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**EXPERIMENTAL HYDROGEOCHEMICAL SURVEYS OF
THE HIGH LAKE AND HACKETT RIVER AREAS,
NORTHWEST TERRITORIES**

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CONTENTS

	Page
Abstract/Résumé	v
Introduction	1
Acknowledgments	3
Analysis	3
High Lake area reconnaissance	4
High Lake follow-up sampling	7
Hackett River area	10
East Cleaver Lake zone	10
Boot Lake zone	10
"A" zone	10
Major element comparisons	12
Controls on the mobility of copper and zinc in northern lake waters	12
Solubility of copper	12
Solubility of zinc	13
Control by iron and manganese oxides	13
The utility of hydrogeochemical methods in the northern part of the Shield	14
Sampling interval	14
Detailed surveys	15
Mechanisms for the mobilization of base metals in permafrost terrain	15
Conclusions	16
References	17
Table 1. Zinc and copper content of lake and river waters	7
2. Selected samples from anomalous lakes in the High Lake area	7
3. Chemical determinations on waters from High Lake, N.W.T.	9
4. Chemical determinations on waters from Camp Lake, N.W.T.	12
5. Comparison of the composition of selected lake waters from Slave Province, N.W.T.	13
6. Comparison of samples collected from the same sites on July 9 and 30, 1974, Hackett River area, N.W.T.	16

Illustrations

Figure 1. Dispersion of zinc in lake sediments and waters from the Agricola Lake massive sulphide prospect	1
2. Geology of Bear and Slave provinces of the Canadian Shield	2
3. The pH of lake waters, High Lake area, N.W.T.	4
4. Zinc content of lake waters, High Lake area, N.W.T.	5
5. Copper content of lake waters, High Lake area, N.W.T.	6
6. Distribution of pH, zinc and copper in 285 lake waters from the High Lake area, N.W.T.	8
7. Location of water samples, High Lake, N.W.T.	9
8. Distribution of zinc and copper, in ppb, and pH in lake waters from the Hackett River area, N.W.T.	11
9. Equilibrium diagram for copper	14

Abstract

(In 1974 surface lake waters were sampled using a helicopter from the High Lake and Hackett River areas, Northwest Territories. Both areas are in the zone of continuous permafrost and are underlain by granites, metavolcanic rocks and metasediments.) The former area contains a zinc-copper massive sulphide body, and Hackett River several zinc-lead-silver massive sulphides.

One thousand square miles around High Lake were sampled at a density of one per 3.5 square miles. At Hackett River 12 square miles were sampled at a density of two per square mile. (The pH and the zinc and copper contents of the waters were analyzed in field laboratory equipped with atomic absorption spectrometer. A variety of elements (SiO₂, Al, Fe, Mn, Ca, Mg, Na, K, HCO₃, SO₄ and Cl) were later analyzed in Ottawa.)

The waters have a very low content of dissolved solids. The pH of the waters correlates well with bedrock composition, being somewhat greater than neutral for volcanic rocks, including those containing calcareous beds, and slightly less than neutral for granitic rocks. The median content of zinc in the 285 waters from the High Lake area is 8.8 ppb and for Cu less than 1 ppb. Lakes near sulphide mineralization have much greater contents of these metals, which testifies to their active, present-day oxidation in this permafrost terrain. The low iron and manganese contents of the water contribute to the mobility of zinc and copper. Limited data are given on seasonal variation, which may be significant for weakly anomalous lakes.

(Hydrogeochemical methods of mineral exploration will likely be used more widely in this northern permafrost environment. As well as the active oxidation of sulphides and the migration of indicator metals, factors contributing to their utility are the wide availability of water in lakes, streams and seeps, and the ease and rapidity of sampling, sample preparation and analysis.)

Résumé

En 1974, on a prélevé, à l'aide d'un hélicoptère, des échantillons d'eau à la surface des lacs dans les régions du lac High et de la rivière Hackett, dans les Territoires du Nord-Ouest. Ces deux régions sont situées dans la zone de pergélisol et reposent sur du granite, des roches métavolcaniques et des métasédiments. La région du lac High renferme un gisement massif de sulfures de zinc-cuivre, tandis qu'autour de la rivière Hackett, on retrouve plusieurs dépôts massifs de zinc-plomb-argent.

Dans la région du lac High, on a couvert une surface de mille milles carrés où on a prélevé un échantillon par 3.5 milles carrés, tandis qu'autour de la rivière Hackett, on a prélevé deux échantillons par mille carré sur une surface totale de 12 milles carrés. Le pH ainsi que la teneur en zinc et en cuivre de l'eau ont été analysés dans un laboratoire mobile équipé d'un spectromètre à absorption atomique. Une variété d'éléments (SiO₂, Al, Fe, Mn, Ca, Mg, Na, K, HCO₃, SO₄ et Cl) ont été analysés par la suite à Ottawa.

Ces échantillons d'eau ont une très faible teneur en solides dissous. Leur pH correspond bien à la composition des roches de fond; il est légèrement basique dans le cas des roches volcaniques, y compris celles qui renferment des dépôts calcaires, et légèrement acide dans le cas des roches granitiques. La teneur moyenne en zinc des 285 échantillons d'eau prélevés dans la région du lac High est de 8.8 parties par milliard, alors que la teneur en cuivre est inférieure à une partie par milliard. Dans les lacs situés à proximité des zones de minéralisation de sulfures, la teneur en ces métaux, est beaucoup plus importante, ce qui prouve qu'ils s'oxydent de façon active dans le pergélisol. La faible teneur en fer et en manganèse de l'eau contribue à la mobilité du zinc et du cuivre. On a recueilli peu de données sur les variations saisonnières, lesquelles peuvent revêtir une grande importance dans le cas des lacs qui présentent de faibles anomalies.

Il est probable que l'on fera appel plus souvent aux méthodes hydrogéochimiques pour l'exploration minérale dans le pergélisol. Outre l'oxydation active des sulfures et la migration des indicateurs métalliques, les facteurs qui rendront ces méthodes encore plus utiles sont la grande quantité d'eau dont on dispose dans les lacs, les rivières et aussi les eaux de filtration, ainsi que la facilité et la rapidité avec lesquelles on recueille, prépare et analyse les échantillons.

EXPERIMENTAL HYDROGEOCHEMICAL SURVEYS OF THE
HIGH LAKE AND HACKETT RIVER AREAS, N. W. T.

INTRODUCTION

Hydrogeochemical methods, as discussed by Boyle *et al.* (1971), have been used infrequently in the Canadian Shield. Features that have discouraged such use are the relatively impermeable nature of Shield rocks, low topographic relief and the various effects of glaciation. Moreover, there has been a widespread belief that the oxidation processes necessary for mobilization and dispersion of metals in solution from sulphide mineralization were not active in northern permafrost areas of the Shield.

In 1974, follow-up investigations on the 1972 Bear-Slave Lake sediment reconnaissance were performed in the Agricola Lake area, Northwest Territories (Cameron, 1975a). This work drew attention to the active nature of oxidation processes in this permafrost environment and, therefore, to the possible utility of hydrogeochemical methods for mineral exploration in the northern part of the Shield. Figure 1 summarizes the dispersion of zinc in the surface drainage, one of the most mobile components of the massive sulphide

mineralization in the Agricola Lake area. This figure shows that the zinc content of stream and lake waters is greatest near the source and decreases rapidly down-drainage. By contrast, the maximum zinc content of lake-centre and nearshore sediments occurred several kilometres from the source and anomalous levels of zinc in these materials continued for several miles before background concentrations were reached. For this drainage system these relationships were governed by pH controls on precipitation, by dilution of the zinc-rich waters, and possibly, by down-drainage transportation of particulate matter onto which zinc has been sorbed or precipitated. In other areas, where carbonate rocks are well developed, the left-hand portion shown in Figure 1 may be truncated because of the buffering effect of the carbonate on pH. However, the basic pattern of dispersion illustrated in this figure may be fairly typical of the organic-poor, permafrosted areas of the Shield.

The importance of the distribution patterns shown in Figure 1 is to illustrate the respective rôles of lake sediment and lake water geochemistry in mineral

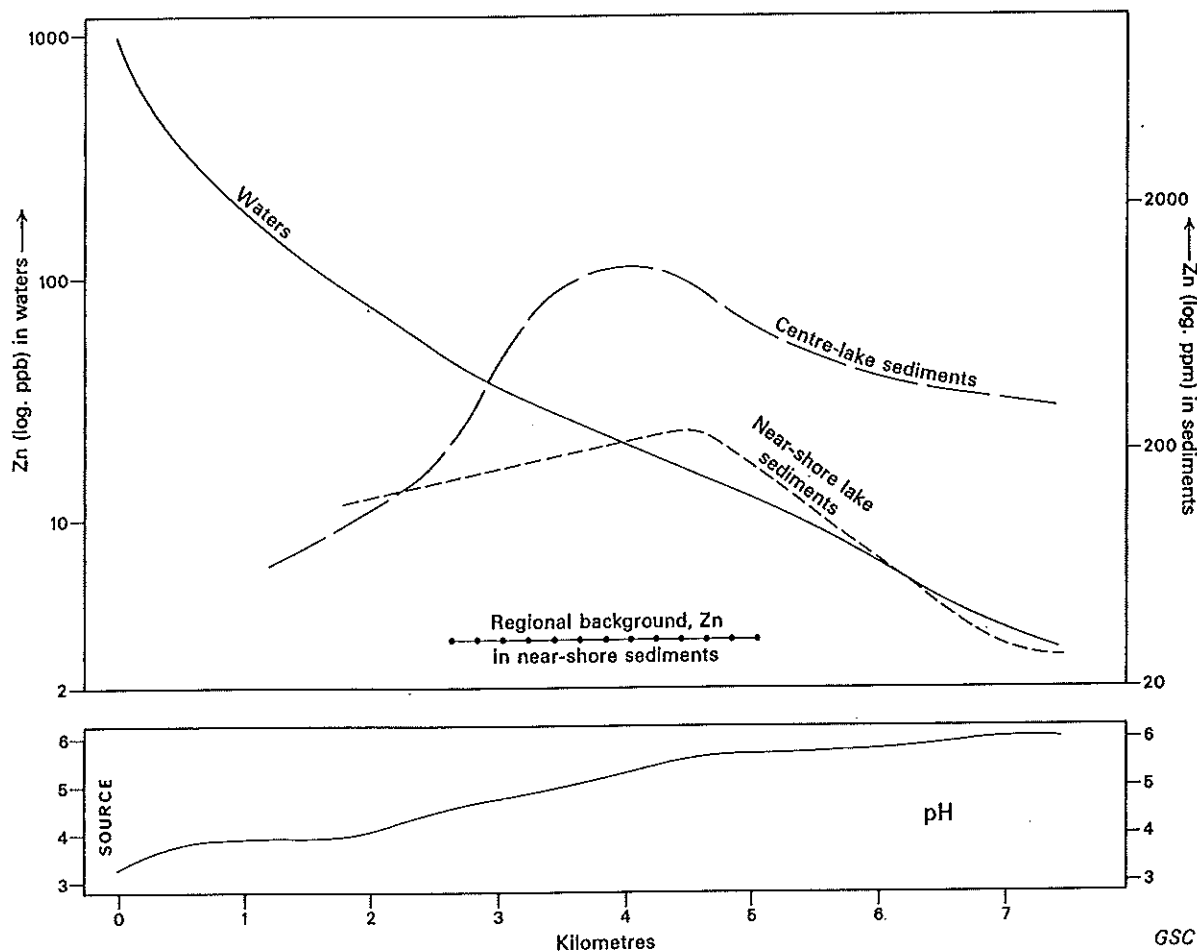


Figure 1. Dispersion of zinc in lake sediments and waters from the Agricola Lake massive sulphide prospect.

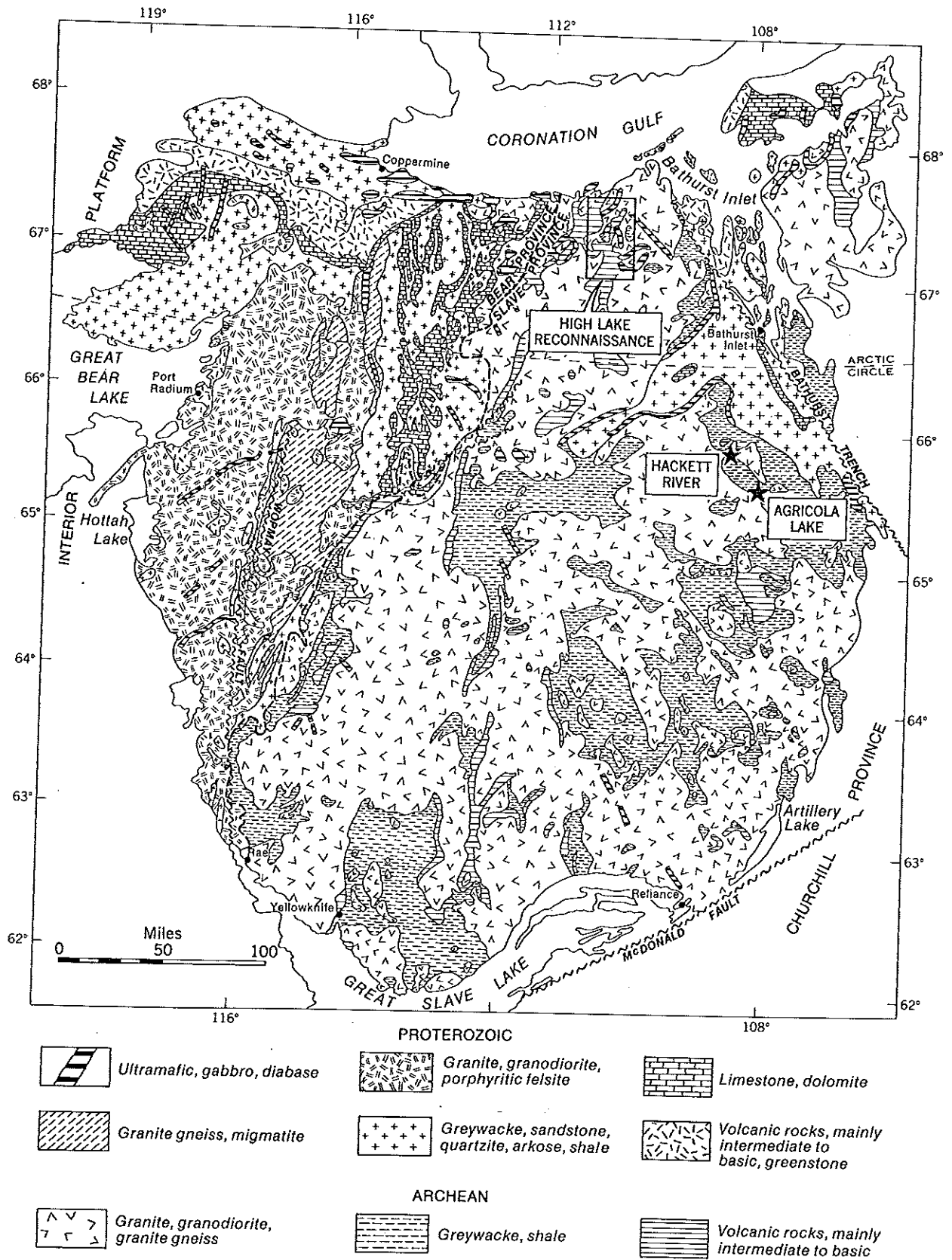


Figure 2. Geology of Bear and Slave provinces of the Canadian Shield, showing location of study areas.

exploration in the northern part of the Shield. Since anomalous levels of mobile metals, such as zinc, may be found in lake sediments some distance from actively oxidizing mineralization, this is the method of choice for wide-interval, reconnaissance surveys. The Bear-Slave operation (Allan *et al.*, 1973) sampled nearshore lake sediments at a density of one sample per 10 square miles. (Current studies suggest that lake-centre sediments may be even more suitable for reconnaissance surveys in the northern part of the Shield. In the organic-rich environment of the southern part of the Shield lake-centre sampling has been used more extensively.) Compared to sediments, waters reach background levels much more quickly by the combined effects of precipitation and dilution. Water samples are inherently less suitable for reconnaissance surveys since they require a higher sample density but for following-up reconnaissance surveys, or for more detailed surveys, hydrogeochemistry has a number of important advantages, including ease of sampling, sample preparation and analysis.

Hydrogeochemistry may be of most use in areas of high, but undefined, mineral potential. The volcanic belt in the Northwest Territories, in which the High Lake zinc-copper massive sulphide deposit is located, is such an area. This belt was mapped by Fraser (1964) with areas of it described recently by Padgham (1974). Felsic volcanics with associated gossans are common; indeed, there are many hundreds of gossanous outcrops in the area studied by authors. This volcanic terrane has a rugged local relief (up to 100 m) which gives rise to an abundance of lakes and ponds.

On July 6 and 7, 1974, 285 surface lake water samples were collected from a 1000 square mile (2590 km²) area centred on High Lake (Figure 2). Sampling was carried out from a float-equipped, turbine-powered, Hughes 500 helicopter in 13.75 hours for a sampling rate of 21 per hour which included time spent travelling to and from the fueling base at High Lake. The waters were obtained by filling a 500 ml plastic bottle from the float of the helicopter. Substantially improved sampling rates could be achieved by slightly more sophisticated methods of sample collection. After the pH was determined and each sample was analyzed for zinc and copper in a field laboratory located in the Agricola Lake area (Figure 2), follow-up sampling was carried out on July 18 and 19, 1974.

The Hackett River area (Figure 2), which is now being actively explored, contains a number of zinc-copper-lead-silver massive sulphide bodies (MacNeill, 1973). Lake sediments were collected in this area during both the 1972 Bear-Slave reconnaissance (Allan *et al.*, 1973) and the 1973 follow-up studies (Cameron and Durham, 1974b). On July 9, 1974, 40 water samples were collected from lakes in the vicinity of this camp.

Acknowledgments

We wish to thank Mr. Richard Bailes and the management of Kennco Exploration (Canada) Ltd. for the hospitality they offered at their High Lake camp. Mr. Paul Wilton of Caminco Ltd. facilitated our sampling of the Hackett River area.

Part of the water sampling was carried out by Mr. Robert Benson. Mr. Robert Watson very capably piloted the helicopter. The field analyses were performed by Mr. R. E. Horton, Miss Elizabeth Ruzgaitis and Miss Sue Costaschuk. The laboratory analyses were completed by Mr. J. J. Lynch, Mr. G. Gauthier and Ms. Alice MacLaurin. Drs. R. W. Boyle and I. R. Jonasson kindly read the manuscript and provided much useful comment.

Analysis

The water samples were collected in 500 ml polyethylene bottles. Within two to three days of collection the pH value and the zinc and copper contents of each sample were determined in a field laboratory. The waters were invariably clear and were not filtered prior to analysis. Acids or other preservatives were not added to the samples at any time. The pH was measured at ambient temperatures of 15 to 20°C. Analysis for zinc and copper was by atomic absorption spectrometer after extraction with APDC-MIBK (Horton and Lynch, 1975). Several samples were returned to the Ottawa laboratories and reanalyzed several months later; they included 36 of the 285 High Lake reconnaissance samples, many of the High Lake follow-up samples, and all of the Hackett River samples. These samples were extracted with APDC-MIBK and analyzed for zinc, copper, lead, nickel, and cobalt. The elements manganese and iron were determined by direct aspiration of the water into the flame of an atomic absorption spectrometer. The detection limit for each of these elements was (in ppb): zinc 1, copper 1, lead 2, nickel 2, cobalt 2, manganese 5 and iron 10. The elements, lead, nickel and cobalt, which were not detected in any of the samples, will not be discussed further.

The data obtained for zinc and copper in the Ottawa laboratories were similar to the field data except that higher values were formed for a number of samples which appears to have been due to incomplete extraction of the metals in the field laboratory.

The data given in the following pages for the different groups of samples were obtained as follows:

- (a) High Lake area, 285 reconnaissance samples: all pH, zinc and copper values determined in field laboratory.
- (b) High Lake area, follow-up samples: pH data from field laboratory; other data from Ottawa laboratory.
- (c) Hackett River area: pH data from field laboratory; other data from Ottawa laboratory.

In addition to these determinations a few critical samples were analyzed for the major components: Ca, Mg, Na, K, Cl, Al, SO₄, alkalinity as HCO₃, and SiO₂. Because of the limited amount of water available not all of these components were analyzed in each sample. Analysis was by conventional techniques (Lively, 1974). Specific conductance, corrected to 25°C, was measured on most samples returned from the field.

High Lake Area Reconnaissance

The distribution of pH zinc and copper values in these waters is shown in Figures 3, 4 and 5. Geological boundaries are based on a map by Fraser (1964). Histograms of the variables are given in Figure 6.

The major regional control on the pH of the waters appeared to be bedrock composition. Thus, areas underlain by volcanic rocks had pH values of 7.0 or greater. Carbonate horizons were common within the

volcanics (Padgham, 1974) and probably contributed to this distribution of pH. Waters from areas underlain by granitic rocks had a slightly lower pH, in the range 6.7 to 7.0. The second most important control on pH was the presence of oxidizing sulphides. Several areas with pH values of 6.6 or less (Figure 3) were in volcanic terrane.

Only 14 per cent of the water samples had a zinc content less than the detection limit of 1 ppb. The median zinc content of 8.8 ppb appeared to be average

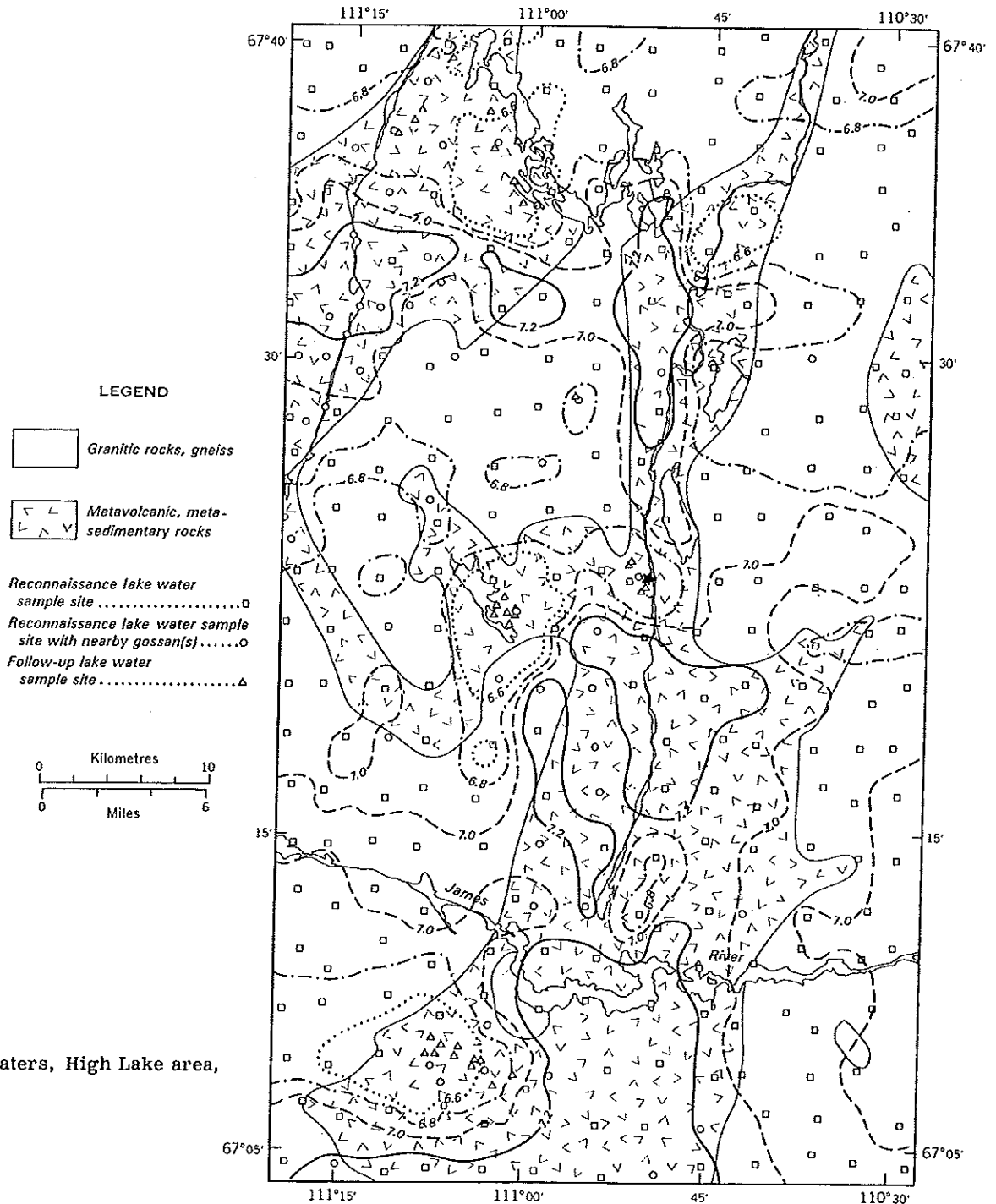


Figure 3
The pH of lake waters, High Lake area,
N. W. T.

compared to data from elsewhere in the world given in Table 1. However, it should be recognized that these northern waters are relatively purer than the majority of waters from more temperate regions. The 36 reconnaissance water samples returned to Ottawa had a median value for specific conductance of 29 micromhos. Using the relation of specific conductance (specific conductance $\times 0.6 =$ dissolved solids in ppm), this is equivalent to only 17 ppm dissolved solids. For North America, Livingstone (1963) gives a mean dissolved

solids content of 142 ppm for fresh waters. Thus, in terms of the total dissolved solids, the zinc content of these waters was relatively high.

Zinc values greater than 20 ppb occurred at or near the margin of the metavolcanic belt (Figure 4). The highest values on the reconnaissance sampling were found in High Lake (250 ppb) and in a pond 8 km west of High Lake. Data on the latter sample and other samples collected during reconnaissance sampling with a zinc content greater than 50 ppb are presented

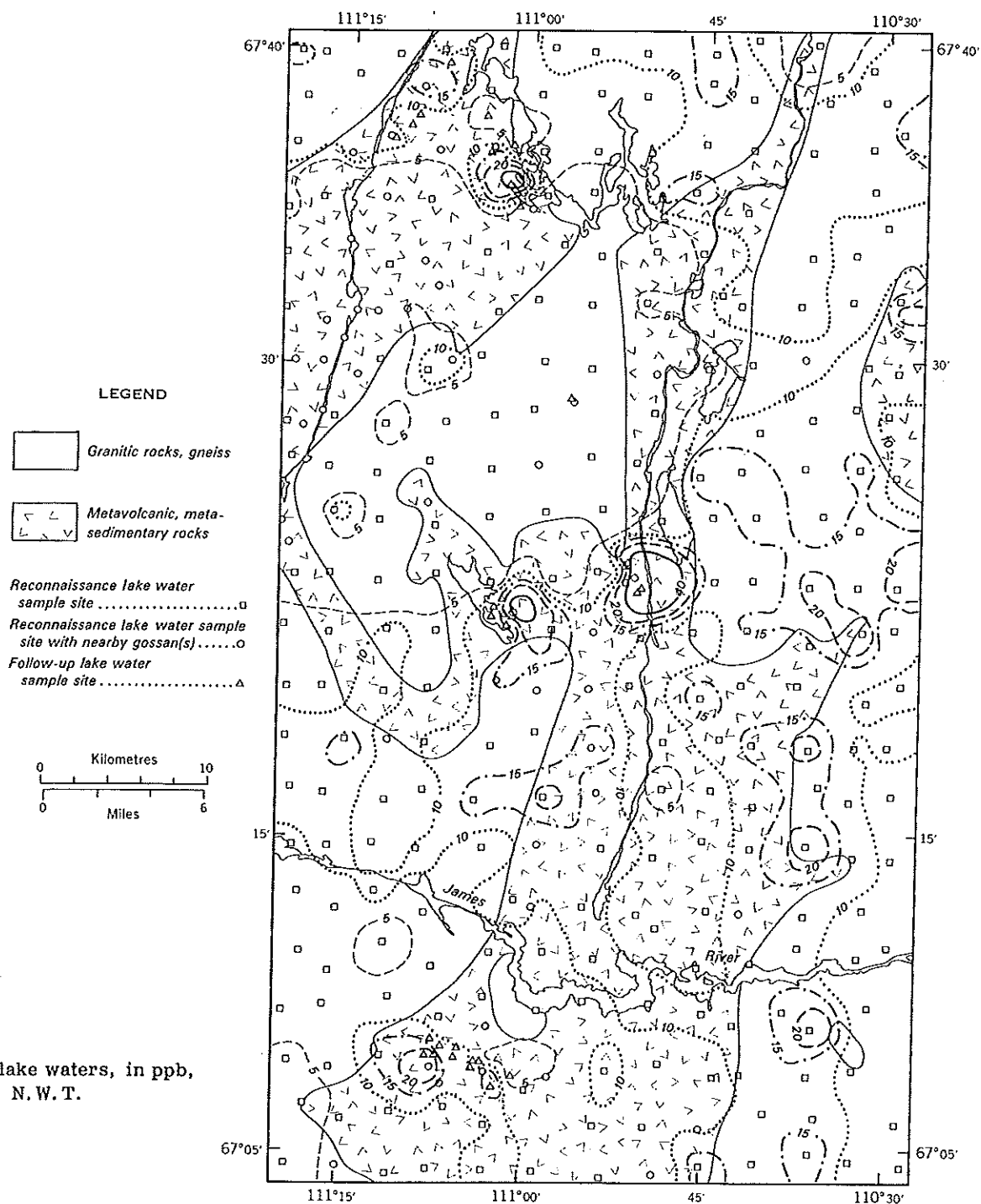


Figure 4
Zinc content of lake waters, in ppb,
High Lake area, N. W. T.

in Table 2. Enhanced levels of zinc and copper were associated with water of low pH derived from oxidizing sulphides.

The general level of abundance of copper was approximately one order of magnitude lower than for zinc. More than half of the samples contained less than the detection limit of 1 ppb copper (Figure 6). There are two probable reasons for this. The first is that the rocks of the region contained more zinc than copper by a factor of approximately two (Allan *et al.*,

1973). Secondly, more detailed hydrogeochemical studies in the Agricola Lake area of the Slave Province (Cameron and Durham, 1974a, 1974b; Cameron and Lynch, 1975; and Cameron, unpublished report) have shown copper to be less mobile in the surface drainage than zinc. Thus once in solution it was more easily precipitated than zinc. In the Agricola Lake drainage system, precipitation of copper from water containing about 50 ppb copper took place about pH 4, whereas similar levels of zinc precipitated most strongly about

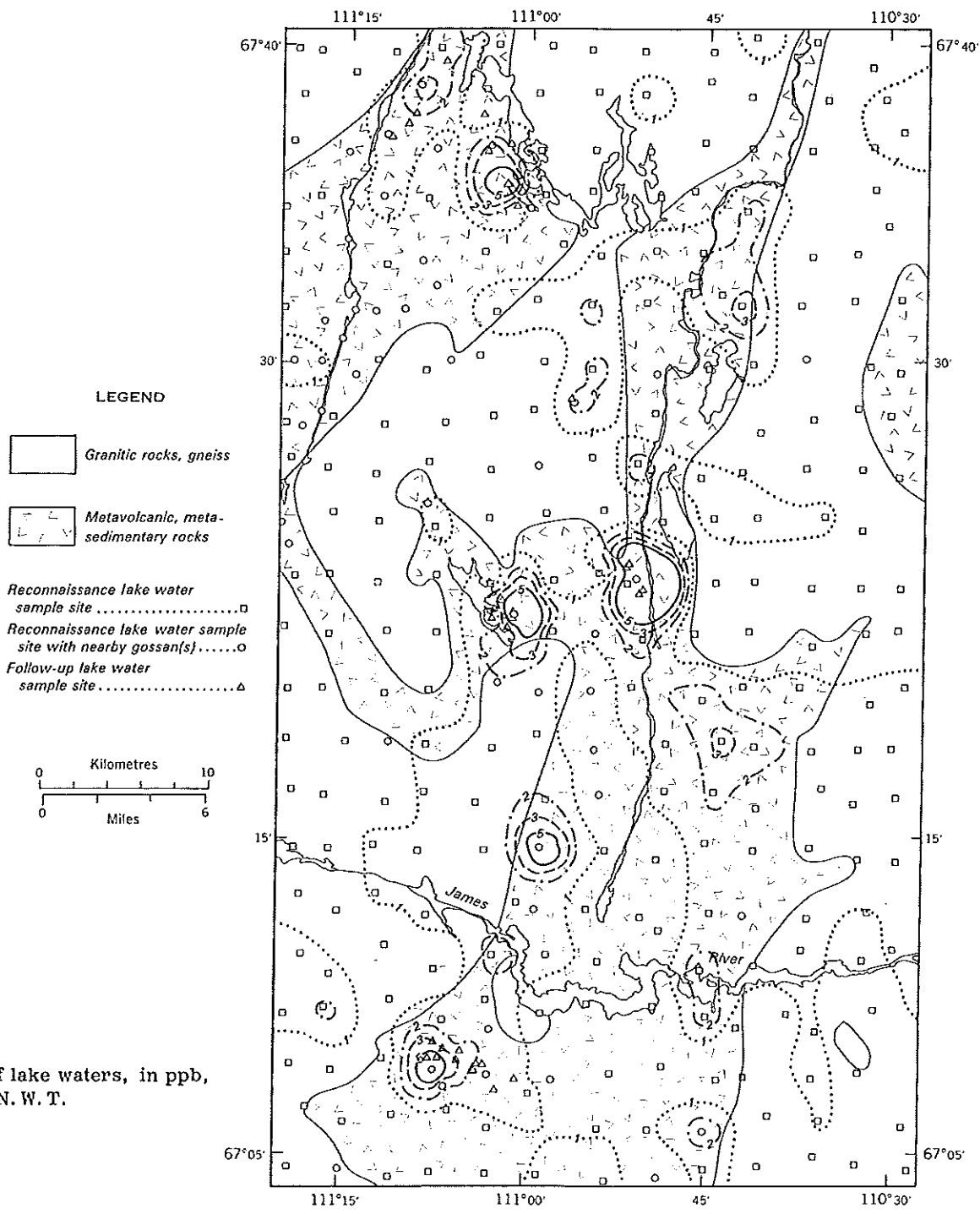


Figure 5
Copper content of lake waters, in ppb,
High Lake area, N. W. T.

pH 5.5. The pioneer work of Boyle *et al.* (1955) showed that zinc travelled farther than copper in surface waters derived from oxidizing sulphide veins in the Yukon. Only 7 of the 285 water samples contained 5 ppb copper or greater. Like zinc, the samples with higher values of copper (> 2 ppb) occurred at or near the margins of the volcanic belts (Figure 5). There is a good, but not perfect, spatial correlation between the higher values for zinc and copper.

Hornbrook (*in Boyle et al.*, 1971) found that the regional content of zinc and copper in the Kaminak Lake area, Northwest Territories, to be "much less than 1 ppb." This area is similar to that around High Lake in that it contains a granitic/volcanic/sedimentary assemblage and is in the zone of continuous permafrost. The much higher zinc content of many of the waters from the High Lake area may have been derived from

oxidizing sulphides present within the volcanic rocks. If this occurred, it may indicate that there is a greater potential for zinc-bearing sulphides in the High Lake area than at Kaminak Lake.

High Lake Follow-up Sampling

A limited follow-up of the areas containing the more anomalous water samples was completed on July 18, 1974. This was done to confirm their anomalous nature, not to explain their cause. However, it was readily apparent that in all cases the anomalies were associated with gossans. A few samples of these gossans were obtained but these cannot be considered representative of the sites. Chemical data on the reconnaissance waters and the more anomalous of the follow-up waters from these areas are given in Table 2 along with data for

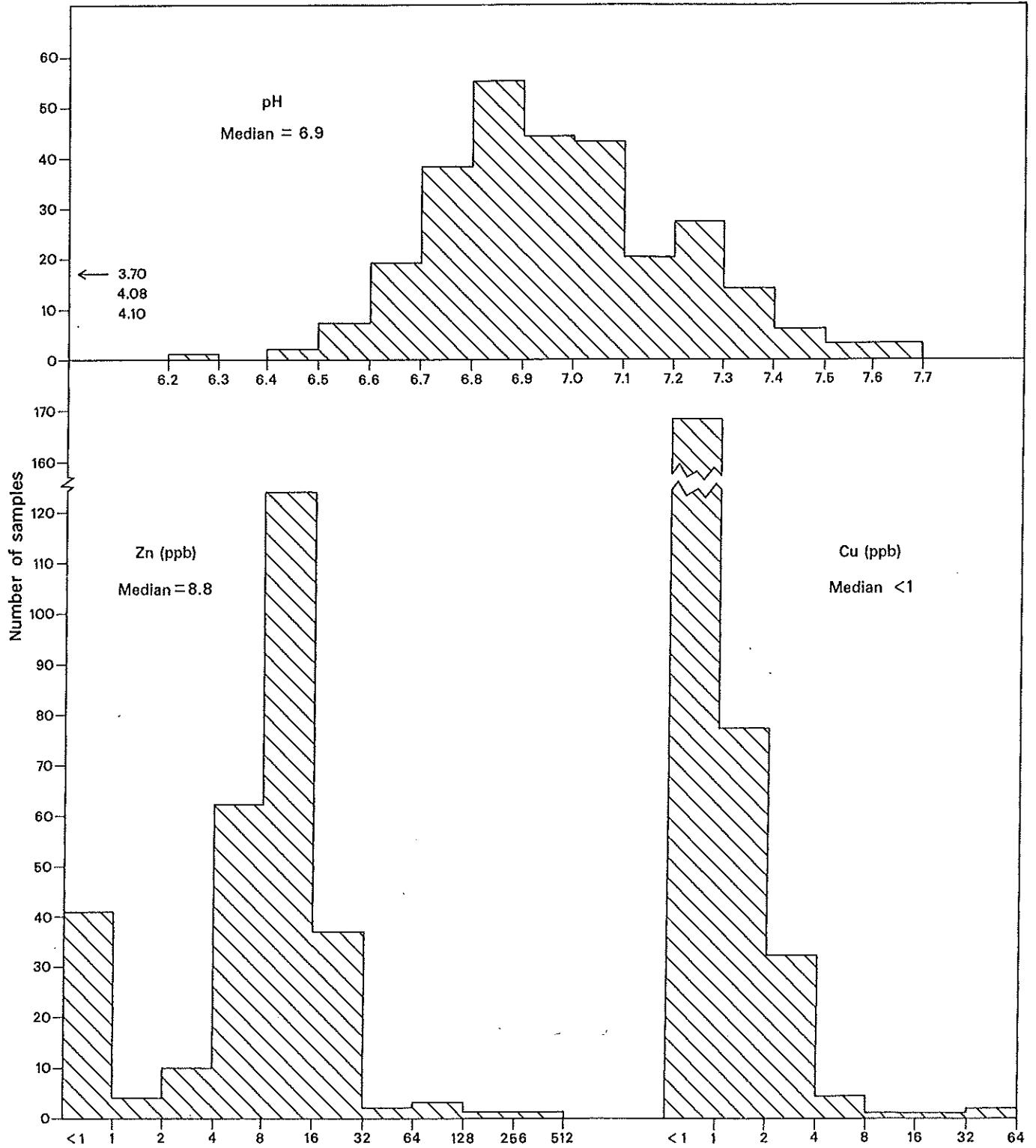
Table 1
Zinc and copper content of lake and river waters

Location	Number of Samples	Zinc		Copper		Reference
		Range ppb	Mean ppb	Range ppb	Mean ppb	
Mackenzie River drainage	100	<1 - 10	1 ⁽¹⁾	<1 - 10	2 ⁽¹⁾	Reeder <i>et al.</i> (1972)
Rivers, U.S.A.	726		20 ⁽²⁾			Durum, in Hem, (1972)
Rivers, Siberia	4 374	0.1 - 5 770	13	0.1 - 20 710	10.3	Udodov and Parilov (1961)
Lakes, Maine	440	0.25 - 34	2.5	0.07 - 140	11.6	Kleinkopf (1960)
Lakes, Sierra Nevada	170	0.3 - 100	1.5	0.4 - 5	1.2	Bradford <i>et al.</i> (1968)
Lakes, Japan	31	1.3 - 79	13.2	0.5 - 7	1.9	Morita (1955)
Rivers, Japan	12	1.5 - 9.4	5.0	0.4 - 3.2	1.4	Morita (1955)
High Lake area	285	<1 - 354	8.8 ⁽²⁾	<1 - 61	<1 ⁽²⁾	This report

Table 2
Selected water and gossan samples from vicinity of anomalous lakes located during hydrogeochemical reconnaissance, High Lake area, N.W.T.

Sample Number	U.T.M. Co-ordinates	Zn ppm	Cu ppm	pH	Sample Number	U.T.M. Co-ordinates	Zn ppm	Cu ppm	Pb ppm	Ag ppm
742378	499200E7472400N	354	61	3.7	747003	499200E7472000N	209	81	629	2.7
740177	499100E7472100N	280	96	3.7	747004	499400E7472100N	95	11	70	14.2
747007	499200E7472100N	388	208	3.6	747009	499100E7472100N	191	371	60	6.1
					747010	499000E7472200N	91	27	60	25.2
742386	498000E7445300N	57	5	6.9	740184	494400E7445500N	16	32	114	0.8
742398	494600E7445600N	90	19	4.1	740198	498200E7445500N	103	293	2	0.9
740185	494600E7446200N	116	20	4.1						
742214	501000E7496900N	76	0.4	7.0	740166	497800E7501800N	50	55	229	1.0
742215	498900E7497300N	94	13	4.1	740167	498300E7500600N	21	278	15	3.4
740173	498400E7498000N	124	14	4.0						
742232	493600E7503300N	53	5	6.7	740161	491200E7500600N	320	946	4 000	39.9
740152	495200E7504900N	16	2	6.4						

Note: (Reconnaissance water samples are 742xxx)



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Figure 6. Histograms showing the distribution of pH, zinc and copper in 285 lake waters from High Lake area, N. W. T.

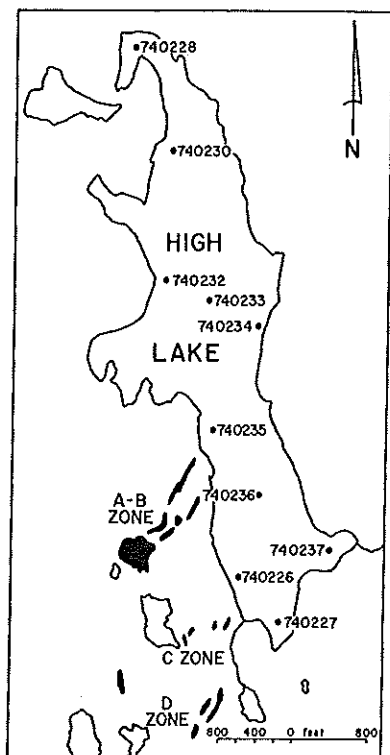


Figure 7
Location of water samples, High Lake, N. W. T.

the gossan samples containing the greatest amounts of lead or silver. As has been previously shown for this region (Cameron and Durham, 1974a, 1974b), zinc and copper were largely removed during the formation of gossans over base metal rich sulphides. Sulphide zones enriched in the metals zinc, copper, lead and silver were characterized by gossans anomalous in the latter two metals and by nearby lake waters and sediments enriched in zinc and copper. Gossan samples from areas A and D were anomalous for lead and highly anomalous for silver.

On July 18 and 19, samples were also collected from High Lake. The locations of these water samples are shown on Figure 7 and the corresponding data in Table 3. The pH data were obtained within two days of collection. The remaining data were obtained in the Ottawa laboratories several months later. Zinc and copper were measured by atomic absorption spectrometry after extraction with APDC-MIBK. Manganese and iron were measured by direct aspiration of the waters into the flame. Again it should be noted that these waters were at no time filtered or acidified.

From the consideration of using hydrogeochemistry for mineral exploration, the most important feature apparent from the data in Table 3 is the uniformity of zinc and copper in waters collected at different sites across the surface of the lake. This indicates that surface mixing was thorough, and that in lakes of moderate size, the site chosen for sampling is not critical. This confirmed data obtained elsewhere in the Slave Province including the Agricola Lake area (Cameron and Lynch, 1975) and the Hackett River massive sulphide camp (see below). Of equal practical

Table 3.
Chemical determinations on waters from High Lake, N.W.T.

Sample Number	pH	Parts per billion			
		Zn	Cu	Mn	Fe
740226	6.2	204	51	<5	18
740227	6.3	195	54	<5	17
740228	6.4	191	48	<5	14
740230	5.8	197	55	<5	17
740232	6.4	202	56	<5	15
740233	6.5	202	61	<5	11
740234	6.2	208	61	<5	12
740235	6.4	200	60	<5	12
740236	6.5	200	58	<5	15
740237	6.6	208	60	<5	15

importance was the excellent reproducibility of the data, despite the fact that the samples were neither filtered nor acidified. Treatises discussing water sampling, particularly for trace element measurements, almost universally recommended filtering (through 0.45 μm filters or finer) and acidification. Filtering was to remove suspended material and acidification was to prevent the sorption of dissolved constituents onto the container walls. The zinc and copper values shown in Table 3 are generally comparable with the field results, although they were somewhat lower and less reproducible because of incomplete extraction of some samples by the field procedure. Since the manganese and iron are total determinations they indicate that the amount of suspended solids (e.g., clays, iron and manganese hydroxides) present were very low. Indeed, the levels measured are not incompatible with all manganese and iron in the waters being in the dissolved state (Kennedy *et al.*, 1974; Jones *et al.*, 1974). Some 36 of the 285 reconnaissance water samples from the area were also analyzed for manganese and iron. For waters of pH 6.2 or greater the maximum iron content measured was 20 ppb and most waters were found to contain less than the detection limit of 10 ppb. Similarly, for these waters, most manganese determinations were less than the 5 ppb detection limit and ranged up to only 7 ppb. However, the three acid waters sampled contained much more of these elements, for example, up to 267 ppb manganese and 225 ppb iron, at pH 3.7 in sample 742378.

The apparent absence of major sorption of trace metals onto the container walls may be related to the purity of the waters. Waters containing significant amounts of suspended or dissolved solids may lose trace metals when these are sorbed onto clays or iron hydroxides that become coated on the container walls. Careful tests to assess the loss of metals from the northern waters during storage are planned for the 1975 field season.

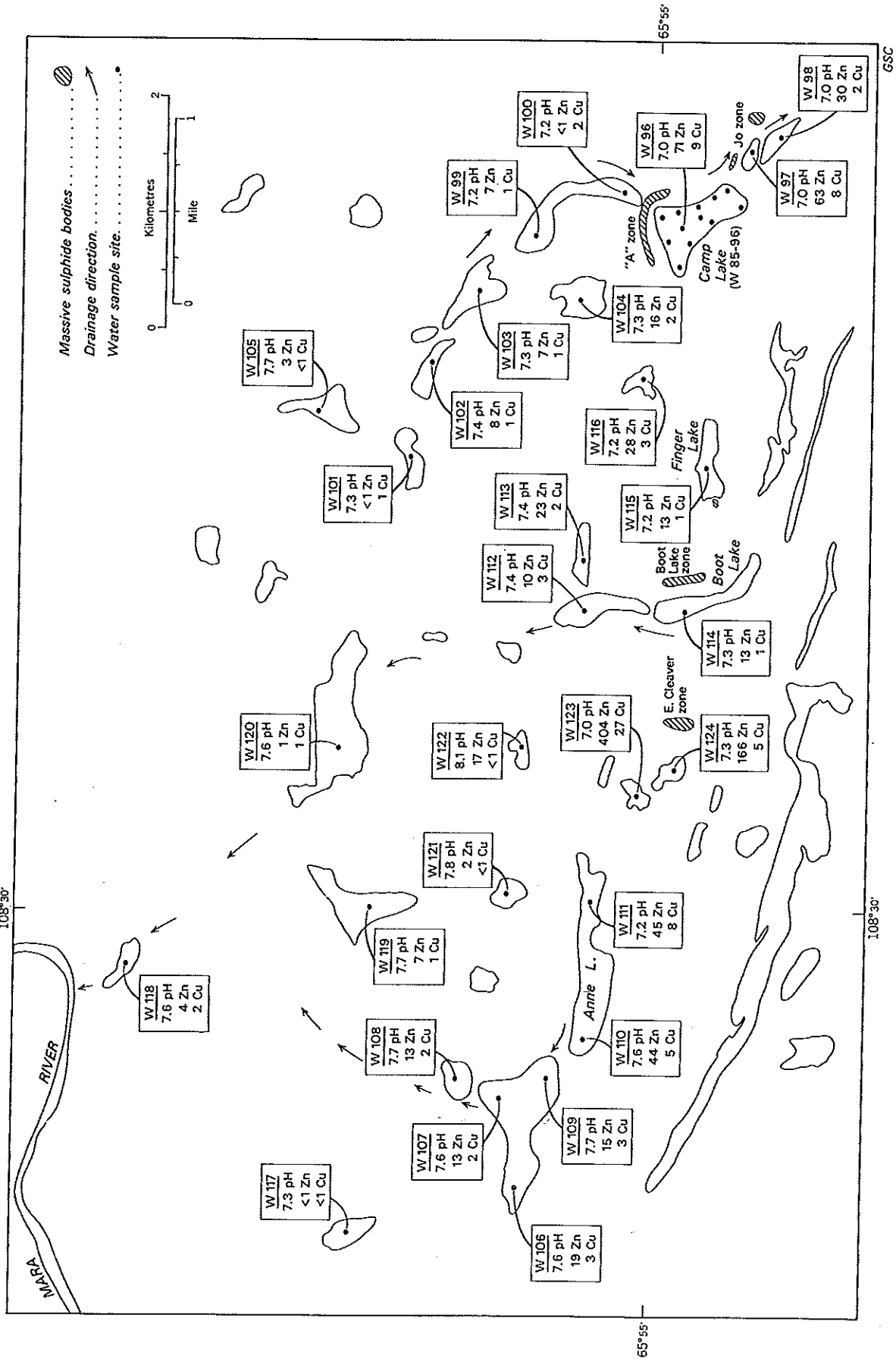


Figure 8. Distribution of zinc and copper in ppb, and pH in lake waters from the Hackett River area, N.W.T.

The waters in High Lake result from the mixing of regionally "normal" waters with metal-enriched, sulphate-bearing waters derived from the oxidation of the flanking sulphides. Water flowing into the north (unmineralized) end of the lake measured 4 ppb zinc and 2 ppb copper at pH 6.7, whereas two waters flowing from the A-B zone (Figure 7) measured 1800 ppb zinc and 1000 ppb copper at pH 3.8, and 16 000 ppb zinc and 68 000 ppb copper at pH 3.0 respectively. Limestone beds, exposed along the shore of the lake, keep the pH of the lake waters near neutral despite the addition of acid waters. In this respect High Lake differs from the acid waters of the Agricola Lake area (Cameron and Lynch, 1975) where carbonate rocks are not as well developed.

The High Lake deposit was discovered in 1955 and contains 2.4 million tons of 5.4 per cent copper, 1.1 per cent zinc and 0.03 oz/ton gold in the A-B zone and 2.8 million tons 2.0 per cent copper, 3.6 per cent zinc, 1.1 oz/ton silver and 0.02 oz/ton gold in the D zone (Figure 7). Although some trenching activity has contributed to modern oxidation of the deposit there is abundant evidence of present day oxidation over parts of the deposit unaffected by trenching. White sulphate encrustations are common and at one site copper-rich solutions had been drawn to the surface of the soil by capillary action where blue copper salts had precipitated. High Lake appears to receive a much higher flux of metals from the copper-rich A-B zone than from the D zone. The high zinc to copper ratio of 3.6 for High Lake waters may be caused by solubility control over the dissolved copper. In fact green copper stain was observed on boulders below the water line near the A-B zone.

Hackett River Area

The Hackett River area lies 200 km south-southeast of High Lake (Figure 2) and is being actively explored. Drilling has proved a number of lenses of lead-zinc-silver-bearing massive sulphides along an 8 km strike. Little information has been published on the geology of the area, but the sulphide mineralization is located in felsic volcanics. Prominently associated with the volcanics are carbonate horizons and disseminations, presumably of exhalative origin.

As presently defined, sulphides occur in a number of lenses extending from the south of Anne Lake to the Jo zone southeast of Camp Lake (Figure 8). The three most important zones are:

East Cleaver Lake Zone

MacNeill (1973) estimated 4 million tons of ore grading approximately 7.1 per cent zinc, 1.1 per cent lead, 0.45 per cent copper and 185 ppm silver. There is a further estimate of 4 million tons of lower grade material containing approximately 1.08 per cent zinc, 0.84 per cent lead, 0.48 per cent copper and 33 ppm silver. On average, there is 20-25 feet of overburden.

Boot Lake Zone

Recent estimates by the holder of the claims, Bathurst Norsemines Ltd., give a minimum of 5 million tons to the 800 foot depth. Hole NB 74-4 intersected 112 feet grading 7.5 per cent zinc, 1.1 per cent lead, 0.32 per cent copper and 182 ppm silver; and 61 feet grading 0.43 per cent zinc, 0.05 per cent lead, 1.29 per cent copper and 49 ppm silver. There appears to be a thick overburden cover on this zone.

"A" Zone

This contains two main lenses averaging about 8.5 per cent zinc, 1.4 per cent lead, 0.25 per cent copper and 240 ppm silver (MacNeill, 1973).

Most lakes in the vicinity of the prospective area were sampled. The data for pH, zinc and copper are given on Figure 8. Drainage directions are shown where possible; for some lakes it was difficult to judge the direction of drainage. Twelve samples were taken from Camp Lake. These were collected to estimate the homogeneity of the waters within a single mineralized lake. The samplings were evenly distributed across the surface of the lake. These data are given in Table 4.

The determinations on the Camp Lake samples, as for High Lake, showed a marked homogeneous distribution of trace metals in the waters. Examining the distribution of trace metals in this and other lake water samples, the zinc content clearly outlined the main mineralized zones, but the results were variable depending on local conditions. Thus sample 123, from a small lake margined by gossanous outcrops and near the East Cleaver Lake zone, contained 404 ppb zinc. By contrast, sample 114 adjacent to the overburden-covered Boot Lake zone contained only 13 ppb zinc. However, even this value was anomalous because zinc values in lake waters away from the mineralized zones ranged from 1 to 7 ppb. This was consistent with earlier data on low background base metal content of rocks (Allan *et al.*, 1973) and lake sediments (Cameron and Durham, 1974b) from this area.

With the exception of sample 123 with 27 ppb, the copper content in Hackett River lake waters ranged from 1 to 9 ppb. Copper was not as effective an indicator of mineralization as zinc, although the higher values occurred only near the mineralized zones. Copper was much less abundant in Hackett River lake waters than in High Lake waters (e.g. the zinc to copper ratio for Camp Lake is 7.9 compared to 3.6 for High Lake). This may reflect the copper-poor nature of the mineralization at Hackett River or, alternatively, the greater pH of Hackett River waters.

Anomalous levels of zinc and copper did appear to have been carried down-drainage from one lake, to another, with an inevitable decrease in metal content (e.g. Figure 8 samples: samples 111-110-109-108; samples 114-112; and samples 96-97).

One of the most interesting aspects of data from this area is the universally neutral to slightly alkaline pH of the lake waters. The area contains many gossans

Table 4
Chemical determinations on waters from
Camp Lake, N.W.T.

Sample Number	pH	Parts per billion			
		Zn	Cu	Mn	Fe
740085	6.9	63	9	<5	<5
740086	6.8	71	9	<5	<5
740087	6.9	69	9	<5	<5
740088	6.9	70	9	<5	<5
740089	7.0	71	10	5	<5
740090	7.0	70	9	<5	<5
740091	7.1	69	9	<5	<5
740092	7.1	74	10	<5	<5
740093	7.0	72	9	6	<5
740094	7.0	80	9	7	<5
740095	7.0	77	9	10	<5
740096	7.0	71	9	<5	<5

derived from both barren iron sulphides as well as base metal sulphides. Therefore, it would not have been surprising to find acidic waters locally, particularly in the smaller lakes but these waters differ markedly from the acidic waters of the Agricola Lake area 40 km to the south. The difference was caused by the abundant development of carbonate material within the volcanic sequence at Hackett River. At Hackett River such minerals as sphalerite, chalcocopyrite and galena can be found at the surface. These are preserved by the neutralizing effect of the carbonates and account, in part, for the early discovery of the mineralization. At Agricola Lake the acidic environment has almost entirely removed all but pyrite from the outcrop, although sphalerite, chalcocopyrite and galena are found at depth (Cameron, 1975a).

It is of significance for geochemical exploration in such carbonate-rich environments that the mobilization and migration of zinc has not been unduly restricted by the neutral to alkaline pH of surface waters. One of the factors favouring migration is that the pH has greatly reduced the solution (and subsequent precipitation) of manganese and iron (Tables 4 and 5). Jenne (1968) has shown that freshly precipitated manganese and iron hydroxides are powerful adsorbers of zinc and copper in solution, particularly at the relatively high pH levels found in these lakes. Their scarcity, therefore, allows the greater migration of zinc.

Major Element Comparisons

In Table 5 a more extensive suite of components is shown for selected water samples from the High Lake, Hackett River and Agricola Lake areas. Sample 740002

is from the immediate vicinity of the Agricola Lake massive sulphide prospect (Cameron, 1975a). The two other samples, 740006 and 740029, are some distance down the Agricola Lake drainage from this source and show the effects of metal precipitation and of dilution with base metal poor waters.

One of the more obvious features of these data was the higher amounts of sodium and chlorine found in the samples from the High Lake area. This can be accounted for by the close proximity of these lakes to the Arctic Ocean (Figure 2) from which salt-bearing precipitation is, no doubt, derived.

Another feature of interest was the varying amount of sulphate ion present in the samples. The Agricola Lake drainage chain, with its acidic leaching regime, had abundant sulphate. The relatively low calcium content of these waters attest to the absence of limestone to neutralize the acidic waters. Sample 742215, one of the three acidic samples collected from the High Lake area, had a high sulphate content also, but the acidic character of the water has apparently been partially neutralized by limy material. Similarly, sample 740111 showed evidence of limestone having neutralized originally more acidic waters, and, to a lesser extent, samples 740226 and 740233 from High Lake.

Controls on the Mobility of Copper and Zinc in Northern Lake Waters

Solubility of Copper

In a study of waters from certain Connecticut lakes, Riley (1939) showed that the amount of copper present in organic (including colloidal) and sestonic (including particulate) forms was greater than that present in soluble (ionic) form. The relatively low organic productivity of these northern waters, therefore, may serve to restrict the total quantity of copper carried.

For waters of typical composition and pH from the High Lake and Hackett River areas, the stable form of copper was the basic carbonate, malachite (Figure 9) but in a few of the waters there may have been sufficient SO_4^{2-} present for the basic sulphate, brochantite, to be the stable form (Rickard, 1970).

Silman (in Schmitt, 1962, p. 119-127) calculated the total activity of copper in natural waters, represented by the soluble forms to be: Cu^{2+} plus $(\text{CuCO}_3)^0$ plus $(\text{Cu}(\text{CO}_3)_2)^{2-}$. His equilibrium diagram for water with a sulphate activity of 10^{-4}M is shown in Figure 9. This diagram encompasses the compositions of most of the waters from the High Lake and Hackett River areas. From the data given in Table 5 the total activity of copper may be derived. Since the waters have an ionic strength of 0.001, a mean activity coefficient of 0.9 can be assumed. The calculated solubility of copper in these waters is well in excess of the actual amounts present. The calculation of solubilities, however, is not an exact science and it remains possible that the mean content of copper in High Lake waters, 56 ppb, is solubility controlled. In an earlier study it was shown that copper was extremely abundant in

Table 5

Comparison of the Composition of Selected Lake Waters from the Slave Province, N.W.T.

SAMPLE AREA	HIGH LAKE						HACKETT RIVER					AGRICOLA LAKE		
	HIGH LAKE		RECONNAISSANCE				CAMP LAKE							
SAMPLE SITE	740226	740233	742150	742190	742210	742215	740085	740095	740097	740100	740111	740002	740006	740029
SiO ₂ , ppm	1.50	-	0.75	-	2.61	3.39	1.73	1.73	-	-	2.39	14.41	2.93	1.09
Al, ppm	-	-	-	-	-	-	-	-	-	-	-	2.6	0.24	0.01
Fe, ppb	18	11	<10	<10	<10	72	<10	<10	<10	<10	15	875	<10	29
Mn, ppb	<5	<5	<5	<5	5	<5	<5	<5	<5	<5	<5	92	25	9
Cu, ppb	51	61	<1	<1	<1	10	9	9	8	2	8	867	8	2
An, ppb	204	202	3	<1	1	95	63	77	63	<1	45	1080	43	12
Ca, ppm	5.70	5.85	2.39	6.43	7.78	20.0	2.51	2.51	2.63	2.81	20.0	5.58	1.72	0.94
Mg, ppm	1.71	1.73	0.62	0.68	2.55	3.09	0.81	0.79	0.81	0.77	1.88	2.38	0.90	0.52
Na, ppm	1.46	1.46	1.12	1.80	2.10	3.79	0.49	0.49	0.52	0.49	0.55	1.56	0.52	0.40
K, ppm	0.47	0.47	0.24	0.21	0.59	0.76	0.47	0.47	0.47	0.47	0.71	0.94	0.68	0.28
Acidity as ppm CaCO ₃	-	-	-	-	-	-	-	-	-	-	-	48.6	4.3	-
Alkalinity as HCO ₃	8.9	9.1	-	-	-	-	4.4	3.2	-	-	-	-	-	-
SO ₄	12.4	12.0	5.7	2.0	4.6	79.6	4.6	5.3	6.7	2.8	22.3	76.7	13.6	7.5
Cl	3.0	2.9	1.7	3.3	3.3	6.1	0.9	0.4	0.6	0.2	0.4	0.56	0.56	0.22
Specific Conductance (25°C)	59.6	59.6	27.1	48.7	75.8	200	30.3	30.3	30.3	27.1	84.5	230	31.0	15.0
pH	6.2	6.6	6.8	7.3	7.6	4.08	6.9	7.0	7.0	7.2	7.2	3.2	4.1	5.5

(- = not measured)

the sediments of this lake. Nine nearshore sediments evenly distributed across High Lake averaged 3700 ppm copper and 1791 ppm zinc (Allan *et al.*, 1973). As noted earlier green copper precipitates were noted on submerged rocks in High Lake near the A-B zone. The much lower copper content of Camp Lake, averaging 9 ppb, probably was caused by the weaker copper mineralization of the area, rather than the higher pH of the lake (averaging 7.0) compared to High Lake (pH 6.3).

Solubility of Zinc

Hem (1972) found the solubility of both zinc carbonate and hydroxide to be too high to control the zinc concentration of natural, oxygenated waters. If solubility control does exist, Hem felt that it was more likely to be determined by that of the silicate, willemite. The solubility of willemite decreases rapidly with increasing pH, but in waters of pH 7.5 with 6 ppm SiO₂ and an ionic strength of 0.001 there is still an equilibrium concentration of 70 ppb zinc. Thus, as for copper, the amounts of zinc present in the most anomalous lake waters were less than the calculated solubilities.

Control by Iron and Manganese Oxides

Jenne (1968) has argued that the principal control on the fixation of zinc, copper and other heavy metals in fresh waters to be the hydrous oxides of iron and manganese. These oxides may exist as discrete

particles or as coatings on other minerals. Only small amounts of these oxides are necessary to exert control because of their presence as coatings with a high surface area and because of their high sorption capacity. In the case of hydrous manganese oxides at pH 8 this may approach 1 mole per mole capacity (Morgan and Stumm, in Jenne, 1968, p. 344).

As was noted briefly above, the influence of iron and manganese oxides on the mobility of zinc and copper may vary markedly with the local geology and surface environment. Thus in the Agricola Lake area the scarcity of limy material in conjunction with the prevalence of sulphides allowed the development of an acidic surface environment. In this environment, iron and to a lesser extent manganese were mobilized from a variety of surface rocks as well as from the base metal sulphide mineralization. High zinc and copper levels in acidic lake waters coexisted with relatively high amounts of iron and manganese (e.g., sample 472 (Cameron and Lynch, 1975) contained 186 ppb zinc, 59 ppb copper, 71 ppb manganese and 182 ppb iron). The iron and manganese carried into the drainage in solution then may have precipitated at suitable conditions of pH and water composition where they serve as a sink for the sorption of zinc and copper from the waters. By contrast, the abundant limy beds found both in the High Lake and Hackett River areas restricted the development of acidic environments to the most actively oxidizing sulphide zones. The mobilization of iron and manganese was not as extensive and high zinc and copper levels coexisted in waters with background levels of iron and manganese (Tables 3-5). Thus in

these neutral environments there was less iron and manganese available to reprecipitate and scavenge the waters of zinc or copper which partially compensated for the reduced mobility of these heavy metals in a neutral environment.

The Utility of Hydrogeochemical Methods in the northern part of the Shield

Sampling Interval

This is one of the most important practical considerations in geochemical exploration, since it determines both the cost and the effectiveness of any exploration program. In discussing the sampling interval it is first necessary to define what is the nature of the target.

Some mineral deposits are associated with rocks containing greater or much greater than average concentrations of the elements in question. An example of this is the copper deposits of the Coppermine District. These occur within a thick sequence of basalts with a much greater than average copper content (Cameron and Baragar, 1971). Allan (in Boyle et al., 1971) outlined large areas of these copper-rich basalts containing copper prospects by analyzing the lake waters for copper. For the purpose of geochemical reconnaissance these copper-rich basalts may be considered the primary target, with more detailed follow-up surveys concentrating on the discovery of copper sulphide bodies within the areas outlined during the reconnaissance. Since the copper-rich basalts were large targets, occurring over several tens of square

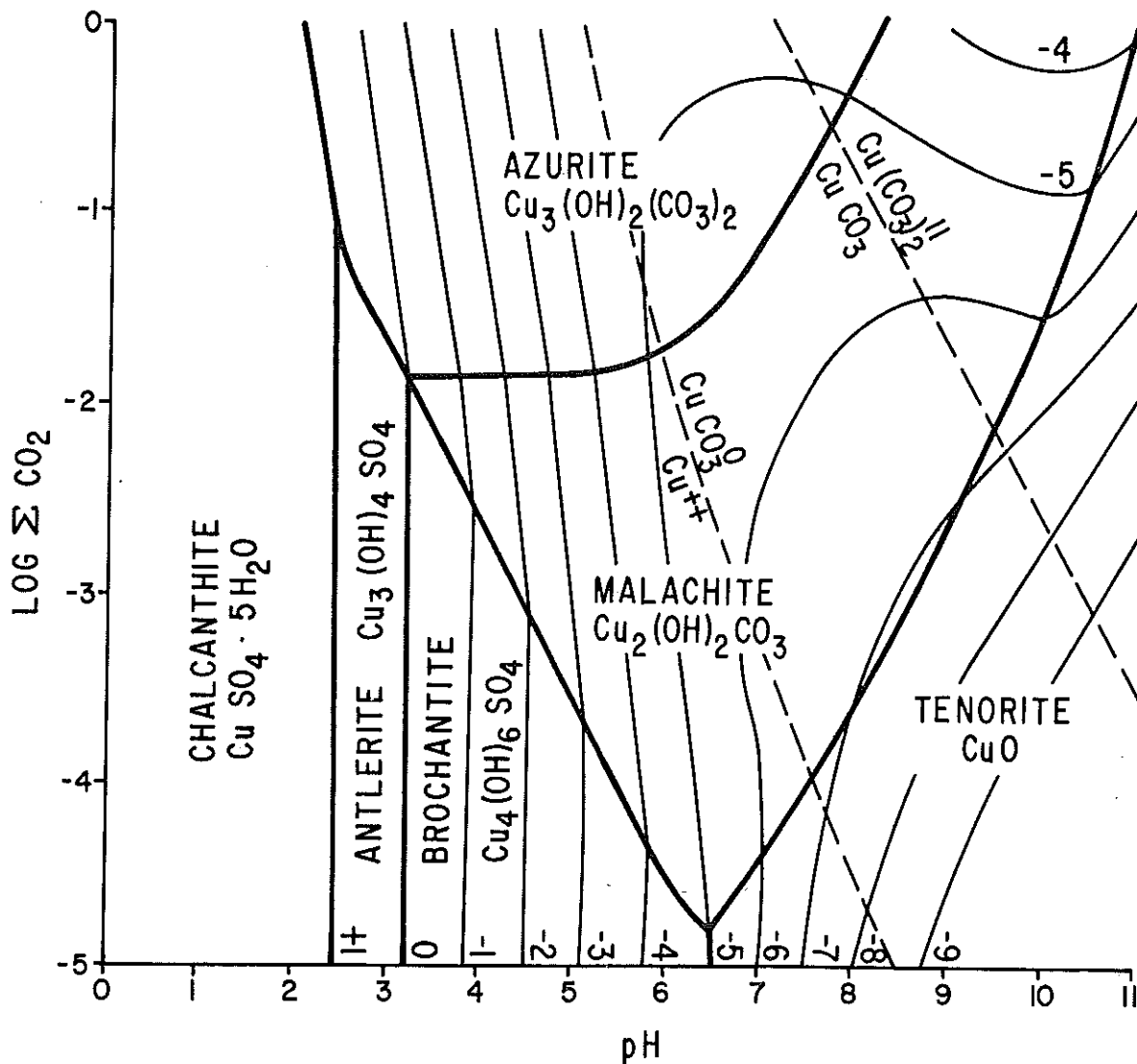


Figure 9. Equilibrium diagram for copper as functions of total carbonate.

miles in the case of the Coppermine Group rocks, a wide sampling interval could be used.

Most mineral deposits in the Canadian Shield, however, are not associated with rocks of distinctive metal content. In particular, this applies to the volcanogenic massive sulphide type of deposit. As Cameron (1975b) has demonstrated, base metal enrichment is confined to the deposits, to the narrow feeder pipe, and to the thin stratigraphic horizon contemporaneous with the deposition of the massive sulphide body. The vast bulk of the enclosing volcanic rocks do not contain unusual contents of base metals. The mineralization at High Lake and Hackett River is of this type and the geochemistry of the volcanics, studied by the senior author (Allan *et al.*, 1973), showed that the base metal content of the volcanic rocks at Hackett River was quite low away from the mineralized zones.

Because the massive sulphide mineralization, commonly found in the Canadian Shield, is not associated with metal rich rocks, it is not possible to use the latter as the primary target in reconnaissance surveys. Instead, the much more restricted target of the massive sulphide bodies must be used. This can be observed in the Hackett River area (Figure 8). Lake waters with anomalous levels of zinc are distributed along a west striking stratigraphic interval that contains the massive sulphide bodies. The lakes to the north, away from the mineralization, had very low zinc contents that reflect the base metal poor nature of the non-mineralized rocks.

Twenty-five lakes were sampled from an area of about 12 square miles (31 km²) at Hackett River. Of these, fourteen lakes contained 13 ppb zinc or more, which might be considered as the threshold value for this area. Thus, if a sampling interval of 1 per 10 square miles had been used, the probability of obtaining one anomalous sample would have been greater than 50 per cent. This area, however, formed a relatively large target with a number of base metal sulphide bodies occurring along a stratigraphic zone. Most areas containing massive sulphide prospects will present a smaller target.

Other features that influence the sampling interval for hydrogeochemical surveys are pH and other controls on metal precipitation discussed previously, and the relief and continuity of the drainage. The latter determine how far and how rapidly the drainage waters travel.

To estimate the optimum sampling interval one must integrate all of these features and relate this to the cost of sampling and analysis. At present these estimates are inexact and based on the very minimum of information. For the areas in question (e. g., High Lake region) a suggested minimum density required for reconnaissance or semi-reconnaissance hydrogeochemical surveys would be 1 sample per 2 to 3 square miles. When using lake sediments the minimum density required to give equivalent results would be at least one half this density (1 per 4 to 6 square miles). This judgment, however, is highly subjective and requires substantiation by detailed studies of lake water and sediment geochemistry, such as the on-going study in the Agricola Lake area.

Detailed Surveys

It is for geochemical surveys with a sampling density of 1 per 2 square miles or denser, that hydrogeochemistry is likely to be of most importance in the northern part of the Shield. The great abundance of lakes in most areas allows detailed surveys to be undertaken. In this study the Hackett River area was sampled at a density of 2 samples per square mile but because of the large number of lakes available a greater density would have been possible. In many parts of the region surrounding High Lake, a minimum sampling density of 4 per square mile is possible. Once anomalous lakes are identified, it is possible to sample the streams and seeps that supply these lakes to localize the source of the metals. In permafrost terrain, the latter are abundantly developed on the slopes bordering lakes.

The 1972 Bear-Slave lake sediment reconnaissance showed a number of anomalous areas for uranium and base metals. Several of the latter in the eastern part of the Slave Province were studied in 1973 by Cameron and Durham (1974a, 1974b). In following-up the 1972 results, lake sediments were sampled in greater detail and then soil samples were taken in areas presumed to be anomalous. In the light of experience gained in 1974 hydrogeochemical sampling would have been a much more efficient and economical approach, in part, because of the ease of sample preparation and analysis but there are other important reasons. Firstly, waters are obviously more easily and rapidly sampled and are more widely distributed than lake or stream sediments. In permafrost terrain, clearly defined streams and stream sediments are infrequent. Much water travels underground or across the surface of the active layer along poorly defined channels. Secondly, mobile metals such as zinc and copper may be leached from soils and stream sediments in areas of sulphide mineralization (Cameron and Durham, 1974a, 1974b, 1975), and this may even apply to lake sediments in an acidic environment (Figure 1). Further, the use of springs or seeps on detailed surveys provides samples that may have had access to concealed orebodies.

Mechanisms for the Mobilization of Base Metals in Permafrost Terrain

It is, at first sight, surprising that oxidation of sulphides and the resulting dispersion of metals in solution is so active in permafrost regions. The critical factor in understanding how chemical weathering takes place was the discovery that in frozen ground thin films of water are present along the boundaries of mineral grains or ice crystals (Tyutyunov, 1960, 1961). Ionic mobility within these films of water is only slightly less than in normal aqueous solution (Anderson and Morgenstern, 1973) allowing chemical reactions to proceed along grain boundaries. The water in these films moves in response to various gradients; e. g., gravitational, pressure, temperature, compositional, and electrical. One of the most important of these are thermal gradients which cause the movement of water and contained ions in the films from warmer to cooler areas (Ferguson *et al.*, 1964).

Table 6
Comparison of samples collected from the same sites on
July 9 and 30, 1974, Hackett River area, N.W.T.

SAMPLED JULY 9, 1974				SAMPLED JULY 30, 1974			
Sample No.	Zn, ppb	Cu, ppb	pH	Sample No.	Zn, ppb	Cu, ppb	pH
96	71	9	7.0	721	66	9	6.8
98	30	2	7.0	720	28	2	6.8
113	23	2	7.4	727	12	2	7.3
114	13	1	7.3	728	9	1	7.1
112	10	3	7.4	726	7	2	7.5
103	7	1	7.3	723	1	1	7.2
120	1	1	7.6	725	1	1	7.4
100	<1	2	7.2	722	3	2	7.0
101	<1	1	7.3	724	1	1	7.4

During polar winters, water and dissolved salts move towards the colder front, i. e. the surface of the soil. The salts often precipitate near this surface. Some water and salts, however, continue to move up into the overlying snows (Jonasson and Allan, 1973). During the summer thaw the snow and the active layer melt causing a run-off of water containing soluble salts (Shvartsev, 1972; Jonasson and Allan, 1973). In areas of oxidizing sulphides lake waters may, by these processes, have elevated contents of sulphates and other constituents during the spring or summer thaw (Stremyakov, 1958; Chernyshev and Vlasov, 1970). The enhancement of metals in waters during the spring has been reviewed by Jonasson and Allan (1973). Shvartsev (1972) noted that the contrast of metal anomalies is greater in the first half of the summer.

Surface run-off is not, of course, the only source of metals for lake waters. Seeps or springs also contribute metals. Thawed channels or "taliks" pass through permafrosted ground and may be particularly well developed where there are oxidizing sulphides. Little is known of seasonal variations in the composition of such waters, but they are subject to large variations in flow depending on freeze and thaw conditions or rainfall.

From this brief discussion it is apparent that a potential exists for marked seasonal variations in the metal content of waters feeding lakes. For this reason, Boyle *et al.* (1955) suggested restricting stream water sampling in the Yukon to the latter half of the summer after flow had stabilized. In comparison to stream waters, lake waters have the advantage that their capacity tends to equalize short-term variations in the flux of metals. The degree to which they attain this is obviously related to a number of factors including their size, their rate of recharge and the speed at which the metal is precipitated.

Allan (*in Boyle et al.*, 1971) has studied the variation of copper in lake waters in the Coppermine area

over the period July 5 to August 24, 1970. Copper concentrations were virtually constant during the period. Rainfall caused no systematic change in the content of background lakes, but did increase the copper content of anomalous lakes.

A limited amount of resampling was carried out at Hackett River on July 30, 1974. These results are compared with earlier data obtained from samples collected on July 9, 1974 (Table 6). The location of the sites are shown on Figure 8. Examination of this table shows that the highly anomalous Camp Lake had maintained a virtually uniform zinc and copper content during July. Similarly, background lakes (1 ppb zinc and/or copper) had remained constant. Only lakes that might be classified as high background to weakly anomalous for zinc (7 to 23 ppb) had shown a downward trend during July. It is possible that these waters derived their metal content by upward migration through bedrock during the winter, and then, during early summer, these metals were flushed into the lakes. By contrast, the highly anomalous lakes may have derived their metal content from groundwater flowing along taliks through actively oxidizing sulphide zones which probably provided a more constant flux of metals.

Conclusions

Active, present-day oxidation of sulphide mineralization has been shown to be the norm in northern Canada, both in the Yukon and in the Canadian Shield. Mobile metals, such as zinc, are readily dispersed in solution from such mineralization. This, in conjunction with the abundance of lakes, ponds and springs in the northern part of the Shield, provide the basis for a largely ignored method of mineral exploration: hydrogeochemistry.

There are certain clear advantages to the use of lake waters for semi-reconnaissance or detailed sampling

(i. e. 1 sample per 2 square miles to 4 samples per square mile) in this region. The most important of these are the speed and ease of sampling, the absence of sample preparation, and rapidity of analysis, particularly in field-based laboratories.

The Geological Survey is constructing a helicopter-mounted sampling apparatus. By using a high volume pump it is hoped that only 10 to 15 seconds need be spent on the surface of lakes, allowing sampling rates of 30 sites or more per hour to be achieved. Sensors built into this apparatus will determine pH, conductivity and water temperature during travel to the next sampling site.

The ease of sample preparation is of particular importance if analysis is to be carried out in the field. Compared to the drying and sieving required for lake sediments or soils, water analysis allows higher productivity and a reduced time between collection and analysis. Provided that analysis is restricted to a few critical elements, field determinations may be made speedily. By using the techniques described for field laboratories (Horton and Lynch, 1975), zinc and copper levels were measured at a rate of 150 samples per day by two experienced analysts. The low content of dissolved matter and the apparent lack of particulate matter in these northern lake waters allows the filtration step to be avoided and acidification does not seem to be required for later analysis. This, however, will be examined further during 1975.

The most important restrictions on the method are the requirement for a closer sampling interval than for lake sediments; possible seasonal variations in lake water composition; and the obvious requirement that only the more mobile elements, such as uranium and zinc, or those of moderate mobility, such as copper, may be utilized. The first restriction probably does not apply to semi-reconnaissance and detailed surveys as defined above. On the basis of the limited evidence available to date, seasonal variation in the metal content of lake waters does not appear to be unduly restrictive. This possible disadvantage is compensated by the seeming homogeneity of lake waters compared to lake sediments. This, however, requires a more thorough study. As far as the restriction to the mobile elements is concerned, this is perhaps the most serious disadvantage. Most mineral deposits, however, contain one element that is mobile in lake waters which, therefore, may serve as an indicator.

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