements measured. In Fig. 11, the areas of *low* values for Ca are shaded to emphasise its migration from areas of low pH. It should be noted that, in part, the low levels of this element in the central area may reflect metasomatic leaching of Ca from the rocks of the alteration zone (Cameron and Durham, 1974b).

AGRICOLA LAKE MASSIVE SULPHIDE PROSPECT

GRID IN METRES

CONTOUR LEVELS: 5.0% Fe, 10.0% Fe, 15.0% Fe,
20.0% Fe

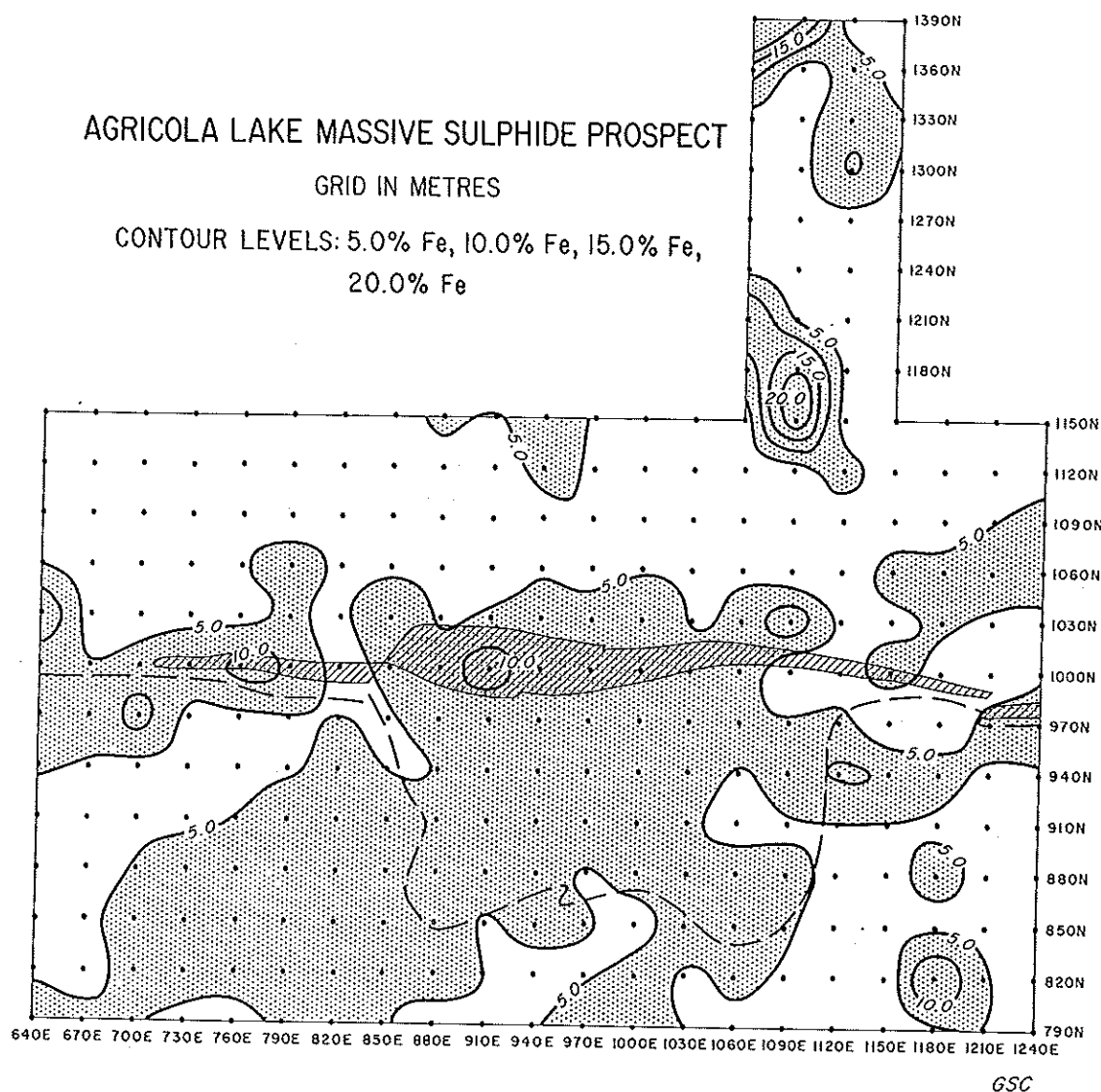


Fig.9. Distribution of iron in soils.

Manganese and nickel

The variance of Mn is distributed over a large number of factors (Table II). Its distribution (Fig.12) shows that it is enriched in the soils of the alteration zone and to the west. It is apparent that any Mn which passes into solution is not being reprecipitated in any quantity along the drainage channel.

Only background concentrations of Ni are found in the area. Its distribution (not shown) reflects variations in bedrock composition. The rock units below the sulphide-rich zone contain more Ni and are, therefore, probably more mafic than the units above.

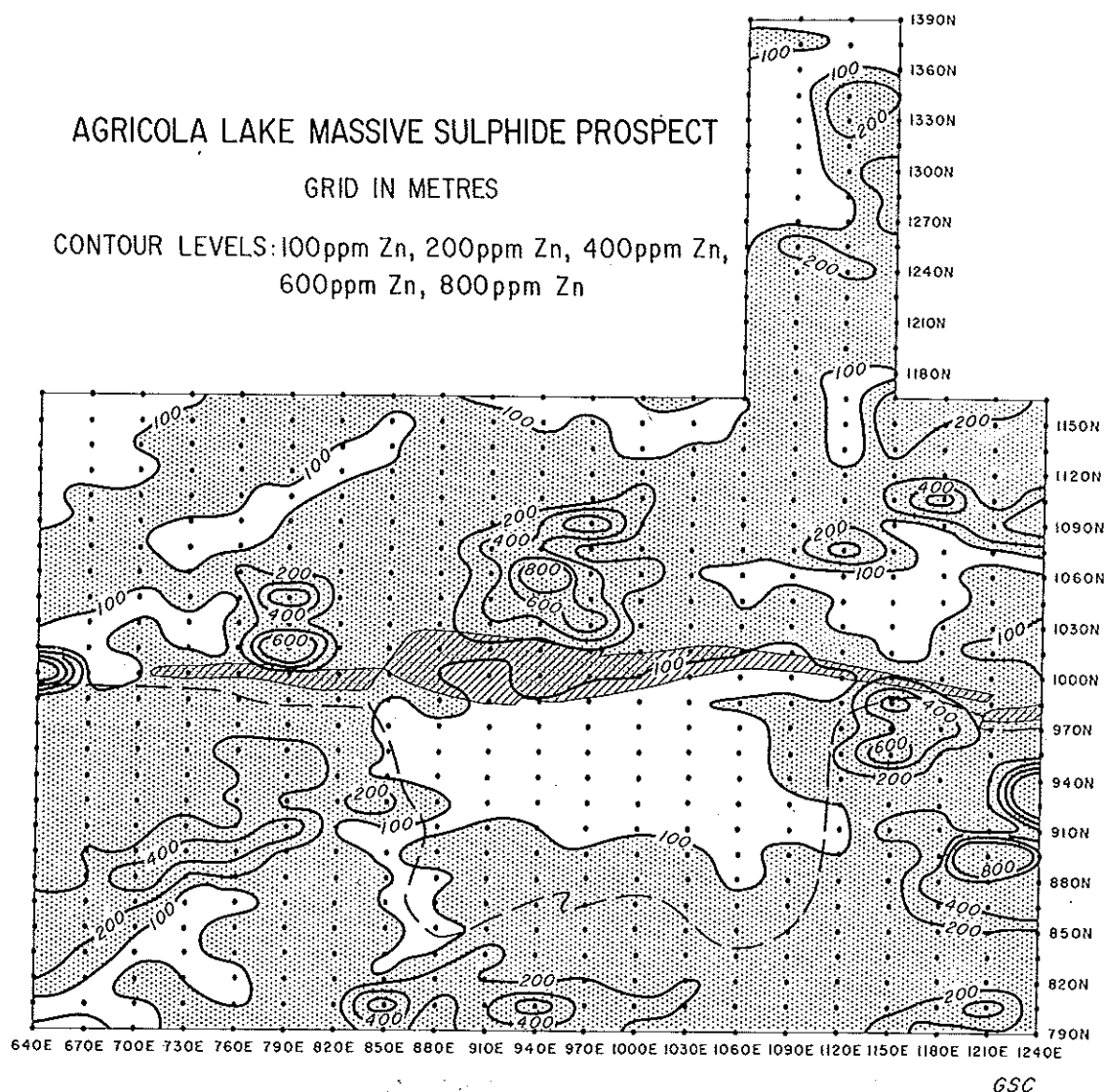


Fig.10. Distribution of zinc in soils.

RELATION OF ELEMENT DISTRIBUTION TO MECHANICAL AND MINERALOGICAL COMPOSITION

Detailed studies have been carried out on selected samples. Data for two of these are reported here. Sample 742466 (885E, 1020N) lies directly over the sulphide body. Sample 741199 (1090E, 1150N) is from a portion of the drainage channel where there is notable precipitation of Fe.

The samples were separated into various size fractions and these were finely ground. These were analysed using a hot HF-HNO₃-HClO₄ attack and again after a hot aqua regia attack. The method giving the highest values for any element is considered a "total" extraction. For Zn, Cu, As, Fe and Mn this was the HF method and for Pb and Ag, aqua regia (Figs. 13B and 14B). For Hg, the HNO₃-HCl procedure was used. The fractions were then re-

AGRICOLA LAKE MASSIVE SULPHIDE PROSPECT

GRID IN METRES

CONTOUR LEVELS: 0.5% Ca, 1.0% Ca

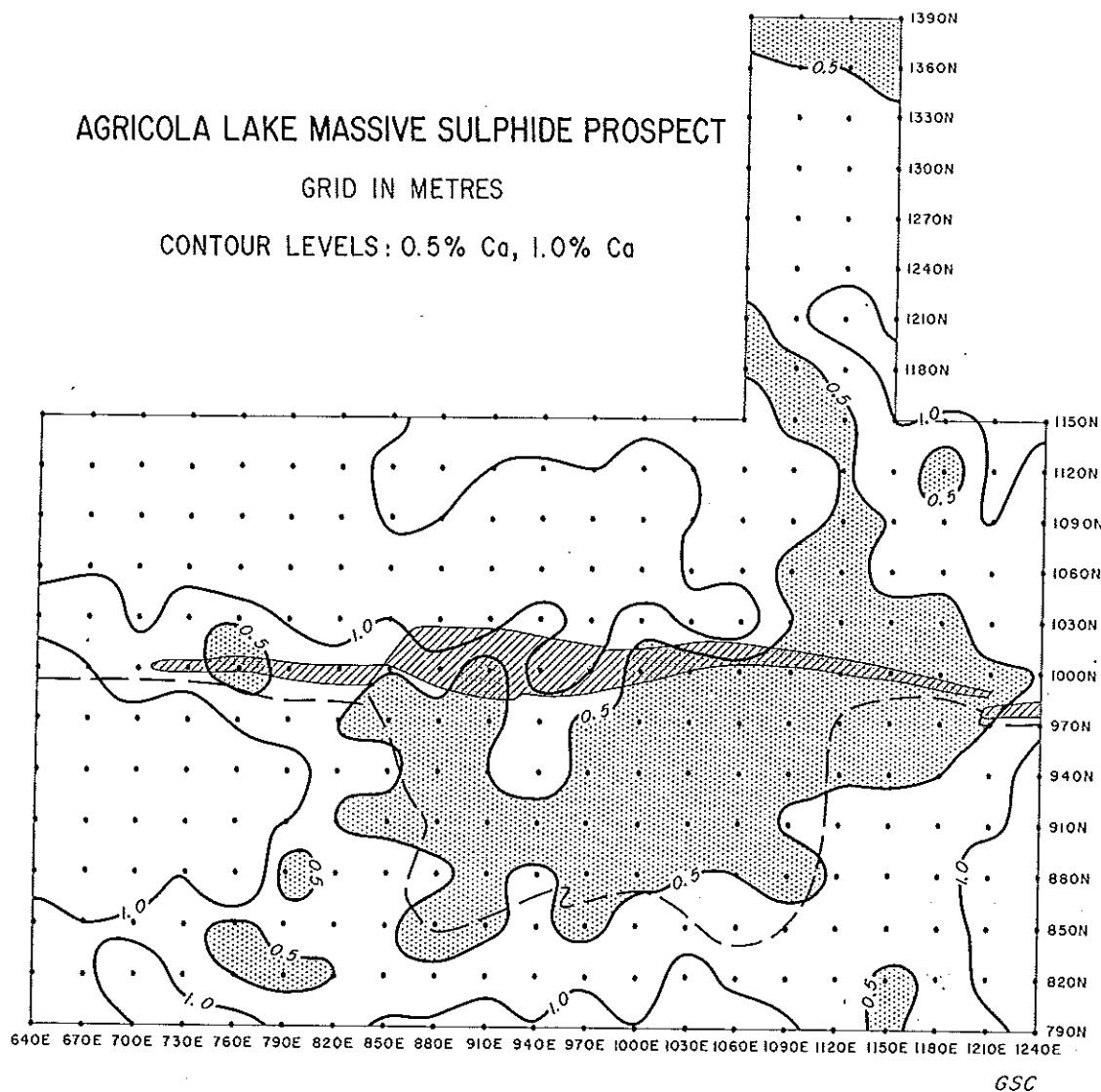


Fig.11. Distribution of calcium in soils.

analysed using *cold* 1M HCl and these data expressed as a ratio to the total extraction (Figs. 13A and 14A). Partial extractions were not made for Hg.

In addition, selected fractions were examined by microscope, X-ray diffraction and electron microprobe by G.J. Pringle and A.G. Plant.

Soil overlying mineralization

Sample 742466 is principally composed of rock fragments with compact brown crusts and extensive outer coatings of a very fine grained yellow-brown powder. Also present are goethite pseudomorphs after pyrite. The crusts are mixtures of anglesite and quartz while the outer coatings are intimate mixtures of quartz, jarosite and plumbojarosite. The relationship suggests the plumbojarosite is secondary to anglesite, being the final product of

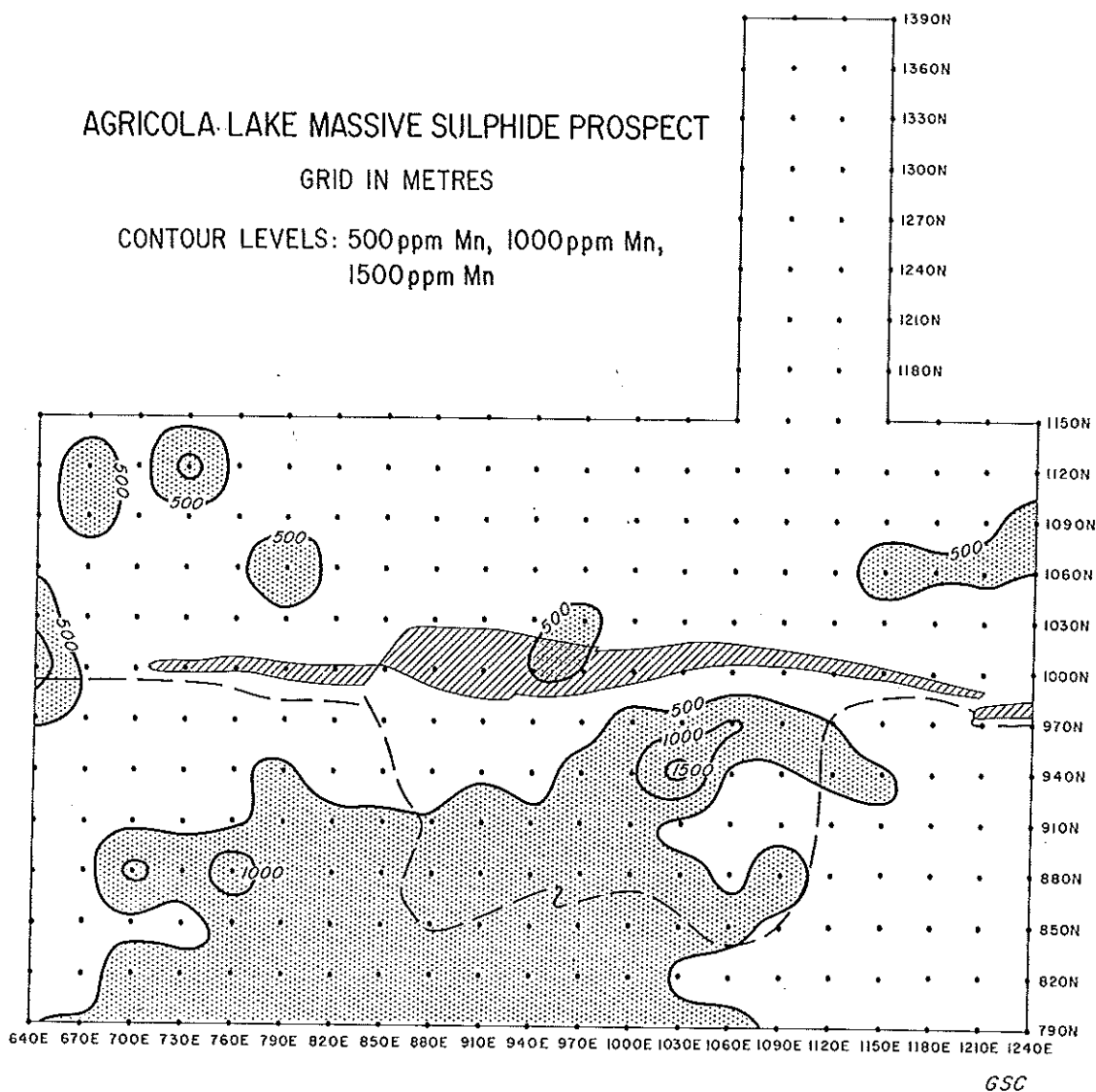


Fig.12. Distribution of manganese in soils.

the weathering of galena. Plumbojarosite has previously been identified in these soils (Cameron and Durham, 1974a). The higher Pb content of the finer soil fractions (Fig.13B) is consistent with the powdery nature of this mineral and also possibly that of anglesite. Note that Pb is readily extracted with cold, weak acid (Fig.13A). In addition to the major constituents, Pb, Fe and SO_4 , plumbojarosite may contain significant amounts of other elements, including Ag, Cu, As and Zn (Boyle, 1965).

While the elements decrease in concentration from the finest fraction, most elements show an increase in fractions coarser than 0.21 mm (Fig.13B). This is particularly noticeable for Ag that reaches 3020 ppm in the 0.62-mm fraction. Mineralogical examination of this fraction showed silver and lead sulphides as black, metallic inclusions in quartz grains. However, this fraction

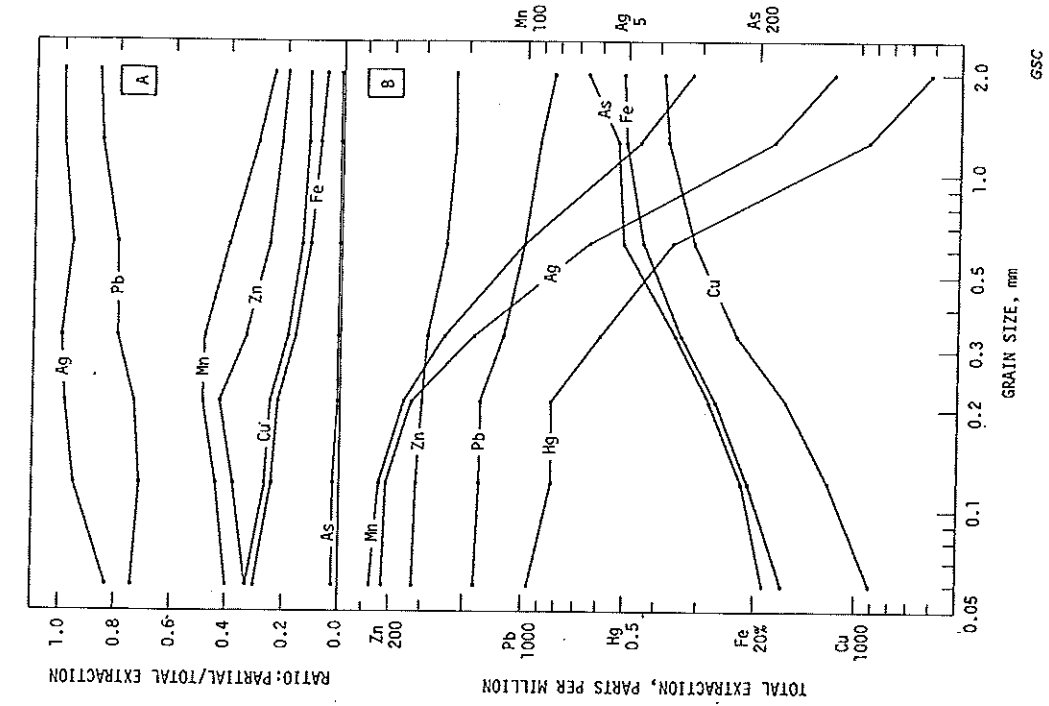


Fig.13. Distribution of elements in size fractions of mineralized soil.

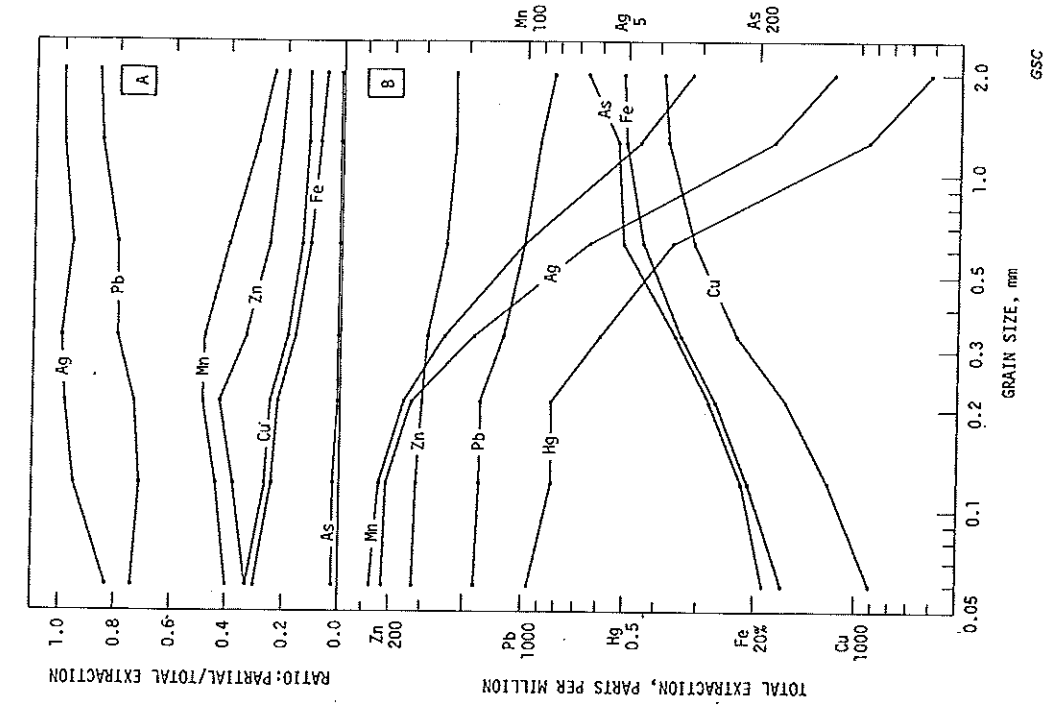


Fig.14. Distribution of elements in size fractions of sample from drainage channel.

is a relatively minor component of the total sample.

In summary, the distribution of chalcophile elements in the soil suggests their concentration in the fine-grained weathering products, but with residual concentrations of primary minerals, notably silver sulphide, in the coarser-grained particles.

Drainage channel sample

Sample 741199 from the intermittent stream channel should properly be considered a stream sediment, although it differs little in appearance from nearby soils. As shown in Fig. 14 the distribution of elements is quite different from the mineralized soil described above. There are three distinct groups of elements. The first group — Fe, As and Cu — show a marked increase in concentration with increasing grain size. The coarsest sizes contain ~ 50% Fe. In contrast, Mn, Ag and Hg show a marked decrease in content with increasing grain size, while elements of the third group — Pb and Zn — decrease only moderately.

The coarsest fractions of this sample consist almost entirely of rounded fragments of goethite. This mineral varies from light friable types to very dark orange, compact forms. All fragments have a thin tan crust. Microprobe analysis with an energy dispersive spectrometer showed the following elements in addition to Fe: variable concentrations of Si and Al; minor but consistent levels of Cu and S; and occasional traces of Ti, K, Ca, Na, As and Zn. In some grains the Cu content is as high as 1%. Mn was not detected in any fragments.

It is clear from these data and Fig. 14 that Cu and As in the sample occur principally as co-precipitates with iron oxide. Note the close similarity in the proportions of these three elements partially extracted by cold 1M HCl (Fig. 14A). It is possible that the goethite fragments grew by slow accretion in the metal-rich waters of the intermittent stream. No discrete minerals were found containing high concentrations of the other five elements shown in Fig. 14.

DISCUSSION

The data indicate that intensive oxidation has occurred in this permafrost environment. That it continues to this day is shown by the acidic nature of the soils and by the high metal and sulphate content of the waters of the prospect (Cameron and Lynch, 1975).

In terms of mobility, the elements directly associated with the mineralization can be subdivided into three broad groups. The least mobile are Au, Hg, Pb and Ag. They are largely retained in the soils close to mineralization or in similar, glacially transported detritus. The second group, Cu and Fe, tend to be removed from the vicinity of the mineralization, but are precipitated in quantity a short distance along the drainage channel. Arsenic is

intermediate in mobility between the two groups. The third group, to which Zn belongs, is of high mobility and in addition to being removed from the mineralized soils, is not precipitated in any quantity in the proximal portion of the drainage system. A general order of mobility may be obtained by comparing for all elements the ratio between the 90th percentile of soils near to the massive sulphide body (lines 910N to 1000N between 820E and 1210E) and the 90th percentile of samples along the drainage system (lines 1150N to 1390N). This gives the following order: $(\text{Zn}) > \text{Cu} > \text{Fe} > \text{As} > \text{Ag} > \text{Pb} > \text{Hg} > \text{Au}$.

These variations in mobility are governed by two factors: the solubility of the immediate products of weathering and the tendency for dissolved ions to be adsorbed on iron and manganese oxides or other materials. Thus the behaviour of Pb is largely controlled by the formation of the relatively insoluble sulphates, anglesite and plumbojarosite. The fate of Ag is less certain. It most probably exists in the mineralized soils as an impurity in these lead sulphates, or even as argentojarosite (Boyle, 1968). Boyle (1965) found >1000 ppm Ag in anglesite samples and $>1\%$ Ag in the only jarosite sample analysed from the Keno Hill area, Yukon.

Lakin et al. (1974) have described conditions in which Au may be dissolved. The condition most appropriate to this prospect is oxidation by chloride in an acidic weathering environment in the presence of MnO_2 . However, the very low chloride content of waters of the area, typically < 1 ppm Cl, militates against such solution of Au. The low chloride content is also not favourable to the migration of Hg as HgCl_2 . The form taken by this element, largely fixed in the soils overlying mineralization, is not known. Like Ag, it may be present in the lead sulphates, or as the basic sulphate, $\text{Hg}_2\text{SO}_4 \cdot \text{HgO} \cdot \text{H}_2\text{O}$ (James, 1962), or adsorbed on to manganese and iron oxides (Aydinyan and Ozerova, 1969). The relative immobility of Hg applied to soils for agricultural purposes is well known (e.g. Gracey and Stewart, 1973).

Turning to those elements that migrate to a greater extent, the composition of a mineralized, acidic spring discharging at 993N, 1035E should be noted (Table III). This and also, perhaps, similar waters concealed beneath adjacent blockfields, mix with waters of higher pH in the main drainage channel to produce waters of $\text{pH} \sim 4$. In the highly oxygenated stream environment, this increase in pH is sufficient to cause precipitation of minerals, most notably ferric oxides. Precipitation of iron proceeds in two main steps, first oxidation of Fe^{2+} to Fe^{3+} , then hydrolysis to hydrous ferric oxide. The first step determines the rate of precipitation (Stumm and Morgan, 1970). At low pH it is relatively slow and is independent of pH. Above this, the oxidation rate increases markedly with pH (100 times per pH unit). Pertinent to this study is that Cu^{2+} , even at the trace quantities present in these waters, has a strong catalytic effect on the oxidation of Fe^{2+} (Stumm and Lee, 1961). In this dynamic system and in waters of this critical pH, changes in stream flow rate, water oxygenation, Fe or Cu content may exert considerable influence on the distance which Fe, and the elements that co-precipitate with Fe, can migrate along the drainage system.

TABLE III

Analysis of mineralized spring water (* includes contamination from drilling fluids)

| | |
|---|-------|
| SiO ₂ (ppm) | 18.3 |
| Ca (ppm) | 18.9* |
| Mg (ppm) | 5.0 |
| Na (ppm) | 1.5 |
| K (ppm) | 0.8 |
| Fe (ppb) | 655 |
| Mn (ppb) | 148 |
| Zn (ppb) | 2000 |
| Cd (ppb) | 10.8 |
| Cu (ppb) | 2100 |
| Pb (ppb) | 510 |
| Ag (ppb) | 1.3 |
| Ni (ppb) | 29 |
| Co (ppb) | 24 |
| SO ₄ (ppm) | 151 |
| Cl (ppm) | 7.0* |
| Specific conductance (μ mhos, at 25°C) | 550 |
| pH | 3.4 |

In the sample from the drainage channel, As and Cu very closely correlate with Fe (Fig.14), indicative of co-precipitation. The adsorption of Cu on goethite is pH-dependent (Grimme, 1968; Forbes et al., 1976). In laboratory systems, adsorption is weak below pH \sim 4.5, but increases rapidly above this value. For Zn, adsorption onto goethite is effective only at pH values of \sim 6.0 or greater, accounting for the lack of notable precipitation of this element in the drainage channel. In the case of As, adsorption is probably followed by the formation of scorodite, $\text{Fe}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$ (Boyle and Jonasson, 1973).

The close correlation of Ag and Hg to Mn and antipathetic relationship to Fe in sample 741199 suggests that the former two elements were adsorbed onto MnO₂ coatings. It is not possible to directly confirm the presence of MnO₂ because of the low concentration of Mn. However, there is persuasive circumstantial evidence in that Ag^{2+} and Hg^{2+} are known to be strongly adsorbed onto MnO₂, and greatly in preference to goethite in the presence of both oxides (Dyck, 1971; Chao and Anderson, 1974; and Anderson et al., 1973, for Ag; Lockwood and Chen, 1973, 1974, for Hg). The amounts of Ag and Hg present are well within the adsorption capacity of Mn, if it is largely present as MnO₂. While there can be little doubt from the lithology of the sample that Fe, Cu and As migrated to this sample site largely in solution, the concentration of Mn, Ag and Hg in the finest fractions may indicate precipitation upstream, followed by transport as particulates. It should be noted that the antipathetic behaviour of Mn and Fe (Fig.14) in drainage sediments is common (Subramanian, 1973).

The availability of Pb in solution (Table III) and its presence in moderate concentration in the coarse, Fe-rich fraction of 741199 (Fig.14) indicate that it is being precipitated in the drainage channel.

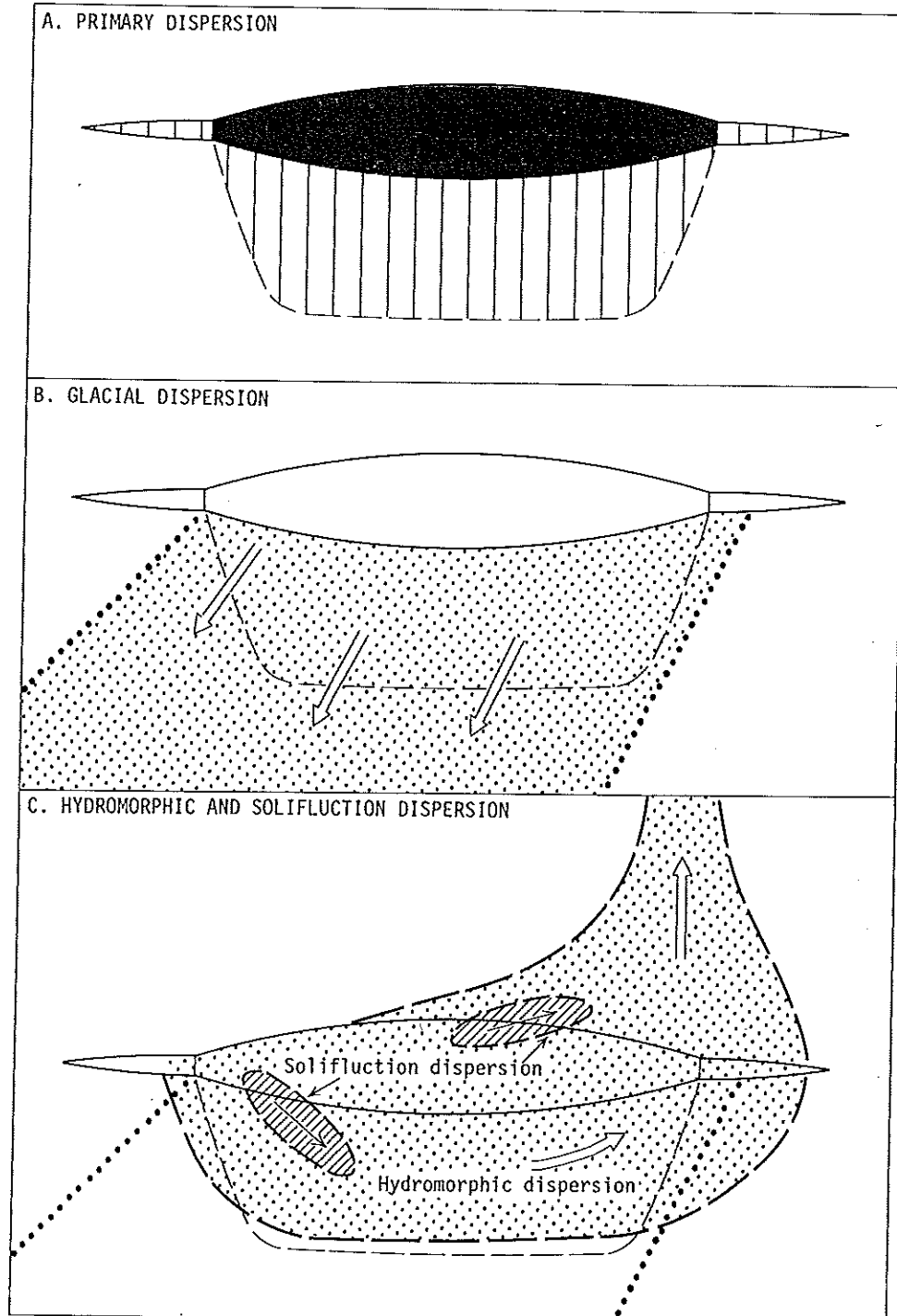


Fig.15. Historical sequence of dispersion processes within study area.

CONCLUSIONS

The main features of primary and secondary dispersion in the prospect area are summarized in Fig. 15. The following conclusions may be applied to geochemical exploration in permafrost terrain of the northern Shield.

(1) Permafrost is no deterrent to active oxidation of sulphide bodies. In fact O_2 is more soluble in cold water and the exothermic nature of many oxidation processes provides a continuing energy source. In frozen ground, thin, intergranular water films allow chemical processes to be active, even in winter (Cameron, 1975b). The presence of springs and sink holes in the vicinity of the mineralization show that taliks (thawed channels) exist in the permafrost.

(2) Frost-churned permafrost soils, lacking normal profile development, are well suited for geochemical sampling.

(3) The order of mobility in this acid-weathering environment has been established as $Zn > Cu > Fe > As > Ag > Pb > Hg > Au$. This allows the selection of indicator elements appropriate to reconnaissance, intermediate and detailed levels of geochemical exploration.

(4) In addition to soil anomalies of elements directly associated with the mineralization, well developed anomalies exist for major rock-forming elements, such as the Mg enriched in the massive sulphide feeder pipe.

(5) Glacial dispersion may involve the movement of previously oxidized material, deficient in the more mobile metals.

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REFERENCES

- Allan, R.J. and Cameron, E.M., 1973. Zinc content of lake sediments, Bear-Slave operation, District of Mackenzie. Geol. Surv. Can. Prelim. Map, 9-1972.
- Allan, R.J., Cameron, E.M. and Durham, C.C., 1973. Reconnaissance geochemistry using lake sediments of a 36,000 square mile area of the northwest Canadian Shield (Operation Bear-Slave, 1972). Geol. Surv. Can. Pap., 72-50: 70 pp.
- Anderson, B.J., Jenne, E.A. and Chao, T.T., 1973. The sorption of silver by poorly crystallized manganese oxides. Geochim. Cosmochim. Acta, 37: 611-622.
- Aslin, G.E.M., 1976. Determination of arsenic and antimony in geological materials by flameless atomic adsorption. J. Geochem. Explor., 7: 321-330.
- Aydingyan, N.Kh. and Oserova, N.A., 1969. Certain new data on geochemistry of mercury. Probl. of Geol. of Min. Dep., Petrol. and Min., Probl. of Genesis and Localization of Min. Dep., Nauka, Moscow, 1: 191-199.

- Boyd, J.B., Gibb, R.A. and Thomas, M.D., 1975. A gravity investigation within the Agricola Lake geochemical anomaly, District of Mackenzie. *Geol. Surv. Can. Pap.*, 75-1A: 193-197.
- Boyle, R.W., 1965. Geology, geochemistry, and origin of the lead-zinc-silver deposits of the Keno Hill-Galena Hill area, Yukon Territory (with short descriptions of the tin, tungsten, and gold deposits). *Geol. Surv. Can. Bull.*, 111: 301 pp.
- Boyle, R.W., 1968. The geochemistry of silver and its deposits. *Geol. Surv. Can. Bull.*, 160: 264 pp.
- Boyle, R.W. and Jonasson, I.R., 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. *J. Geochem. Explor.*, 2: 251-296.
- Butrym, J., Cegla, J., Dzulynski, S. and Nakonieczny, S., 1964. New interpretation of periglacial structures. *Folia Quat. (Krakow)*, 17: 34 pp.
- Cameron, E.M., 1967. A computer program for factor analysis of geochemical and other data. *Geol. Surv. Can. Pap.*, 67-34: 42 pp.
- Cameron, E.M., 1975a. Integrated studies on mineral resource appraisal in the Beechey Lake belt of the northern Shield. *Geol. Surv. Can. Pap.*, 75-1A: 189-192.
- Cameron, E.M., 1975b. Geochemical methods of exploration for massive sulphide mineralization in the Canadian Shield. In: I.L. Elliott and W.K. Fletcher (Editors), *Geochemical Exploration 1974*. Elsevier, Amsterdam, pp. 21-29.
- Cameron, E.M. and Durham, C.C., 1973. Follow-up investigations on the Bear-Slave geochemical operation. *Geol. Surv. Can. Open File*, 175 (November, 1973).
- Cameron, E.M. and Durham, C.C., 1974a. Follow-up investigations on the Bear-Slave geochemical operation. *Geol. Surv. Can. Pap.*, 74-1A: 53-60.
- Cameron, E.M. and Durham, C.C., 1974b. Geochemical studies on the eastern part of the Slave Province, 1973. *Geol. Surv. Can. Pap.*, 74-27: 20 pp.
- Cameron, E.M. and Durham, C.C., 1975. Soil geochemistry of the Agricola Lake massive sulphide prospect. *Geol. Surv. Can. Pap.*, 75-1A: 199-202.
- Cameron, E.M. and Lynch, J.J., 1975. Hydrogeochemical studies in the Agricola Lake area, 1974. *Geol. Surv. Can. Pap.*, 75-1A: 203-208.
- Chao, T.T. and Anderson, B.J., 1974. The scavenging of silver by manganese and iron oxides in stream sediments collected from two drainage areas of Colorado. *Chem. Geol.*, 14: 159-166.
- Dyck, W., 1971. The adsorption and coprecipitation of silver on hydrous oxides of iron and manganese. *Geol. Surv. Can. Pap.*, 70-64: 23 pp.
- Forbes, E.A., Posner, A.M. and Quirk, J.P., 1976. The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. *J. Soil Sci.*, 27: 154-166.
- Frith, R.A. and Hill, J.D., 1975. The geology of the Hackett-Back River greenstone belt - preliminary account. *Geol. Surv. Can. Pap.*, 75-1C: 367-370.
- Gracey, H.I. and Stewart, J.W.B., 1973. The fate of applied mercury in soil. *Proc. Int. Conf. Land for Waste Management*, Ottawa, Ont., 1973, pp. 97-103.
- Grimme, H., 1968. Die Adsorption von Mn, Co, Cu und Zn durch Goethit aus verdünnnten Lösungen. *Z. Pflanzenernähr., Düng., Bodenkd.*, 121: 58-65.
- Horton, R. and Lynch, J.J., 1975. A geochemical field laboratory for the determination of some trace elements in soil and water samples. *Geol. Surv. Can. Pap.*, 75-1A: 213-214.
- James, C.H., 1962. A review of the geochemistry of mercury (excluding analytical aspects) and its application to geochemical prospecting. *Imp. Coll. Sci. Technol.*, London, Tech. Commun., 41: 42 pp.
- Kornik, L.J., 1975. Ground magnetometer survey in the Agricola Lake area, District of Mackenzie. *Geol. Surv. Can. Pap.*, 75-1A: 214-218.
- Lakin, H.W., Curtin, G.C. and Hubert, A.E., 1974. Geochemistry of gold in the weathering cycle. *U.S. Geol. Surv. Bull.*, 1330: 80 pp.
- Lockwood, R.A. and Chen, K.Y., 1973. Adsorption of Hg (II) by hydrous manganese oxides. *Environ. Sci. Technol.*, 7(11): 1028-1034.

- Lockwood, R.A. and Chen, K.Y., 1974. Adsorption of Hg (II) by ferric hydroxide. *Environ. Lett.*, 6(3): 151-166.
- Padgham, W.A., Bryan, M.D.P., Jefferson, C.W., Ronayne, E.A. and Sterenberg, V.Z., 1974. Geology of Agricola Lake. Dep. of Indian Affairs and Northern Development, Ottawa, Ont., 76-G-12, prelim. ed.
- Pearce, T.H. and Lefebvre, D., 1975. Geology of the Agricola Lake area, District of Mackenzie. *Geol. Surv. Can. Pap.*, 75-1A: 219-222.
- Scott, W.J., 1975. VLF resistivity (RADIOHM) survey, Agricola Lake area, District of Mackenzie. *Geol. Surv. Can. Pap.*, 75-1A: 223-225.
- Slaney, V.R., 1975. Colour photography in the Beechey Lake belt, District of Mackenzie. *Geol. Surv. Can. Pap.*, 75-1A: 226.
- Stumm, W. and Lee, F.G., 1961. Oxygenation of ferrous iron. *Ind. Eng. Chem.*, 53(2): 143-146.
- Stumm, W. and Morgan, J.J., 1970. *Aquatic Chemistry, an Introduction Emphasizing Chemical Equilibria in Natural Waters*. Wiley-Interscience, New York, N.Y., 583 pp.
- Subramanian, V., 1973. Mechanisms of fixation of the trace metals manganese and nickel by ferric hydroxide. Ph.D. Thesis, Northwestern Univ., Evanston, Ill., 90 pp.
- Washburn, A.L., 1956. Classification of patterned ground and review of suggested origins. *Bull. Geol. Soc. Am.*, 67: 823-866.
- Williams, J.D.H., 1975. Limnological investigations in the Agricola Lake area. *Geol. Surv. Can. Pap.*, 75-1A: 227-228.