

## HYDROGEOCHEMICAL METHODS FOR BASE METAL EXPLORATION IN THE NORTHERN CANADIAN SHIELD

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### ABSTRACT

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The use of lake waters for base metal exploration has been studied in the northern part of the Slave Geological Province of the Canadian Shield. The area is north of the treeline, within the zone of continuous permafrost, and, like most other regions of the Shield, has a high density of small lakes.

A regional sampling of 1218 lakes established that less than 2 ppb ( $\mu\text{g/l}$ ) Zn or Cu is typical of waters from unmineralized terrane. These samples had a median pH of 6.8 and a median specific conductivity of  $19.5 \mu\text{mhos}$ . Lake waters were also taken from the areas surrounding five massive sulphide occurrences: High Lake, Canoe Lake, Takiyuak Lake, Hackett River and Agricola Lake. In all cases there are unambiguous anomalies for Zn. Anomalies are also present for Cu, but are less intense and extensive. This difference between the two elements is related to the superior mobility of Zn in surface waters and its more consistent presence as a major constituent of massive sulphides.

A water sampling apparatus has been developed and tested on a light turbine helicopter. Using this, thirty sites may be sampled each hour when sampling at a density of 1 site per  $2.8 \text{ km}^2$ . Measurement of pH, conductivity and water temperature are recorded in the helicopter during sampling.

A number of factors have been investigated that may influence the utility of lake water sampling for base metal exploration:

- (1) Seasonal variability, while present to moderate degree, is unlikely to hinder application of the method.
- (2) For the size of lakes sampled ( $2 \text{ km}^2$  or less), elements are homogeneously distributed across the lake surface during the ice-free season. During the initial period of break-up there are marked variations in element content around the ice-free lake margin. Sampling during this period may help define the source of metals for anomalous lakes.
- (3) Study of sample preservation suggests that mobile elements, such as Zn, that are stable in solution within lakes, are also relatively stable when untreated water is stored in plastic bottles.
- (4) Care must be taken to avoid contamination of the samples, particularly from the bottle.

The areal extent of lake water base metal anomalies appears to be less than equivalent lake sediment anomalies. Thus for wide-interval, regional geochemical reconnaissance, lake sediment sampling is the method of choice. Lake waters are an appropriate medium for detailed exploration of areas of interest, such as volcanic belts. For this application, the principal attractions are rapid sampling rates, and hence low costs, high contrast anomalies, and a uniform sampling medium.

## INTRODUCTION

In a review published in 1971, Boyle et al. found that hydrogeochemical methods were poorly developed for use in the Canadian Shield. At that time the majority of the few applications had been to uranium exploration. While the authors listed a number of conditions that were inimical to the success of hydrogeochemistry in this region — impermeable rocks, poor drainage, glacial cover, permafrost — they regarded the future of the method optimistically.

It is now clear that the northern environment is no impediment to the oxidation of sulphides and the dispersion of the soluble weathering products. The cold groundwaters are richer in oxygen than waters of warmer climes and are less likely to have this oxygen depleted by organic activity. Many of the oxidation reactions of sulphides are exothermic and thus do not depend on an external source of heat. The liberation of heat from these reactions frequently causes the development of thawed channels in the permafrost in and around sulphide bodies. Even in frozen ground and during the winter, the presence of thin water films along grain boundaries allows ionic movement (Tyutyunov, 1960, 1961; Anderson and Morgenstern, 1973). The amount of organic activity is less in the north than in the southern Shield. Thus, once liberated into surface waters, metals are less likely to be precipitated by organic matter. Finally, the glaciers that covered the region have, to a greater or lesser extent, exposed a fresh level of sulphides that may be oxidized and their mobile elements dispersed. These same glaciers have carved a myriad of lake basins, allowing convenient and close density sampling of surface waters.

Obstacles to hydrogeochemistry in the northern Shield are more likely to be technical than environmental. Most northern waters are relatively pure and contain only low concentrations of indicator elements. Anomalous contents of such base metals as Zn, Cu and Ni may be less than 10 ppb. These amounts are close to the limits of analytical technology, although rapid progress is being made in the field. At these levels care must be taken to avoid contamination of the waters and to ensure that the elements are retained in solution until analysis has been carried out.

The first part of this paper shows that hydrogeochemical anomalies do exist around known base metal occurrences. This is followed by a discussion of those factors, such as controls on element mobility, sampling and seasonal variability, storage and contamination, and sampling logistics that determine whether this can be a practical approach for mineral exploration. Some of these factors have also been considered in a recent review by Miller (1978).

Attention is given principally to the use of Zn and Cu, since these are relatively mobile in the surface environment and are major constituents of massive sulphides. Elements, such as Pb and As, which also occur in this mineralization, are immobile in most northern waters. The majority of the analyses for Zn and Cu reported in this paper were made in field laboratories within a few hours or days of sampling. Fifty milliliters of unacidified and

unfiltered water were extracted with APDC-MIBK and this extract aspirated into an air-acetylene flame of an atomic absorption spectrometer. Detection limits varied somewhat, but were mostly in the range 0.5–1.0 ppb for both Zn and Cu. The pH of waters collected during 1975 were measured on board the sampling helicopter within a few seconds of sampling. During 1974, similar data were obtained in a field laboratory.

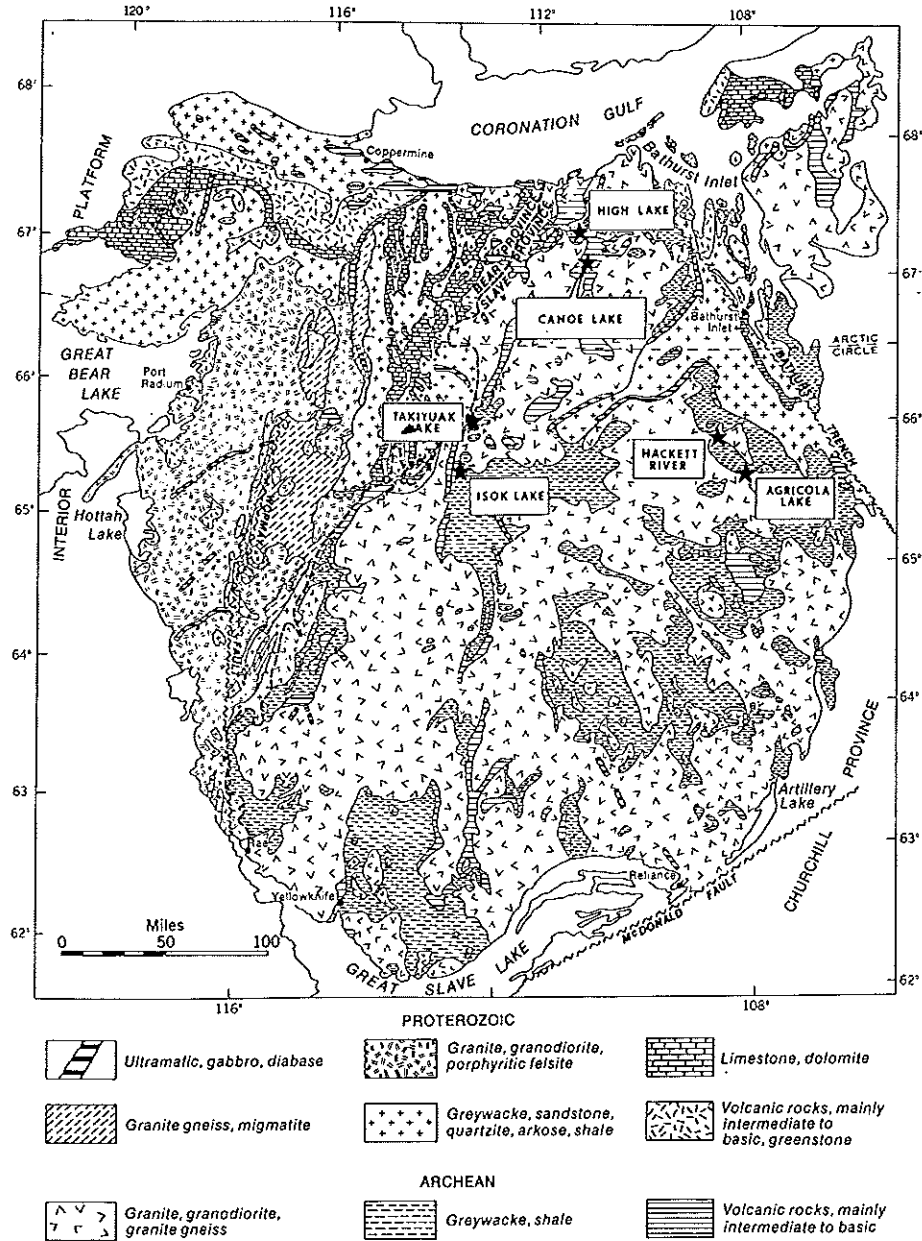


Fig.1. Location of massive sulphide mineralization in the northern part of the Slave Geological Province.

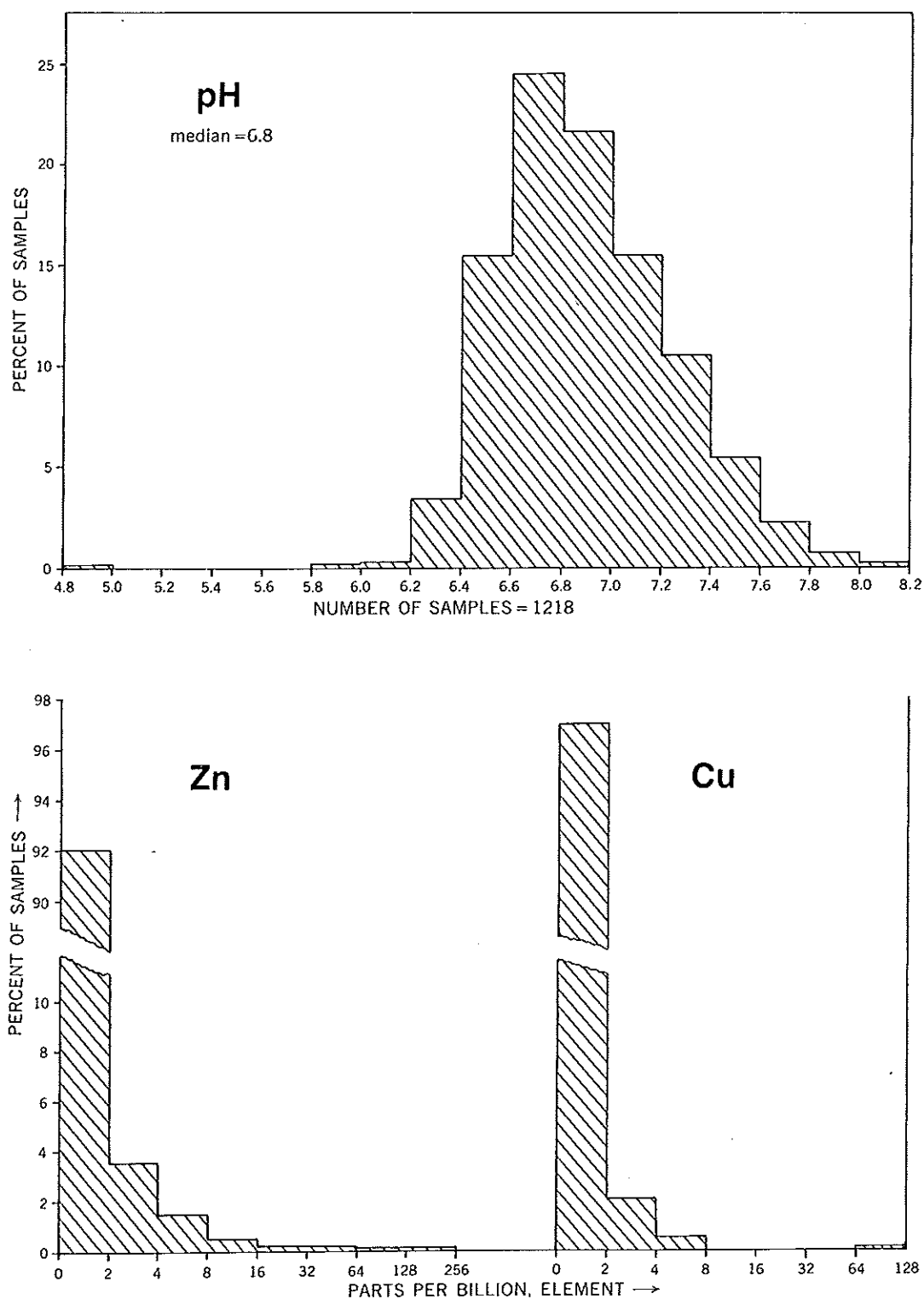


Fig.2. Histograms for Zn, Cu and pH, 1218 lake waters, High Lake region, Northwest Territories.

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## MASSIVE SULPHIDE TEST AREAS

The principal occurrences of massive sulphide mineralization in the northern part of the Slave Geological Province are shown in Fig. 1. Mineralization is in Archean metavolcanic rocks. The High Lake and Takiyuak Lake occurrences are of the Cu-Zn type, with 5.2 million tons of 3.5% Cu, 2.5% Zn at High Lake and 0.5 million tons of 5.0% Cu, 3.5% Zn at Takiyuak Lake. The others are of the Zn-Pb-(Cu) type. At Hackett River, several bodies aggregate a minimum of 20 million tons, the 'A' zone containing 8.5% Zn, 1.4% Pb, 0.25% Cu and 240 ppm Ag. Only preliminary drilling results have been published for Agricola Lake and Canoe Lake.

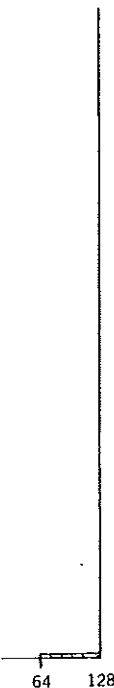
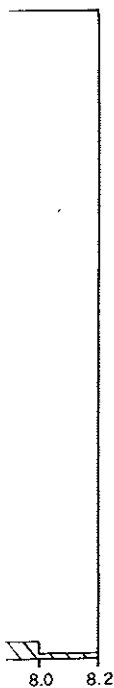
All of these locations lie within the zone of continuous permafrost, north of the treeline. Local relief is generally low, being greatest in the Canoe Lake — High Lake areas, up to 100 m. Relief is usually greatest in the volcanics, so that drainage is away from these areas. Quaternary cover is variable, but most of the bodies discussed show some gossanous outcrop or soils.

Hydrogeochemical data have been obtained for all but the Izok Lake example. None of the massive sulphides have been mined and there is no significant contamination of present surface waters by previous drilling or trenching. At the Agricola Lake occurrence, lake and spring water sampling was carried out before, during and after drilling. This showed that contamination was slight, being confined to  $\text{CaCl}_2$  added to the drilling fluids.

Preliminary hydrogeochemical work at Agricola Lake in 1974 has been described by Cameron and Lynch (1975) and a more detailed description of geochemical dispersion in lake waters and sediments by Cameron (1977). Studies at Hackett River and High Lake in 1974 were published by Cameron and Ballantyne (1975). Then, during the 1975 field season, detailed hydrogeochemical work was carried out at High Lake, Canoe Lake, Takiyuak Lake, Hackett River and Agricola Lake and a reconnaissance lake water survey was made of a 2400-km<sup>2</sup> area centred on High Lake and including the Canoe Lake area. Preliminary aspects of this 1975 work have been described by Cameron and Durham (1976).

## ABUNDANCE OF ZINC AND COPPER IN LAKE WATER

In the 1975 lake water survey of the High Lake region, some 1218 samples were collected at a density of 1 per 2.8 km<sup>2</sup>. The terrane consists of granitic, metavolcanic and metasedimentary rocks. Histograms for Zn and Cu (Fig. 2) show that, for the great majority of the samples, the amounts of Zn and Cu present are near or below the limit of detection. Note that the Zn results are lower than the data obtained in 1974 from the same region published by Cameron and Ballantyne (1975). This is due to contamination of some of the 1974 waters by sample bottles and is discussed in a later section. For this region, and indeed for all of the northern part of the Slave Province, lake waters with Zn and/or Cu contents that are clearly above the detection limit, say, 2 ppb or more, may be considered anomalous.



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In comparing the base metal data for the waters of this area with other waters, it is useful to know the quantity of total dissolved solids. The median value of specific conductance (at 25° C) for the 1218 waters is 19.5  $\mu$ mhos. Using the approximate relationship: specific conductance  $\times$  0.6 = dissolved solids, the calculated median content of dissolved solids is 12 ppm.

The data given in Fig.2 show that while the median pH of the lake waters is close to neutral, moderately acidic and alkaline conditions do occur. The alkaline waters are related mainly to carbonate-bearing metavolcanic and metasedimentary rocks, while the weakly acidic to neutral waters (pH 6–7) chiefly occur in granitic terrane.

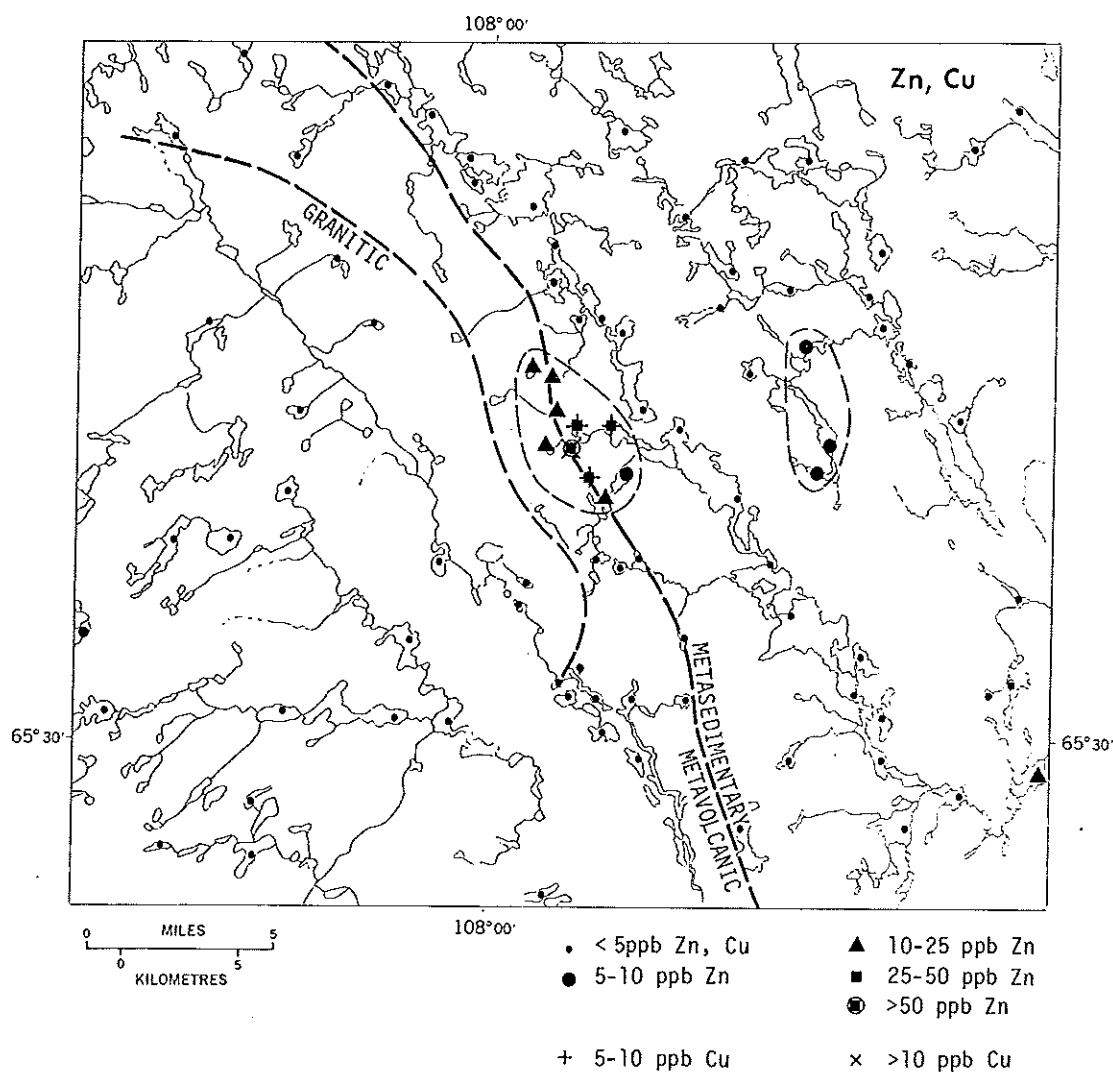


Fig.3. Distribution of Zn and Cu in lake waters, Agricola Lake region, Northwest Territories.

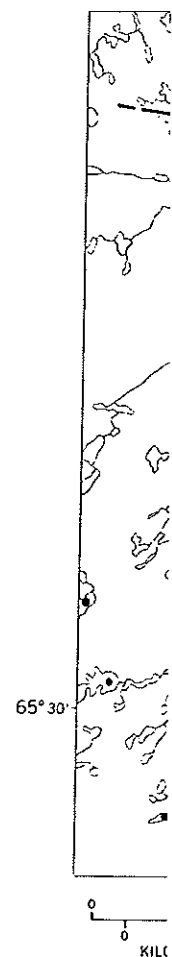


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Both Zn and Cu (Fig.3). The distribution of these metals is graphically related to the geological rocks. The distribution of Zn and Cu is Note that 2/3 of the waters to the east in the region are be disclosed on the basis of pre-existing data. Cameron, 1980, extensive th

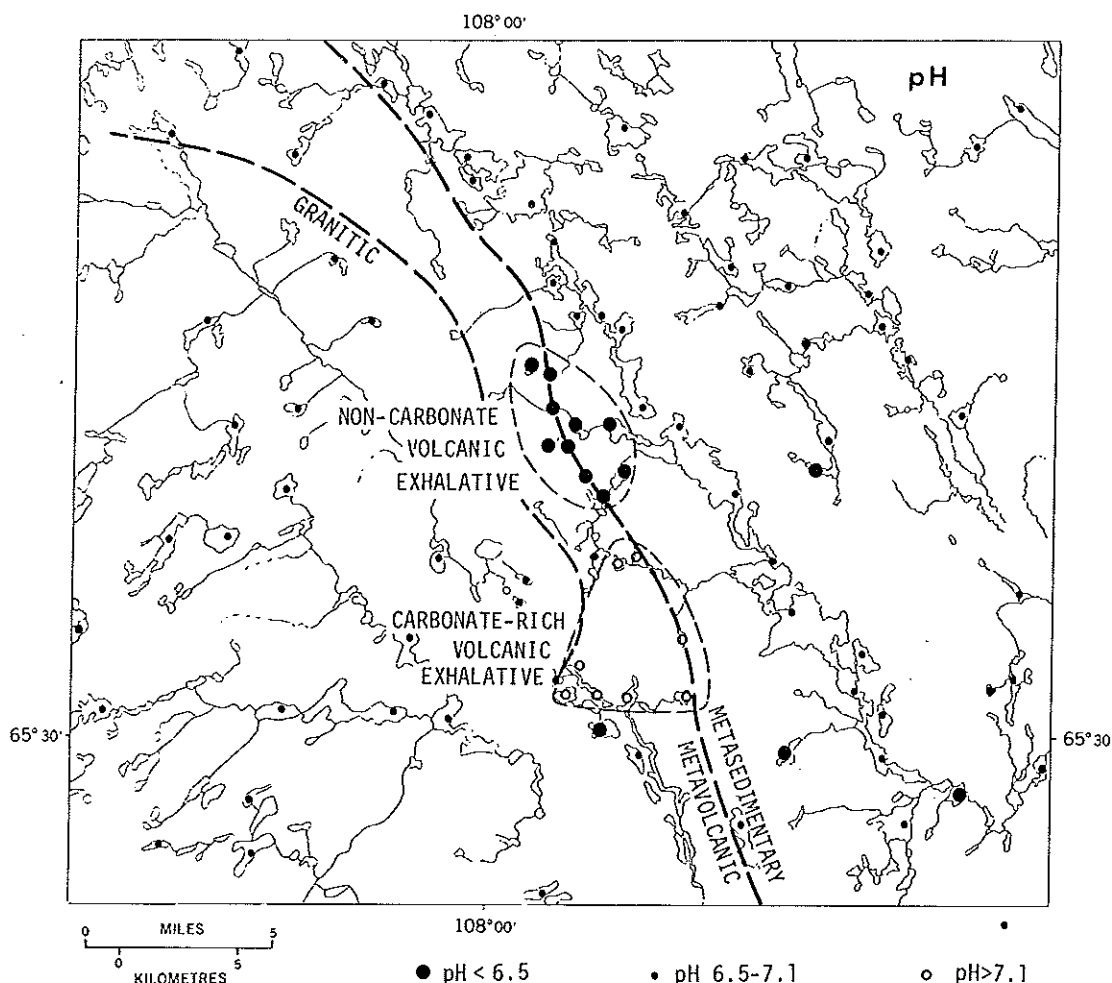


Fig.4. Distribution of pH in lake waters, Agricola Lake region, Northwest Territories.

#### LAKE WATER DATA NEAR TO MASSIVE SULPHIDE MINERALIZATION

##### *Agricola Lake area*

Both Zn and Cu are anomalous in the lakes surrounding this occurrence (Fig.3). The elliptical shape of the main anomaly reflects extensive, stratigraphically-controlled mineralization in the steeply dipping metavolcanic rocks. The Agricola Lake massive sulphide is near the centre of the anomaly. Note that Zn is more extensively distributed than Cu. The weaker anomaly to the east in metasedimentary rocks that overlie the volcanics is believed to be disclosing a slightly younger exhalative event along the same trend. On the basis of previously published data for lake sediments from this area (see Cameron, 1977; Coker et al., 1978), the anomalies in waters are much less extensive than the lake sediment anomalies.

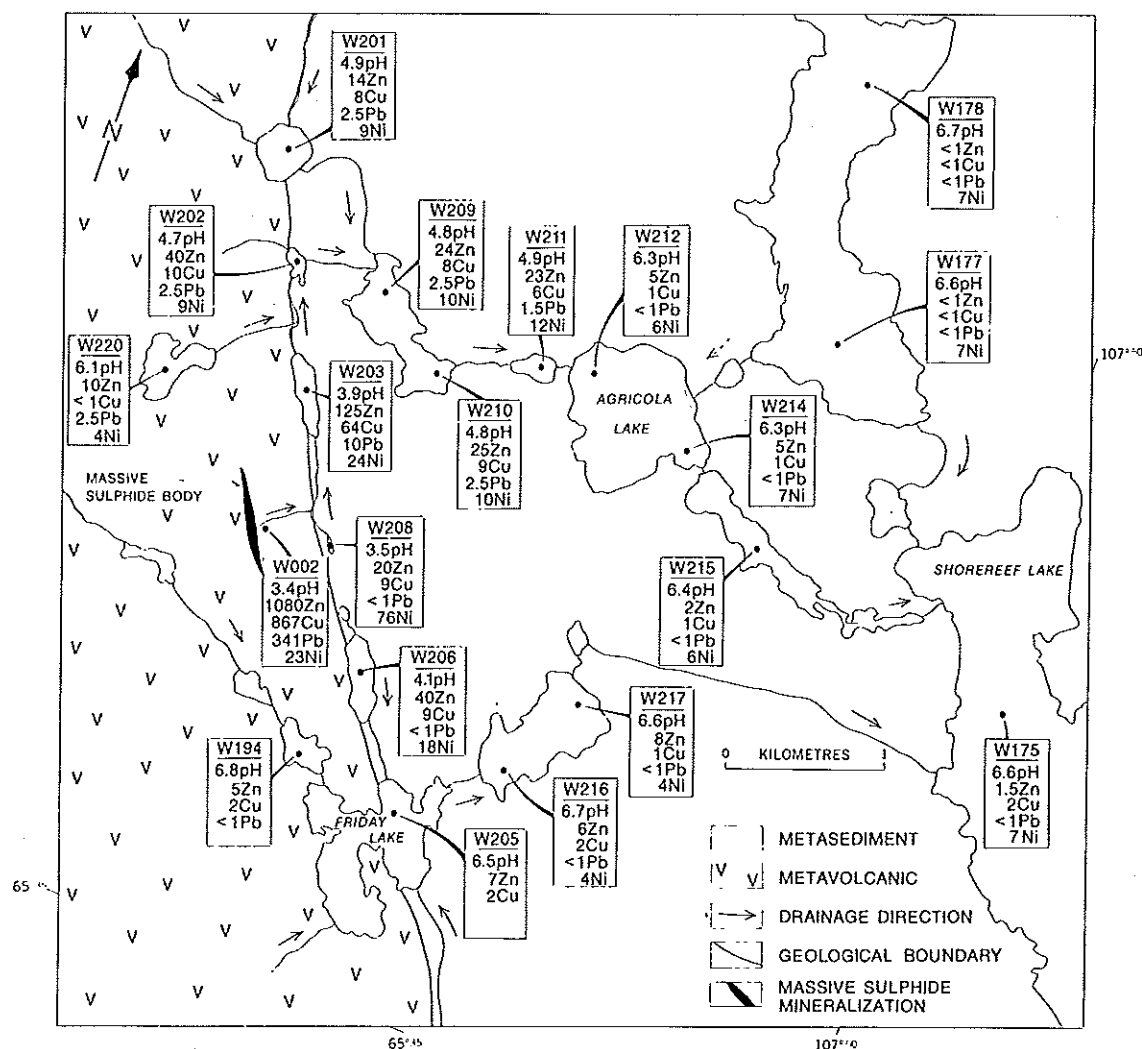


Fig.5. Distribution of Zn, Cu, Pb, Ni and pH in lake waters, Agricola Lake area, Northwest Territories.

The pH of the lake waters from the same 1500 km<sup>2</sup> region, shown in Fig.4, reveal two areas of distinctive pH. The most northerly is around the known sulphide mineralization where oxidation has produced acidic waters. These acidic waters are coincident with the base metal anomaly shown in Fig.3. The other, of weakly alkaline waters, marks a carbonate-rich (and apparently base metal-poor) exhalative event within the volcanic sequence.

More detailed data on the central part of the main anomaly of Fig.3 are given in Fig.5. The principal source of metals is the massive sulphide body, but there are other significant sources of metal in the metavolcanic rocks and also in the metasediments especially near their lower contact.

By dilution and precipitation, the metal content of the waters decreases down-drainage from the mineralization, more rapidly for the immobile element, Pb, than for the mobile Zn. In these acidic waters, absorption on to

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hydrous iron oxide has been cited as a major control on the mobility of the base metals (Cameron, 1977).

Note that while there is little Ni associated with the sulphide body, this element is anomalous over a wide surrounding area, particularly over the metasediments. Elsewhere in the northern Slave Province contents of  $< 2$  ppb Ni are typical of surface waters.

#### *Hackett River area*

In the preceding example the sites of sulphide and carbonate volcanic exhalative activity are separated (Fig. 4). Thus present-day oxidation of the sulphide mineralization produces an acidic environment conducive to the mobilization and widespread dispersion of base metals. At many other Archean massive sulphide occurrences there is no such distinct spatial separation of carbonate and sulphide. Thus lake waters near the mineralization are of neutral to slightly alkaline pH. The Hackett River area is such an example.

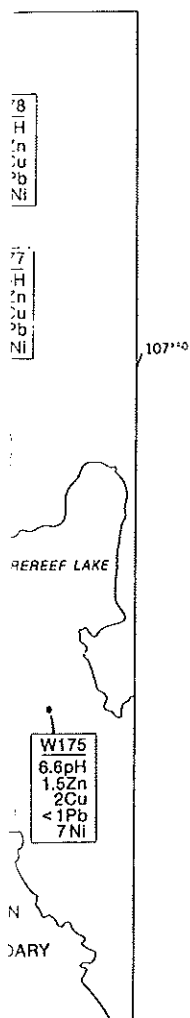
Data from the area was first obtained in 1974 (Cameron and Ballantyne, 1975). The area was resampled on three separate occasions during 1975. Data for the 30 June 1975 sampling are given in Fig. 6. Zn is distinctly anomalous in many of the lakes, but Cu is much less so.

The dispersion of Zn may be traced down-drainage from the massive sulphide bodies; for example, west from the East Cleaver zone through a chain of lakes which includes Anne Lake. In the eastern portion of the map note that sample W 250, immediately up-drainage from the 'A' zone, is low in Zn, but W 251, below this zone, has 61 ppb. All of the sulphide bodies shown in Fig. 6, except for the Boot Lake zone, are marked by gossanous outcroppings or soils. The Boot Lake zone is concealed by a considerable thickness of overburden. The effect of this concealment on depressing the Zn present in Boot Lake waters is apparent when compared to lakes near to other zones. Nevertheless this lake is still distinctively anomalous.

#### *Takiyuak Lake area*

Massive sulphides occur in volcanic rocks near to a granitic contact. In Fig. 7, their position is marked by a solid triangle. This area drains eastwards through a chain of lakes. Note that samples W 678 and W 679, immediately up-drainage, are low in Zn and Cu, but those down-drainage (W 691/W 692/W 693) are distinctively anomalous. The sampling appears to have outlined another sulphide occurrence near sample W 688, several km along the volcanic/granitic contact from the known body.

The neutral to slightly alkaline character of the base metal-rich waters suggests that carbonates are associated with the mineralization.



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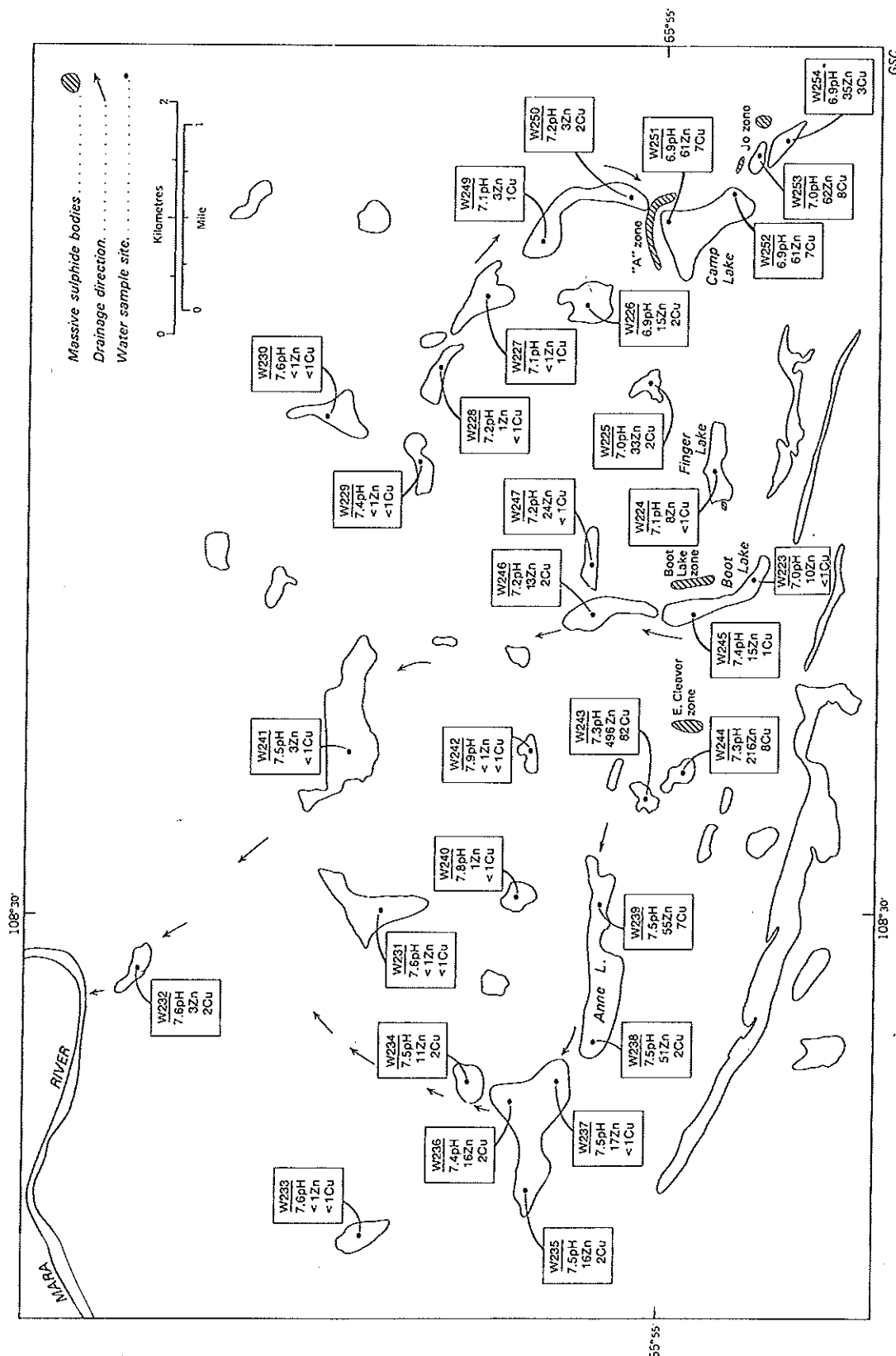


Fig. 6. Distribution of Zn, Cu and pH in lake waters, Hackett River area, Northwest Territories.

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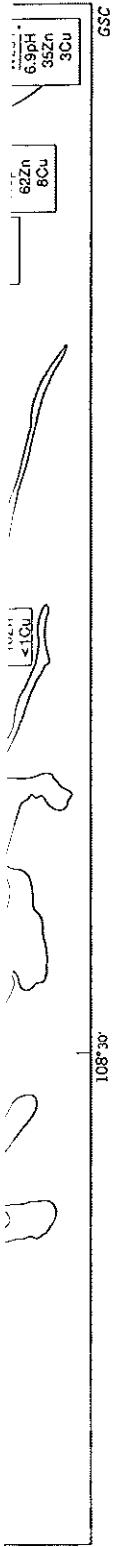


Fig. 6. Distribution of Zn, Cu and pH in lake waters, Hackett River area, Northwest Territories.

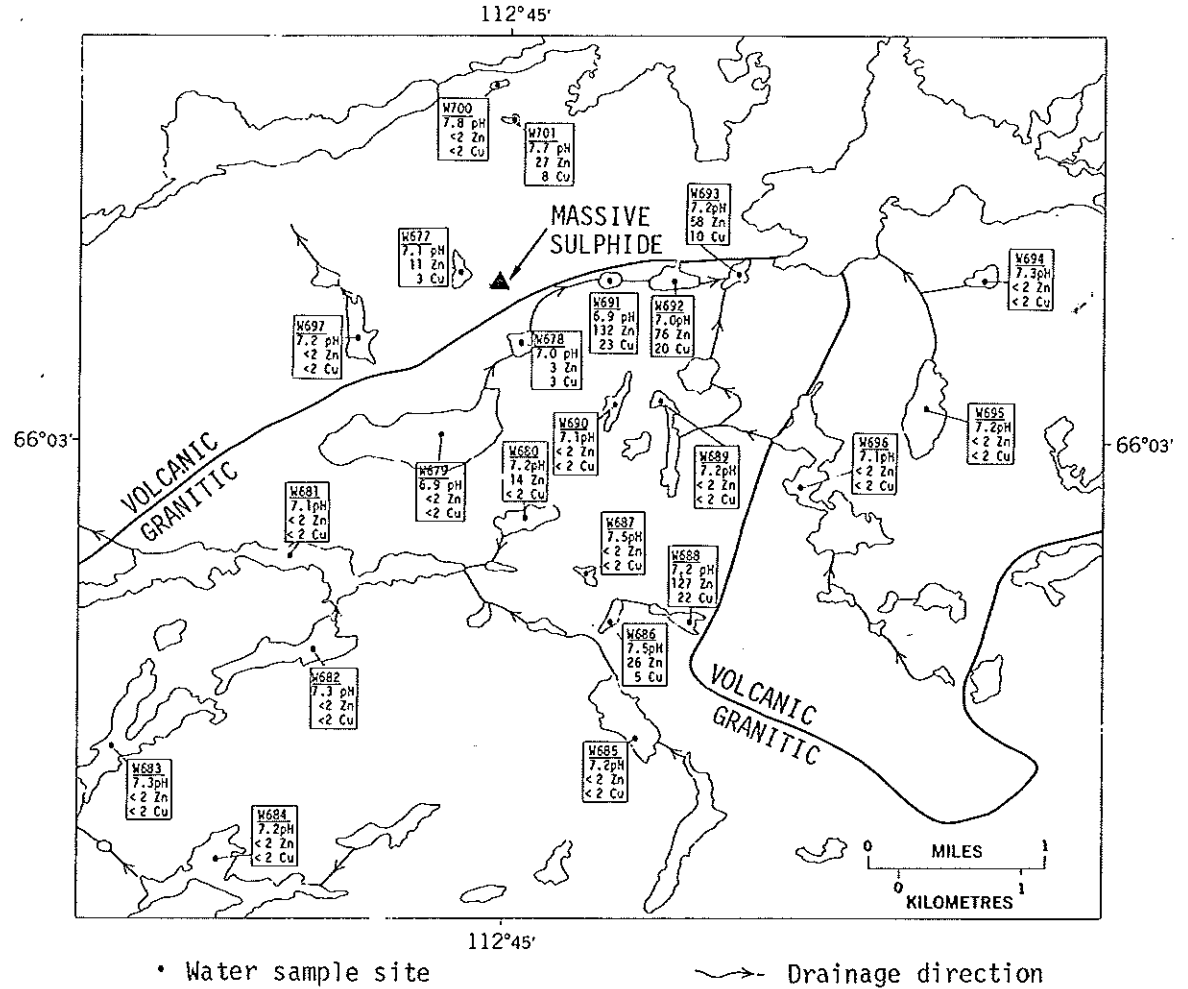


Fig. 7. Distribution of Zn, Cu and pH in lake waters, Takiyuak Lake area, Northwest Territories.

### High Lake area

The occurrence is marked by prominent gossans on the hillside flanking High Lake (Fig. 8). The lake waters are strongly anomalous in Zn and Cu. Although Cu dominates over Zn in the mineralization, the reverse is true of the lake waters. Four samples of centre-lake sediment average 4000 ppm Zn and 12,000 ppm Cu, indicating the strong partitioning of these elements in favour of Zn remaining in solution. Two stream waters flowing from the 'A-B' zone into the lake measured 1800 ppb Zn, 1000 ppb Cu at pH 3.8 and 16,000 ppb Zn, 68,000 ppb Cu at pH 3.0. Despite these acidic inflows, High Lake is only very weakly acidic. Thin limestones, interbedded with volcanics, outcrop along the edge of the lake.

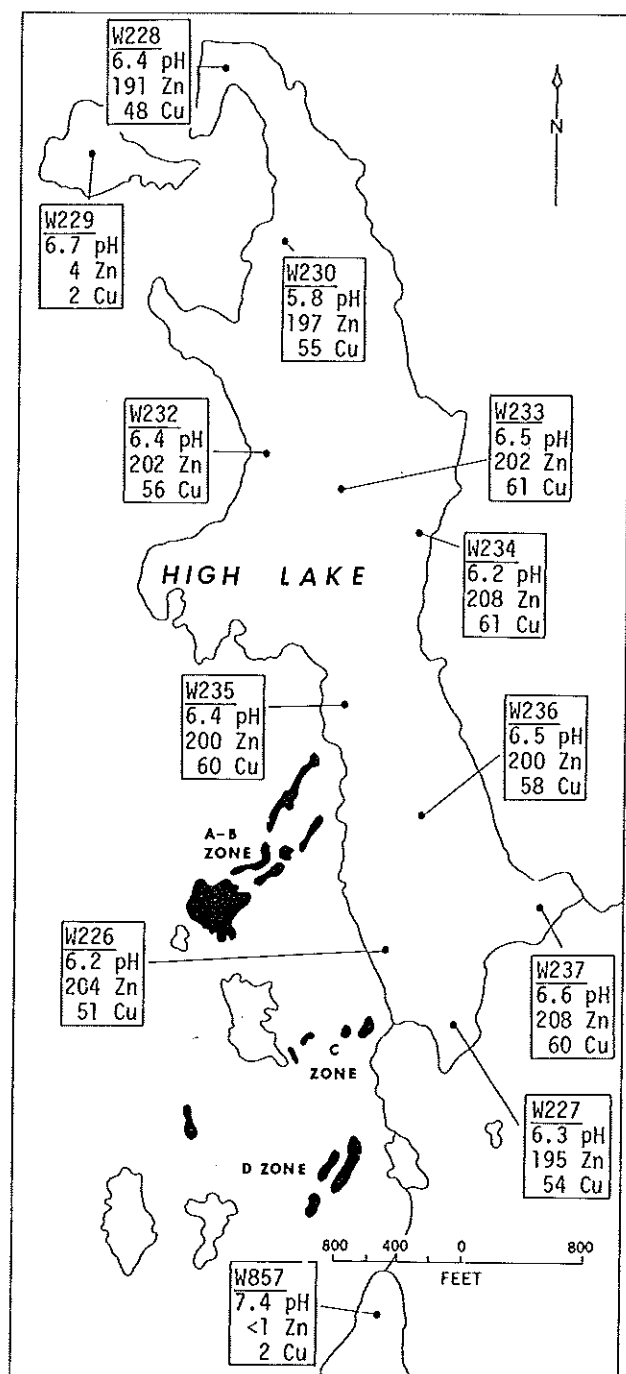
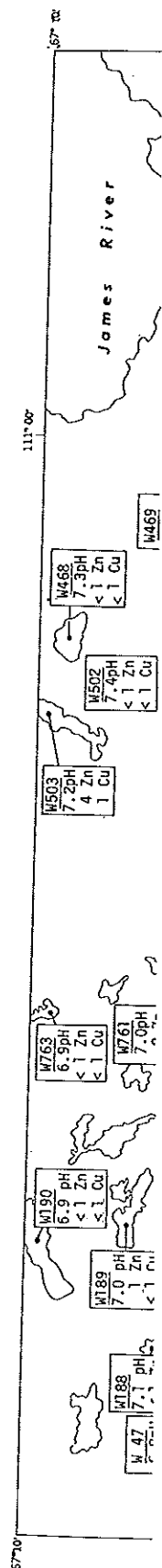


Fig.8. Distribution of Zn, Cu and pH in High Lake waters, Northwest Territories.

#### Canoe Lake area

Data from this area are shown in Fig. 9. A drilled occurrence of massive sulphides is in metavolcanics near the western end of Canoe Lake. Compared to background values of 1 ppb Zn and Cu or less, Canoe Lake is anomalous, particularly for Zn. It drains northwards from its eastern arm and the lakes down-drainage are weakly anomalous.



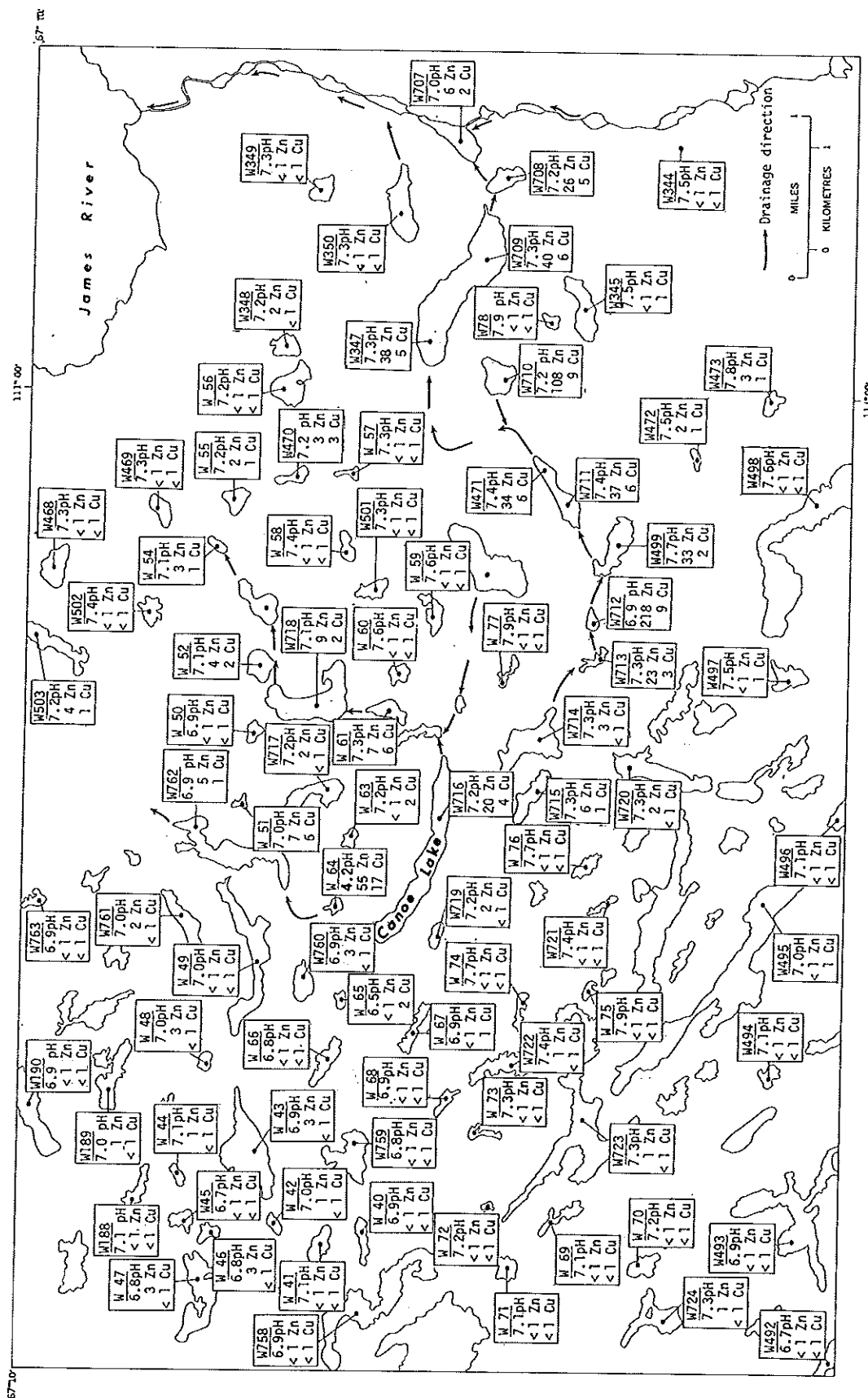


Fig. 9. Distribution of Zn, Cu and pH in lake waters, Canoe Lake area, Northwest Territories (lake waters > 5 ppb Zn shaded).

It is apparent that there is another source of base metals about 2 km south-east of Canoe Lake, situated near samples W712 and W713. This area drains east-northeast along the strike of steeply dipping metasedimentary and meta-volcanic beds. After a rapid decline of Zn down-drainage from W 712, the Zn content stabilizes in the 30–40 ppb range for several km. The probable reason is that there are a number of sources of mineralization along this stratigraphic horizon. Note, for instance, the elevated content of Zn in sample W 710.

With one exception, the anomalous waters shown in Fig. 9 are neutral to weakly alkaline, reflecting the presence of limy beds.

#### CONTROLS ON THE MOBILITY OF ZINC AND COPPER IN NORTHERN LAKE WATERS

The solubility of Zn and Cu in natural waters has been considered by a number of authors (for Cu see Silman, in Schmitt, 1962; Rickard, 1970; Mann and Deutscher, 1977; for Zn see Hem, 1972). These data indicate that the waters described in the preceding section are undersaturated in these metals. High Lake water is possibly closest to being saturated; this in Cu. ('Major' cation and anion data for these waters, needed for solubility calculations, are given in Cameron and Ballantyne, 1975, table 5).

The role of organic matter in the mobilization and fixing of base metals in the northern environment is believed to be low, but there is a dearth of information. Lake and stream waters are clear and the surface of lake sediments is oxygenated within the size of lakes used for sampling. The high winds of the region tend to keep the lake waters well oxygenated and unstratified during the ice-free season.

The principal control on the fixing of Cu, Zn and certain other base metals is believed to be hydrous iron and manganese oxides. Jenne (1968) has cogently argued in favour of the influence of these oxides in fresh waters. Cameron (1977) has shown for the acidic Agricola Lake drainage system, that iron oxides precipitated in the lakes and streams are a major control on the adsorption and co-precipitation of several base metals. This adsorption is pH-dependent, with the adsorption sequence, in order of increasing pH, being correlated with the decreasing tendency for the given cation to hydrolyse. Experimental data illustrating the sequence are shown in Fig. 10, where it should be noted that  $\text{Cu}^{2+}$  is adsorbed at lower pH than  $\text{Zn}^{2+}$ .

It has been shown that hydrous iron and manganese oxides have their greatest adsorption capacities when they are freshly precipitated and, in particular, when the metal to be adsorbed is present at the time of precipitation (Lee, 1975). Freshly precipitated iron hydroxides are certainly present in the acid-weathering Agricola Lake drainage where sample W 002 near the mineralization has 875 ppb Fe and sample W 203, a short distance down-drainage (Fig. 5), has 70 ppb Fe (measurements of 92 ppb and 69 ppb Mn on the same samples indicate that manganese hydroxides are not being substantial-

ly precipitated carbonate at neutral pH, thereby precipitating 15 ppb Fe and < 5 ppb Mn soluble in water that are available for this

#### SEASONAL

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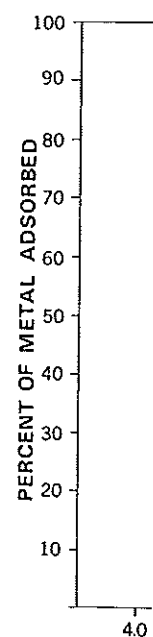


Fig.10. Adsor

ly precipitated in this portion of the drainage). But where there is sufficient carbonate present in the environment to maintain surface waters at a near-neutral pH, there may be much less Fe and Mn available in solution to provide freshly precipitated hydrous oxides. For instance, at High Lake the waters contain 15 ppb Fe and < 5 ppb Mn (pH 6.3) and for Camp Lake (Fig. 6) < 10 ppb Fe and < 5 ppb Mn (pH 6.9). Thus while base metals such as Zn and Cu are less soluble in neutral than in acidic waters, the lower quantities of Fe and Mn that are available for precipitation in these waters, may, in a sense, compensate for this lower inherent mobility.

#### SEASONAL VARIATIONS

If lake waters are to be a viable sampling medium for base metal exploration, it is important that they be reasonably uniform in composition during the field season. For the region sampled the season is limited to three months, July, August and September. Lake ice melts in late June or early July, and in September deteriorating weather makes helicopter sampling operations difficult.

From data obtained in 1974 it was apparent that seasonal change was greatest during the period of thaw. Accordingly, in 1975 many lakes in the Hackett River, Agricola Lake areas, and also between these areas, were sampled on three occasions during the first part of the season. They were first sampled on June 12 when the snow had largely melted, but the lakes were ice-covered except for a zone of water around the shore (Fig. 11a). The lakes were free of

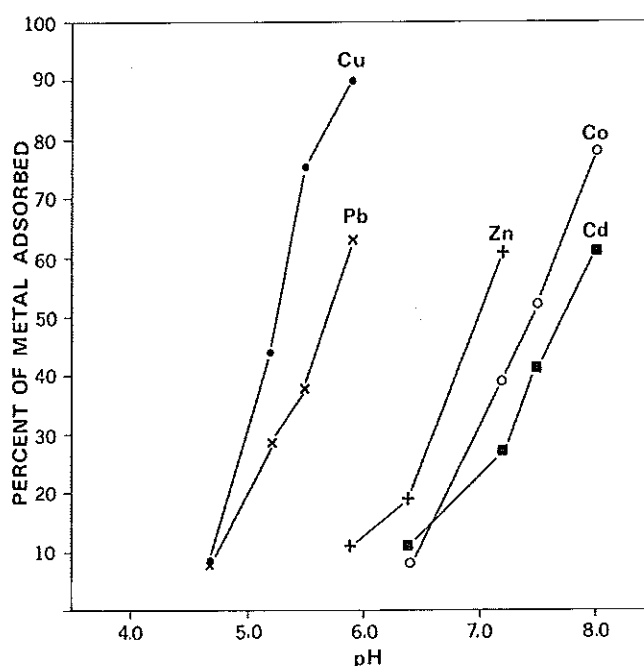


Fig.10. Adsorption of certain metal cations on goethite. (Data from Forbes et al., 1976.)

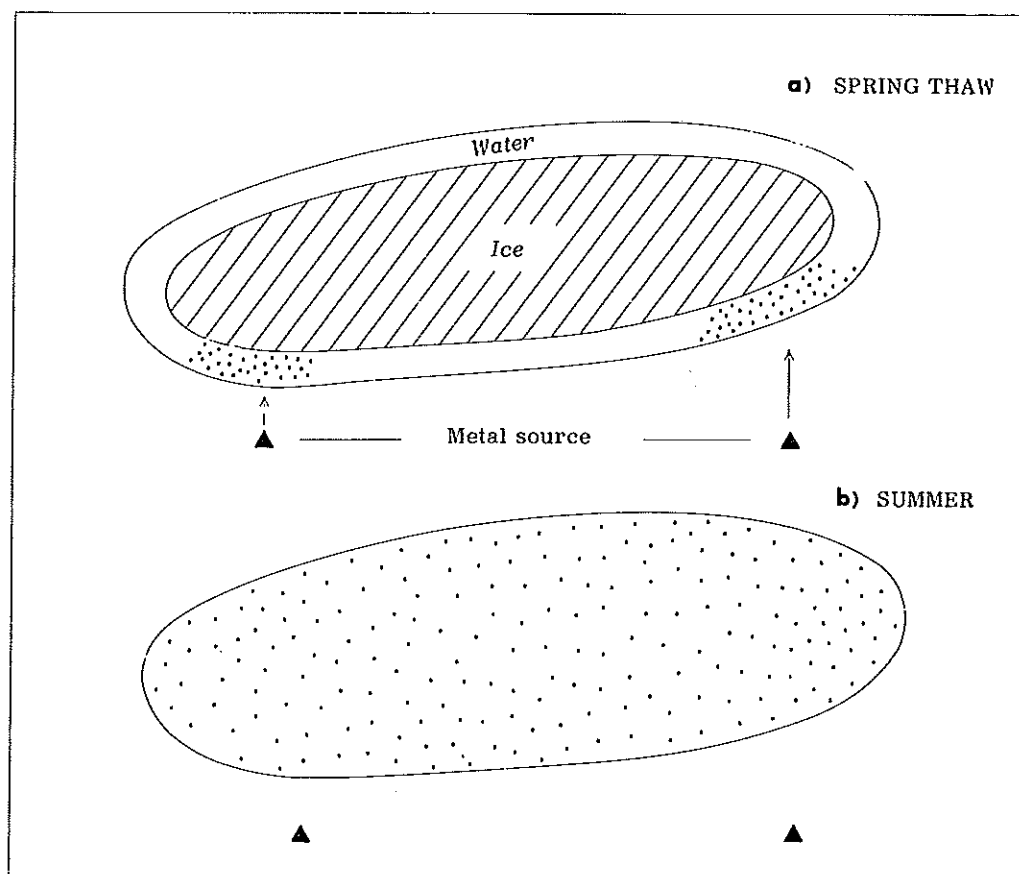


Fig.11. Localized distribution of anomalous base metal contents in lake waters during spring thaw compared to homogeneous distribution during summer.

ice during the two subsequent sampling dates on June 30 and July 18.

The variations observed in the Zn and Cu contents of different lake waters between these three sampling periods are not consistent. They appear to be related to the complex interplay of four major factors:

(1) The snowmelt brings waters with a generally low base metal content to the lakes. This has the effect of diluting the waters of lakes that have an anomalous metal content.

(2) In and around oxidizing base metal mineralization there may be thawed channels in the permafrost through which water flows in the summer. The seeps or springs, at which these waters emerge, do not commence to flow until sometime after the snow has melted, perhaps two weeks. In mineralized areas, these seep waters may be rich in base metals. During the remainder of the summer these seeps decline in volume, but tend to increase in metal concentration. They may be recharged by heavy rains.

(3) Drainage is most often through a chain of lakes. Seasonal changes along the chains vary from system to system, depending on the dynamics of water movement and flow-capacity considerations.

(4) During the ice-free season, the strong winds of the Barren Lands effec-

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tively mix the waters of the dominantly shallow lakes. However, during the initial period of ice melting, when water is present only along the shore, mixing is not effective.

To illustrate compositional variation caused by these factors during and after the break-up period, the contents of Zn in water from the Hackett River area are shown in Fig. 12.

First, examine the drainage from the East Cleaver zone westwards. In samples W 243 and W 244, nearest to the mineralization, Zn was lower on June 12 because of dilution by snowmelt, but is still highly anomalous. The run-off has expelled anomalous waters from these lakes downslope into the eastern end of Anne Lake, so that site W 239 contained more Zn on June 12 than later in the season. The ice cover over most of the lake prevented mixing of this anomalous water with the remainder of the lake. Note that the outflow of Anne Lake (site W 238) had constant Zn throughout all sampling periods. The lake immediately west of Anne Lake shows a similar response. Its eastern arm had greater levels of Zn on June 12 because of inflow from Anne Lake, while the outflow (W 234) was constant throughout the sampling season. The arm receiving snowmelt from unmineralized ground (site W 235) had a lower content of Zn during break-up.

Note that certain of the moderately anomalous sites (e.g., W 224/W 225/W 245) are relatively constant in Zn throughout all sampling periods. The ground in question, between the East Cleaver and the 'A' zones, is quite strongly mineralized and it is possible that snowmelt contains moderately anomalous levels of Zn. Jonasson and Allan (1973) have demonstrated the movement of base metal ions into snow during the winter.

For a longer-term comparison of variability, the data obtained in 1975 and shown in Figs. 6 and 12 may be compared with data obtained in 1974 (see Cameron and Ballantyne, 1975, fig. 8). For most lakes the data obtained during the two years compare closely.

Seasonal changes, therefore, appear to be of relatively minor consequence for exploration purposes. Indeed it may be advantageous to carry out detailed follow-up sampling around the margin of anomalous lakes during the break-up period, in order to pinpoint the source of metal (Fig. 11a). During this period, water cascades down the hillsides into the lakes from all directions, but during the summer permanently flowing streams are sparse.

#### SAMPLING VARIABILITY

Lakes used for hydrogeochemical sampling are small, ranging up to 2 km<sup>2</sup>. Across the surface of these lakes water composition is quite uniform during the ice-free season. This may be demonstrated by data shown in Figs 5, 6, 8 and 12. This homogeneity is a consequence of the high winds characteristic of the Barren Lands and also the shallow, unstratified nature of the water column in these smaller lakes. Choice of sampling sites within lakes is, therefore, not critical.

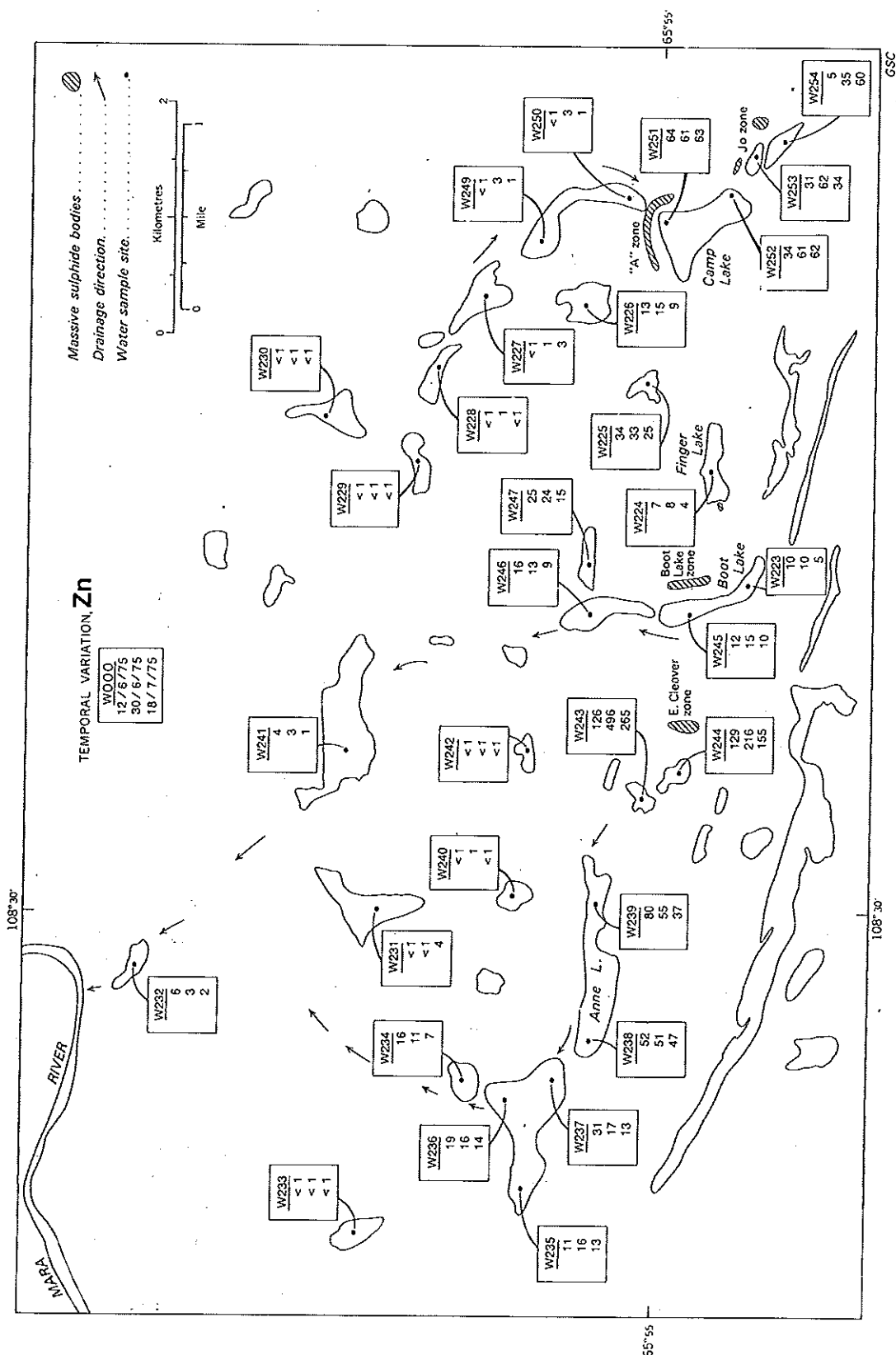


Fig.12. Distribution of Zn in lake waters, Hackett River area, Northwest Territories, at three sampling periods during June and July, 1975.

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## PREPARATION, STORAGE, CONTAMINATION OF WATERS

Waters from the northern Slave Province generally have a very low content of particulates and thus do not require filtering prior to analysis. But on the basis of data obtained from High Lake (Table I), it does appear that a small portion of the Cu in the waters is associated with particulates. These data were obtained by averaging the results of four samples submitted to each of the six treatments.

In hydrogeochemical studies there is a serious possibility that the composition of a sample will change between the time it is collected and when it is analysed. Some constituents may precipitate or be adsorbed on to the container. In addition, the container, or the preservative added to the sample, may contaminate the water.

Many studies have reported a loss of metals from waters held in different types of containers at various pH levels. Most of this work has been based on synthetic solutions, containing base metals at much higher levels than are generally found in nature. While these results may not be directly applied to natural waters, they do show that losses are best prevented by storing samples in plastic bottles at low pH (usually 0.5%  $\text{HNO}_3$ ).

A recent study by Subramanian et al. (1978) provides useful data on the stability of metals in natural and synthetic waters at their natural abundance level. Examination of these data shows that the metals the geochemist would consider as being mobile (see Fig. 10) also tend to be stable in non-acidified waters held in plastic bottles. For example, Cd, Co and Ni showed no loss on storage for 30 days at pH values as high as 8.0. But less mobile elements, such as Pb, were lost at pH levels greater than 1.6 and Cu at pH greater than 4.0.

A representative suite of waters from the northern part of the Slave Province were collected in 1975 and were immediately analysed in the field for Zn and Cu. A separate bottle taken at each site was acidified in the field to 0.5%  $\text{HNO}_3$ . In November of the same year the untreated and the acidified samples were analysed in the Ottawa laboratories. The results given in Table II show

TABLE I

Effect of filtering and acidification on High Lake water

Treatment	Zn (ppb)	Cu (ppb)
Untreated	229	79
Acidified, unfiltered	235	77
Filtered, 0.45 $\mu\text{m}$	227	65
Filtered, 0.22 $\mu\text{m}$	235	66
Filtered, 0.45 $\mu\text{m}$ and acidified	233	67
Filtered, 0.22 $\mu\text{m}$ and acidified	235	66

Fig.12. Distribution of Zn in lake waters, Hackett River area, Northwest Territories, at three sampling periods during June and July, 1975.

TABLE II

Comparison of zinc and copper contents of lake waters analysed immediately after collection in July, 1975, and again in November, 1975, after storage in untreated and in acidified form

Sample	Original pH	Zn (ppb)		Cu (ppb)			
		July unacidified	November unacidified	November acidified	July unacidified	November unacidified	November acidified
865	7.3	3	5	4	< 2	1	1
Friday L.	6.5	11	9	10	4	2	3
866	7.5	16	16	19	< 2	2	3
Agricola L.	6.3	16	14	17	6	4	6
867	7.5	34	28	38	2	3	4
849	7.5	37	24	30	7	3	4
708	7.6	47	43	45	11	6	7
729	7.2	63	58	64	13	—	11
710	7.2	108	94	91	9	5	7
Yava L.	3.9	112	146	140	57	46	44
715	7.4	155	138	145	7	4	5
High L.	7.1	238	244	238	87	70	85
Median loss/gain			-10%	+1%		-33%	-18%

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that Zn is relatively more stable in solution than Cu and that the acidified samples are more stable than the untreated.

However, for exploration purposes, it is suggested that acidification is not required for these waters. It should be emphasized that waters from other areas, differing in composition, may behave differently during storage. It is probable that the mobile elements, which are most useful as indicators of mineralization, will be relatively stable during the short time required between sampling and analysis. Possibly, the same properties of an element which allow it to remain in solution in the lake, also confer stability within the sampling container. The acidification of samples, while being quite practical for research projects, adds to the logistical demands on exploration parties collecting large numbers of samples. Also, each operation on the sample increases the possibility of contamination. If there are any particulates in the water, the acid may dissolve metal from this material.

When the constituent being measured occurs at the low-ppb level, clearly precautions must be taken to avoid contamination. This applies particularly to metals, such as Zn and Cu, that are widely used by society, compared to, say, U that is limited to a few products.

The greatest possibility of contamination comes from the sample container. Most hydrogeochemical research studies now employ plastic bottles that have been soaked in acid, then rinsed several times with ultrapure water. For exploration purposes where large numbers of samples are being collected, it would be desirable if such thorough washing could be avoided. Accordingly, tests were made prior to the 1974 field season to discover if it was adequate to wash 500-ml linear polyethylene bottles (Nalgene brand) once only with sample water at the site. These tests showed that base metal contamination of purified water stored in bottles cleaned this way was negligible (similar results have been obtained for comparable bottles, but acid-washed, by Marchant and Klopper, 1978). The procedure was used during the 1974 season and provided satisfactory results for the majority of the samples. However, one batch of bottles proved to be contaminated, adding approximately 8 ppb of Zn to a full volume of sample water. This caused erroneous results for the 1974 High Lake reconnaissance survey (Cameron and Ballantyne, 1975, fig. 6). This problem has not recurred in several thousand bottles that have been used and tested since 1974, but it is strongly recommended that a representative sample of containers be tested for the metals to be measured prior to their use.

#### SAMPLING LOGISTICS

One of the principal advantages of the use of lake waters for exploration is the high sampling rates possible using helicopters.

Prior to the 1975 field season a sampling apparatus was built and installed on a Hughes 500 model helicopter. A small, high-capacity, immersible plastic pump was placed on the skid of the helicopter below the front portion of the

float. In this position water is drawn from a depth of approximately 20 cm when the aircraft is on the lake. The water then passes up through 2-cm diameter plastic tubing to three 500-ml capacity plastic containers in the rear compartment of the helicopter. One of these containers is used to fill a 500-ml sample bottle, the second holds a pH electrode, and the third, temperature and conductivity probes (Fig. 13). On landing on a lake surface, the operator in the rear compartment flushes water through the system, then allows all three bottles to fill. The helicopter lifts off to the next site. En route, the operator in the rear fills and labels a sample bottle, while the navigator in the front compartment reads pH, conductivity and temperature from an electronic console with digital output. Immediately before landing at the next site the system is drained.

Using this method only 8–12 seconds need be spent on the lake and thirty samples per hour may be collected when sampling at a density of one site per 2.8 km<sup>2</sup>. Sampling rates are determined by the climb rate and manoeuvrability of the helicopter, the skill of the crew, the local relief, and weather.

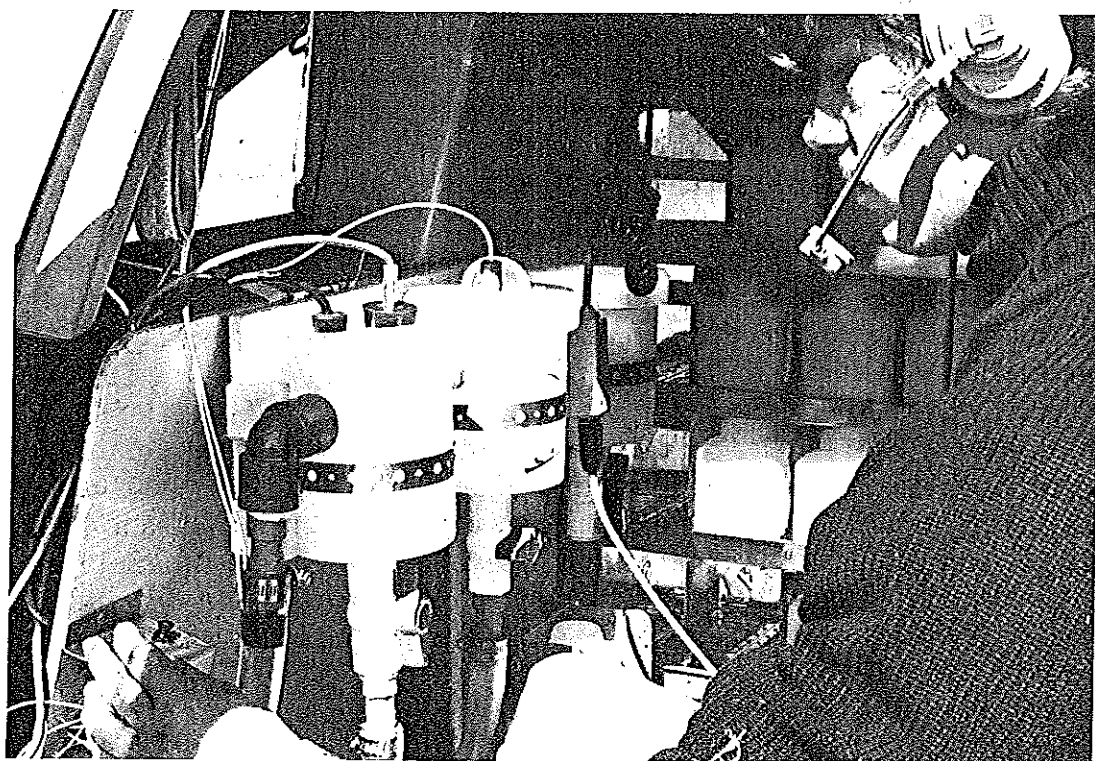


Fig.13. Rear compartment of water sampling helicopter showing plastic containers (left to right): for temperature and conductivity measurement, for pH, and for filling sampling bottles. Operator's left hand is on pump motor switch. Rack with capacity for 200 500-ml bottles in background.

## CONCLUSIONS

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TABLE III

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## CONCLUSIONS

The relative advantages of lake sediments and lake waters for geochemical exploration in northern, permafrosted areas of the Canadian Shield are given in Table III. Centre-lake sediment sampling is the method of choice for wide-interval reconnaissance surveys of large areas, such as the current National Geochemical Reconnaissance Program (Cameron and Hornbrook, 1976). This is because of the wider dispersion characteristic of sediment anomalies and because the sediment samples provide information on a larger suite of elements.

The principal application of lake water surveys is for more detailed investigation of favourable areas, such as volcanic belts. At this level of exploration the effectiveness of the method for base-metal search should be similar to that of lake sediment surveys, but at substantially lower cost because of the rapid rate of sampling possible and the absence of sample preparation. However, the work is technically more demanding at the analytical stage and in avoiding sample contamination.

For massive sulphide exploration, Zn is likely to be the most useful indicator element in lake waters because of its abundance in this mineralization and its mobility in surface waters. For Cu-Ni mineralization, Ni should be considered as an indicator for the same reasons. Cu may also provide useful information, but it is less mobile than either Zn or Ni.

TABLE III

Comparison of centre-lake sediments and surface lake waters as sampling media in the northern Canadian Shield

	Centre-lake sediments	Surface lake waters
Length of dispersion train	often long	short to moderate
Sampling variability within lakes up to 2 km <sup>2</sup>	moderate	low
Seasonal variation	nil?	low to moderate
Availability of samples	most, but not all lakes	all
Sampling costs	moderate	low
Sample preparation	required	not generally required
Possibility of contamination	low	strong
Indicator elements	mobile + immobile	mobile
Analysis (e.g., Zn, Ni, Cu)	rapid	rapid, but requiring care
Field analysis (e.g., Zn, Ni, Cu)	possible	more convenient

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## ACKNOWLEDGEMENTS

The samples were collected at different times in the company of Mr. S.B. Ballantyne, Mr. C.C. Durham and Mr. J. Thomas. Mr. R. Watson was the helicopter pilot in 1974 and Mr. G. Vinet in 1975. Field analytical work was performed by Ms. G.E.M. Hall, Ms. A.I. MacLaurin and Ms. E. Moore. Dr. Peter Bradshaw and Dr. Yvon Maurice provided critical comments on the manuscript. I am most grateful to all these persons.

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