

GEOCHEMICAL DISPERSION IN LAKE WATERS AND SEDIMENTS FROM MASSIVE SULPHIDE MINERALIZATION, AGRICOLA LAKE AREA, NORTHWEST TERRITORIES

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ABSTRACT

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The Agricola Lake area lies within the tundra and is underlain by continuous permafrost. Archean metavolcanic rocks are host to massive sulphide mineralization, which contains Zn, Cu, Pb, Ag, Au, As, Cd and Hg. This mineralization is being actively oxidized, producing acidic waters enriched in a number of metals.

The elements Pb, Ag and Hg are immobile in the surface environment and are largely retained in the soils near the mineralization. Zn, Cd and Cu are mobile and are dispersed in quantity far along the lake-stream system draining the mineralization. Arsenic is relatively immobile, but it has so wide a primary distribution, particularly in metasedimentary rocks overlying the volcanics, that it too is anomalous in sediments throughout the drainage. Ni and Co, derived from these metasedimentary rocks, and as mobile as Zn and Cd, are also strongly anomalous in lake sediments. Fixing of the mobile elements in sediments appears to be determined by their adsorption on iron oxides, Cu being adsorbed at lower pH values and closer to the mineralized source, than Zn, Cd, Ni or Co.

The use of nearshore and centre-lake sediments for reconnaissance-level geochemical exploration is compared. The latter are a more homogeneous, finer-grained sampling medium. Dispersion of mobile indicator elements from their source in centre-lake sediment is greater than for nearshore sediment. This is because nearshore sediments are essentially subaqueous soils, that are not produced by lacustrine sedimentation. Adsorption of metals on nearshore material takes place in situ, so that dispersion trains can be no longer than that of the waters in contact. In the case of centre-lake sediments, it is suggested that metals are adsorbed on fine-grained particulates, which travel downstream before settling in the centre-lake bottoms.

Waters are the most convenient sampling medium for more detailed levels of exploration. Surface waters are homogeneous within any one lake and show only moderate variation in composition throughout the summer ice-free season. Lake waters that are not derived from mineralized areas are very pure, with dissolved solids contents of 10 ppm or less.

INTRODUCTION

The Agricola Lake area lies within the "Barren Grounds", 480 km north-east of the town of Yellowknife. The land is of low relief, dotted by innumerable lakes. This is a tundra landscape, underlain by continuous permafrost.

A reconnaissance lake sediment survey of 93,000 km² carried out by the Geological Survey of Canada in 1972 showed strong base metal anomalies within the area. This led to follow-up work in 1973 and drilling by a company in 1974 which outlined a Zn-Cu-Pb-Ag-Au-bearing massive sulphide body. An integrated geochemical, geophysical, geological study was made of the prospect by the Geological Survey of Canada in the following year. In 1975 a study of seasonal variation in lake water chemistry within the region included this area. A brief historical summary and bibliography of this activity has been given in a companion paper on the geochemistry of the soils of the prospect (Cameron, 1977). The present paper describes the dispersion of elements from the massive sulphide body in lake and stream sediments and waters. In the absence of large amounts of carbonate rocks within the drainage system, dispersion is in waters that are mildly to strongly acidic.

Work within the area has been restricted to ice-free periods of the lakes (July–September), when access is by float plane from Yellowknife. Sampling of the lakes described has been by float-equipped helicopter, usually as part of wider-ranging regional sampling programs.

GEOLOGY, TOPOGRAPHY, DRAINAGE

The massive sulphide body, underlain by an alteration pipe, is enclosed within vertically dipping metavolcanic rocks of Archean age. These rocks are overlain to the east by recessive carbonaceous slates and then by a thick, metamorphosed greywacke-argillite sequence, all steeply dipping (Fig. 1). Maximum elevations, to approximately 410 m, are in the metavolcanic terrain and drainage is eastwards across the metasedimentary sequence. Total relief within the area is approximately 70 m and lakes are shallow, being no deeper than 10 m along the Agricola Lake chain (Fig. 1).

The region has been glaciated, the general direction of ice movement being roughly parallel to the dominant north-northwest strike of the metavolcanic rocks (Wright, 1967). Glacial cover is generally thin. Within the prospect area, mineralized till and soil has been dispersed in a direction slightly north of west (Cameron, 1977).

Several lake and stream systems flow eastwards from the north-northwest-trending volcanic rocks (inset, Fig. 1). A number of these systems are anomalous in base metals and other elements, but less strongly so than the Agricola Lake chain. During the 1972 Bear Slave reconnaissance, one nearshore site was sampled in Agricola Lake. Table I shows that this sediment is anomalous in a variety of elements, notably Zn, Cu, Ni, Co and As. The Agricola Lake system enters Shorereef Lake which is part of a major south-southeast-flow-

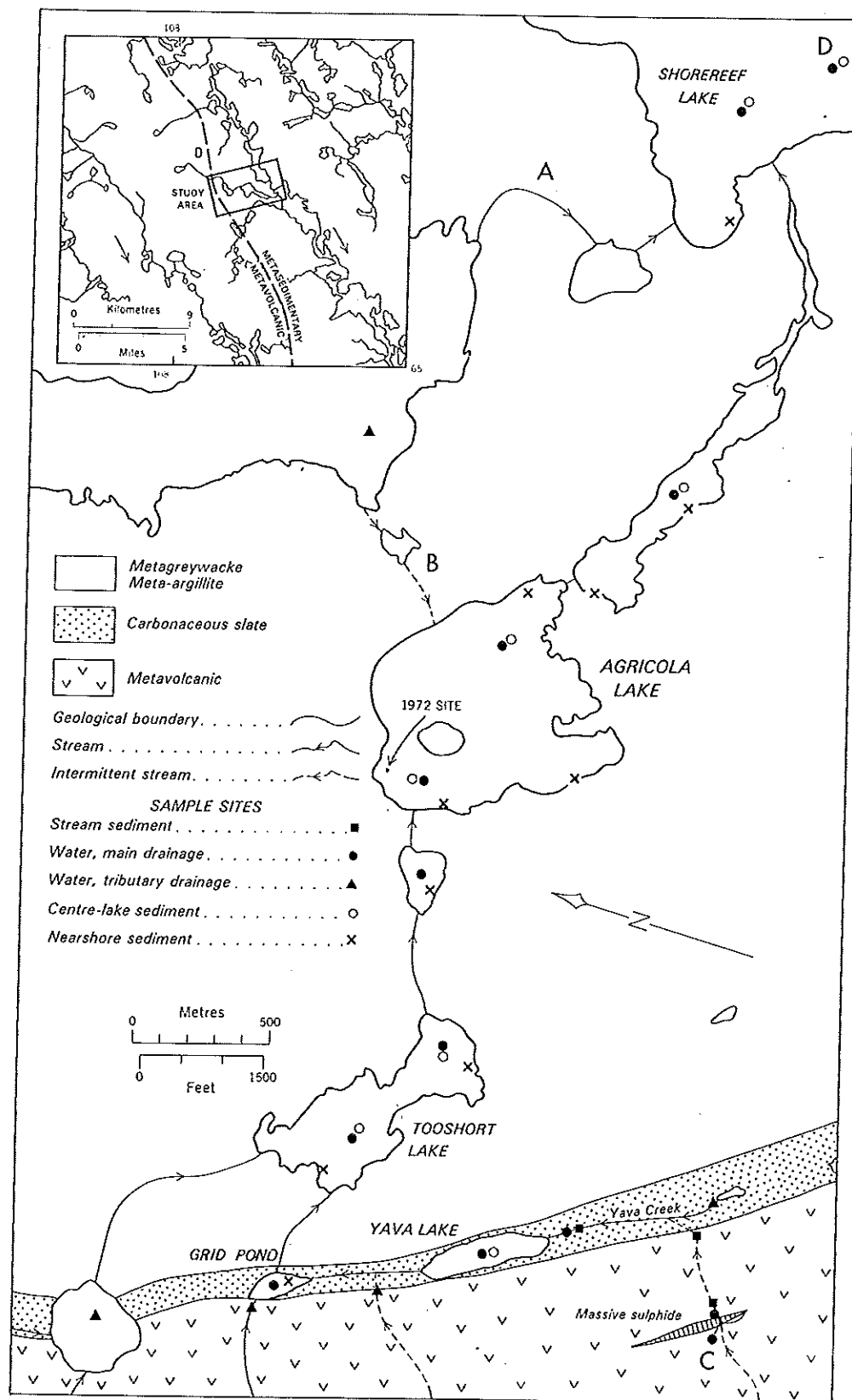


Fig. 1. Sampling sites along the Agricola Lake drainage system. Points C and D define limits of this system shown in Figs. 2-4.

TABLE I

Anomalous nearshore lake sediment sample, Agricola Lake, 1972 Bear Slave Operation (from Cameron and Durham, 1974)

Element	Agricola Lake sample 2890	Sheet 3, Bear Slave survey area (1349 samples)		Ratio 2890/G.M.
		geometric mean (G.M.)	G.M. + log standard deviation	
Li (ppm)	39.0	15.5	28.3	2.5
Be (ppm)	2.0	1.5	2.1	1.3
Mg (%)	1.4	0.66	0.96	2.1
K (%)	2.6	1.86	2.28	1.4
Ca (%)	0.8	1.22	1.49	0.7
Ti (%)	0.28	0.32	0.395	0.9
V (ppm)	95.0	51.8	69.8	1.8
Cr (ppm)	134.0	62.2	91.4	2.2
Mn (ppm)	257.0	89.0	154.0	2.9
Fe (%)	4.7	2.18	2.93	2.2
Co (ppm)	64.0	9.7	16.4	6.6
Ni (ppm)	123.0	23.3	42.7	5.3
Cu (ppm)	161.0	19.6	36.6	8.2
Zn (ppm)	230.0	31.8	58.1	7.2
As (ppm)	28.0	2.3	6.7	12.2
Sr (ppm)	170.0	237.0	283.0	0.7
Y (ppm)	34.0	23.2	32.6	1.5
Zr (ppm)	249.0	273.0	366.0	0.9
Mo (ppm)	1.6	0.55	1.5	2.9
Ag (ppm)	0.3	0.39	0.53	0.8
Ba (ppm)	632.0	586.0	750.0	1.1
La (ppm)	51.0	35.9	52.0	1.4
Hg (ppb)	37.0	11.2	20.0	3.3
Pb (ppm)	18.0	12.9	16.0	1.4
U (ppm)	0.6	0.7	1.8	0.9

ing river-lake system (inset, Fig. 1). The principal channel on this latter system is shown as *A* in Fig. 1. When the area was visited during spring break-up in mid-June, 1975, large volumes of water were also flowing into Agricola Lake along channel *B* (Fig. 1), and thence along the Agricola Lake drainage into Shorereef Lake. The gradient along the Agricola Lake chain is slight, averaging less than 5 m/km between Yava Lake and Shorereef Lake.

Near the sulphide mineralization, much of the water flow is in the sub-surface. Yava Creek disappears into sinkholes near the massive sulphide body and re-emerges in the slate-floored valley to the east. A number of seeps are found in the valley, principally below the cliff that marks the contact of the volcanic rocks with the recessive slates. Between lakes, the course followed by waters is frequently irregular, across or beneath boulder fields.

LAKE SEDIMENTS

Two distinct types of sediment are found in the lakes: that of the immediate nearshore area and that found in deeper water. Large areas of the lakes may be floored by boulders.

The nearshore sediments are subaqueous equivalents of the onshore overburden and soil. These sediments show the same patterned features, such as frost boils and stone stripes. Presumably, these features are also caused by frost-churning action in the active layer (Washburn, 1956). Like the soils, the nearshore sediments are heterogeneous mixtures of material from cobble to clay in grain size. The central, fine-grained portion of subaqueous frost boils was generally chosen for sampling. This may often be gray, unoxidized, in contrast to the oxidized, buff-coloured margins.

The other type of sediment is here termed centre-lake, although it may occur anywhere in the lake, except in the immediate nearshore environment. This type is finer grained and much more homogeneous than nearshore sediments (Table II). The material appears to have been deposited by lacustrine

TABLE II

Mechanical composition, nearshore and centre-lake sediments, Agricola Lake

	Percent > 2 mm	Percent sand (0.063–2.0 mm)	Percent silt (0.0039–0.063 mm)	Percent clay (< 0.0039 mm)
Nearshore sediment	13.0	31.5	37.6	17.9
Nearshore sediment	63.5	5.4	16.8	14.3
Centre-lake sediment	0.0	4.7	60.0	35.3
Centre-lake sediment	0.0	10.4	69.5	20.1

sedimentation, rather than by flooding of overburden as in the case of the nearshore material. Detailed studies by the Great Lakes Institute of Canada, on centre-lake sediments from the area, based on core samples, are not yet published. However, an initial report on this work found two types of sediment that could be distinguished by echo sounder: "Type I, giving a very 'soft' reflection, consisted of a reddish uppermost layer, about 1 cm thick, overlying soupy brownish material down to a depth of at least 30 cm (the maximum length of core recovered by the Phleger corer). The other type, Type II, giving a 'harder' reflection, consisted of bright reddish surface material overlying brownish material over bluish-grey sediment. The last material readily oxidized in the core liners on standing after only a couple of days to a deep black material, inducing the speculation that the bluish material contains $\text{Fe}(\text{OH})_2$ which readily oxidizes to material of the approximate composition $\text{Fe}_4(\text{OH})_{10}$ " (Williams, 1975, p. 227).

The material forming centre-lake sediments is almost certainly derived from both the surrounding land surface and from the nearshore sediments. In the latter case ice and wave action probably removes fine-grained material brought to the sediment-water interface by frost churning.

Because of the shallowness of the lakes and the frequent and strong winds of the "Barren Lands", lake waters are not stratified. Several profiles of O_2 , pH, and conductivity taken by "Martek" analyser showed uniform results throughout the water column. The surface sediments are, therefore, in contact with oxygenated bottom waters.

ANALYSIS

Table III summarizes the methods used in the Ottawa laboratories for the analysis of sediments and waters. The minus 250-mesh portion of the nearshore sediments was used for analysis. For the centre-lake sediments, unsieved material was finely ground. Lake waters were neither acidified or filtered, since previous experience indicated that this was not necessary for these particular waters. Low contents of Fe in background waters (see below) indicate low quantities of particulate material. Analyses for Zn and Cu by atomic absorption in the field, immediately after collection, were essentially similar to analyses made in Ottawa several weeks later. The major element data given in Table IV, exclusive of H_2O , CO_2 and C, were by X-ray fluorescence after fusion with a lithium tetraborate/metaborate mixture.

SEDIMENT AND WATER COMPOSITION AND TEMPORAL VARIATION

Table IV gives major element analyses for three typical centre-lake sediments from Tooshort Lake, Agricola Lake and Shorereef Lake. The low totals of these analyses are probably related, in part at least, to N, O and H associated with organic matter. Features to note in these data are an absence of carbonate and only small amounts of manganese oxides, and the presence of significant quantities of Fe and of organic material. However, the amount of C present is lower than that of typical lake sediments from the forested southern Shield (Coker and Nichol, 1975; Dean and Gorham, 1976). Since all three samples listed in Table IV are a buff, oxidized colour, it is presumed that S is present in forms other than sulphide. The variation in major element composition shown by the samples indicates that centre-lake sediments from the area are only a moderately homogeneous sampling medium.

Table V gives data for water samples from Yava Lake; from the east end of Tooshort Lake; and from Shorereef Lake. Five different sampling periods over two seasons are represented to provide information on temporal variation. Yava Lake is close to the mineralization; east Tooshort Lake is midway along the anomalous drainage system; and the waters of Shorereef Lake may be considered to have background concentrations of elements. It may be seen from Table V that samples from the latter have a low content of total dissolved solids, 10 ppm or less. Waters of this purity are typical of this re-

TABLE III

Analytical methods for waters and lake sediments (AA = atomic absorption)

Constituent	Extraction	Method	Detection limit
<i>Waters</i>			
Fe } Mn }	direct aspiration	AA with computer-controlled background correction, acetylene-air flame	3 ppb 3 ppb
Ni } Cu } Pb } Zn }	APDC-MIBK	50 ml H ₂ O extracted into 6 ml MIBK, then AA with acetylene-air flame	2 ppb 1 ppb 1 ppb 1 ppb
Ca	direct aspiration	AA with acetylene-N ₂ O flame, Sr buffer	10 ppb
Mg } Na } K }	direct aspiration	AA with acetylene-air flame, Sr buffer	10 ppb 10 ppb 10 ppb
SiO ₂		molybdenum blue colorimetric	0.1 ppm
Al		colorimetric, ferron-orthophenanthroline	0.1 ppm
SO ₄		colorimetric titration against BaCl	2 ppm
Cl		thiocyanate, colorimetric	0.1 ppm
Acidity (total)		titration to pH 8.3	0.5 ppm
Alkalinity		titration to pH 4.5 and 4.2	0.5 ppm
<i>Sediments</i>			
Mn } Fe } Co } Ni } Cu } Zn } Ag } Pb }	4M HNO ₃ / 1M HCl, 2 hours at 90°C	AA with acetylene-air flame	1 ppm 1 ppm 2 ppm 2 ppm 1 ppm 1 ppm 0.4 ppm 5 ppm
Hg	hot conc. HNO ₃ / conc. HCl	cold vapour AA	4 ppb
As	hot aqua regia	AA by hydride generation	0.5 ppm

gion (Cameron and Ballantyne, 1975). By contrast, the Yava Lake waters are highly acidic with anomalous levels of sulphate and base metals produced by the oxidation and dissolution of the sulphide mineralization. These acid waters have a greater ability to dissolve rock-forming minerals and the content of SiO₂, Al, Ca, Mg, Na and K is accordingly greater in the Yava Lake samples.

TABLE IV

Major element composition of centre-lake sediments

	Tooshort Lake sample 742504	Agricola Lake sample 742506	Shorereef Lake sample 742510
SiO ₂	63.8	50.6	59.4
Al ₂ O ₃	9.6	14.0	10.8
Total Fe (as Fe ₂ O ₃)	4.1	9.6	5.6
MgO	0.83	1.80	1.68
CaO	0.28	0.70	0.84
Na ₂ O	0.72	1.40	1.21
K ₂ O	0.91	2.08	1.89
TiO ₂	0.18	0.41	0.39
MnO ₂	0.02	0.04	0.04
Total H ₂ O	13.8	13.2	10.9
CO ₂	0.0	0.0	0.0
C	4.2	4.5	4.8
S	0.30	0.65	0.23
P ₂ O ₅	0.10	0.33	0.19
Total	98.8	99.3	98.0

The sampling of 11 June 1975 was during break-up when lakes were ice-covered except for open water along shore lines. At all other times the lakes were ice-free. Note that samples 750025 and 750036, collected during break-up, are more dilute than other samples from the same lakes. At this time shoreline waters contain much snowmelt, which has not mixed with the bulk of the lake waters.

Apart from shoreline dilution during break-up, temporal variation within the lakes shown in Table V is generally moderate. However, where a lake has inflows from two sources of distinctly different composition, and these show variation in flow, then it is possible to have important temporal variation in water chemistry. Thus in 1974 Grid Pond was relatively acidic with a median pH of 3.9, while in 1975 this had risen to 4.7. The increase was caused by a decline in the supply of acidic waters from Yava Lake (partly groundwater-fed) relative to less acidic waters of two other streams (largely surface waters) that supply the pond. The volume of the pond is insufficient to buffer such variations. Also, Agricola Lake waters were less acidic and less mineralized in 1975 because of an increased flow of water along channel *B* (Fig. 1). The plots showing the dispersion of elements in the waters of the Agricola Lake system (Figs. 2–4) are largely based on samples collected on 30 June 1975. These data should be regarded as representing one interval of time in a dynamic system. While the composition of waters within any lake may change with time, the trends in composition along the chain of lakes remains relatively constant.

Sample 740009 was collected from Yava Lake prior to any drilling of the prospect. Samples collected subsequently show higher levels of Cl as a result of CaCl_2 added to drilling fluids.

GEOCHEMICAL DISPERSION

The composition of two spring waters emerging near to the massive sulphide body are shown in Table VI. Sample 740002 was collected prior to any drilling and is not contaminated with CaCl_2 as is 742540. The waters are strongly acidic and are highly anomalous in a number of constituents, notably Cu, Pb, Zn and SO_4 . Such waters are the immediate source of metals dispersed down the drainage system. Because of the highly oxidized nature of the mineralization at the surface, the downstream movement of primary sulphide-rich particulates can be discounted (Cameron, 1977).

Iron and manganese

Fig. 2 plots the distribution of Fe and Mn along the Agricola Lake drainage system. The downstream dispersion of metals as shown begins with water sample 740002 containing 875 ppb Fe. From this point there is a rapid decline in Fe as a result of precipitation and mixing with less mineralized waters. Near to the sulphide body the strongly acidic spring waters, as represented by 740002, enter Yava Creek and mix with the waters of $\text{pH} \sim 4.6$, producing waters of $\text{pH} \sim 4.0$. In the highly oxygenated stream environment, this is sufficient to cause extensive precipitation of Fe, with the coarse fractions of stream sediments containing up to 50% Fe (Cameron, 1977).

Oxidizing sulphides within the carbonaceous slates also produce acidic waters. These join Yava Creek before it enters Yava Lake. The waters of Yava Lake, with $\text{pH} \sim 3.9$, contain significant quantities of Fe, with 48–70 ppb in 1975. Since its centre-lake sediments are not notably high in Fe (Fig. 3), it may be presumed that these levels of Fe are relatively stable in the lake waters. Downstream there is mixing with two tributary streams of pH 6.1 and 6.0 and this causes further precipitation of Fe within Grid Pond, the content of the waters declining to 6–11 ppb Fe. The sediments and boulders flooring this shallow pond are heavily iron-stained.

The nearshore sediments down-drainage from Grid Pond show a steadily declining Fe content, undoubtedly related to the decreasing availability of Fe in the waters for precipitation along the shorelines. Centre-lake sediments show a different pattern, reaching a maximum Fe content 2 km below the maximum value for nearshore sediments. This perhaps indicates the down-drainage transportation of iron-rich particulate material which then settles in the centre-lake bottoms. This is an important consideration for geochemical exploration, since it implies a wider dispersion from a given source in centre-lake sediments than in nearshore samples.

TABLE V

Composition of surface lake waters

		Yava Lake samples				
		740009	742472	750025	750203	752750
Date sampled		1/7/74	23/7/74	11/6/75	30/6/75	18/7/75
SiO ₂	(ppm)	7.1	n.d.	1.30	2.68	3.61
Al	(ppm)	1.75	n.d.	n.d.	n.d.	n.d.
Fe	(ppb)	74.0	162.0	48.0	70.0	56.0
Mn	(ppb)	76.0	71.0	32.0	69.0	91.0
Ni	(ppb)	20.0	26.0	13.0	24.0	29.0
Cu	(ppb)	39.0	59.0	24.0	64.0	90.0
Pb	(ppb)	15.0	18.0	6.0	10.0	11.0
Zn	(ppb)	179.0	186.0	73.0	125.0	195.0
Ca	(ppm)	2.50	3.17	0.95	2.32	3.40
Mg	(ppm)	1.42	1.30	0.50	1.33	1.53
Na	(ppm)	1.00	1.08	0.64	0.76	1.10
K	(ppm)	0.58	0.52	0.60	0.40	0.71
SO ₄	(ppm)	40.6	41.1	13.2	26.5	37.5
Cl	(ppm)	0.30	2.4	1.0	2.1	3.3
Acidity as CaCO ₃	(ppm)	26.5	n.d.	11.4	22.8	26.0
Alkalinity as HCO ₃	(ppm)	n.d.	n.d.	n.d.	n.d.	n.d.
Specific conductance	(μmhos)	112.0	141.0	59.0	104.0	127.0
pH		3.5	3.8	4.1	3.9	3.9

n.d. = not determined.

The mineralized spring waters listed in Table VI contain less Mn than Fe by an order of magnitude. The downstream decline in this element is less marked than for Fe, which is attributable both to this lower content and to the higher pH required for Mn precipitation than for Fe. The nearshore sediments show a definite peak in Mn within Agricola Lake 2.5 km down-drainage from the nearshore Fe peak (Fig. 2). The centre-lake sediments also reach a maximum in Agricola Lake, but continue at this level to the end of the sampled drainage system, again perhaps indicative of transportation of fine-grained particulate material on which Mn has precipitated. Note that for both Fe and Mn the maxima in nearshore sediments coincide with a rapid decrease in their content in water.

Lead, silver and mercury

These elements are relatively immobile and are retained in the soils overlying the mineralization. Maximum values of 15% Pb, 1200 ppm Ag and

East Tooshort Lake samples					Shorereef Lake samples			
740025	742486	750036	750210	752767	742491	750047	750175	752783
2/7/74	23/7/74	11/6/75	30/6/75	18/7/75	23/7/74	11/6/75	30/6/75	18/7/75
2.97	n.d.	0.72	1.12	1.29	n.d.	0.49	0.35	0.25
0.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
36.0	29.0	13.0	5.0	< 3.0	15.0	3.0	< 3.0	< 3.0
36.0	27.0	35.0	30.0	34.0	4.0	< 3.0	< 3.0	< 3.0
8.0	11.0	10.0	13.0	14.0	5.0	5.0	7.0	4.0
7.0	11.0	5.0	9.0	13.0	2.0	2.0	2.0	1.0
1.0	1.0	2.5	2.5	2.5	1.0	< 1.0	< 1.0	< 1.0
32.0	34.0	12.0	25.0	30.0	2.0	2.0	2.0	< 1.0
1.80	1.84	0.95	0.86	1.96	0.97	1.14	0.80	1.07
0.94	0.92	0.50	0.45	0.89	0.49	0.55	0.40	0.47
0.60	0.66	0.50	0.38	0.75	0.48	0.74	0.38	0.63
0.48	0.41	0.38	0.30	0.50	0.22	0.30	0.26	0.22
14.0	12.2	6.5	10.1	11.0	3.0	4.9	3.4	3.5
0.22	0.10	< 0.1	< 0.1	0.10	0.10	< 0.1	< 0.1	< 0.1
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d.	n.d.	0.5	0.5	1.9	1.3	2.8	2.3	1.8
31.0	41.0	21.0	30.0	34.0	19.5	17.9	14.4	14.8
4.5	4.7	5.0	4.9	5.0	6.1	6.9	6.6	6.7

135 ppm Hg have been measured in one soil sample (Cameron, 1977).

Downstream from the mineralization the Pb content of the waters rapidly declines (Fig. 3). Not one of the nearshore sediment samples can be considered anomalous relative to the regional geometric mean of 13 ppm Pb (Table I). This indicates a lack of Pb in solution, available for precipitation along the lakeshore. For the centre-lake sediments and waters, only samples from Yava Lake, closest to the source, and the most acidic, can be considered anomalous (Fig. 3).

In the stream sediment sample 741199, shown closest to the mineralization in Figs. 3 and 4, there is 43 ppm Ag and 636 ppb Hg. Downstream in Yava Lake, centre-lake sediment contains only 3.2 ppm Ag and 76 ppb Hg. All other centre-lake sediments sampled contain <1 ppm Ag; while Hg in this material is relatively uniform along the drainage, declining to ~50 ppb in Agricola Lake and the same in Shorereef Lake. Nearshore samples contain a maximum of 104 ppb Hg in Grid Pond, declining to <20 ppb in Shorereef Lake. All nearshore samples contain <0.4 ppm Ag.

TABLE VI

Composition of mineralized surface waters near Agricola Lake massive sulphide prospect

Date sampled	Sample 740002	Sample 742540
	29/6/74	24/7/74
SiO ₂ (ppm)	14.4	18.3
Al (ppm)	2.6	n.d.
Fe (ppb)	875.0	655.0
Mn (ppb)	92.0	148.0
Co (ppb)	n.d.	24.0
Ni (ppb)	23.0	29.0
Cu (ppb)	867.0	2100.0
Pb (ppb)	341.0	510.0
Zn (ppb)	1080.0	2000.0
Ca (ppm)	5.6	18.9*
Mg (ppm)	2.4	5.0
Na (ppm)	1.56	1.49
K (ppm)	0.94	0.82
SO ₄ (ppm)	77.0	151.0
Cl (ppm)	0.56	7.0*
Acidity as CaCO ₃ (ppm)	49.0	190.0
Specific conductance (μmhos)	230.0	550.0*
pH	3.4	3.4

* Contamination by drilling fluids. n.d. = not determined.

Zinc, cadmium and copper

By contrast, Zn, Cd and Cu are relatively mobile. Cu in waters shows a steady decline in content from 1 ppm at the source to a background level of 1 ppb in Agricola Lake, 4 km downstream (Fig. 4). In stream sediments the maximum concentration of Cu is found close to the mineralized body, and for the nearshore sediments, it is in Grid Pond. Both these maxima coincide with maxima for Fe in the same media. For the stream sediment, co-precipitation of Cu and As with Fe has been demonstrated (Cameron, 1977). The data given for nearshore sediments in Fig. 4 indicate that precipitation of Cu along the lakeshore is continuous as far downstream as Agricola Lake. All these samples are strongly anomalous compared to the regional geometric mean of 20 ppm Cu (Table I). There is a rapid decrease of Cu in the nearshore samples downstream from Agricola Lake, coincident with a similar decline in the Cu content of the waters. The centre-lake sediments reach a maximum in Agricola Lake but continue to be strongly anomalous downstream, in contact with waters of background concentration. Again, this provides evidence of downstream transportation of metal-rich particulate material, which settles to the lake bottoms.

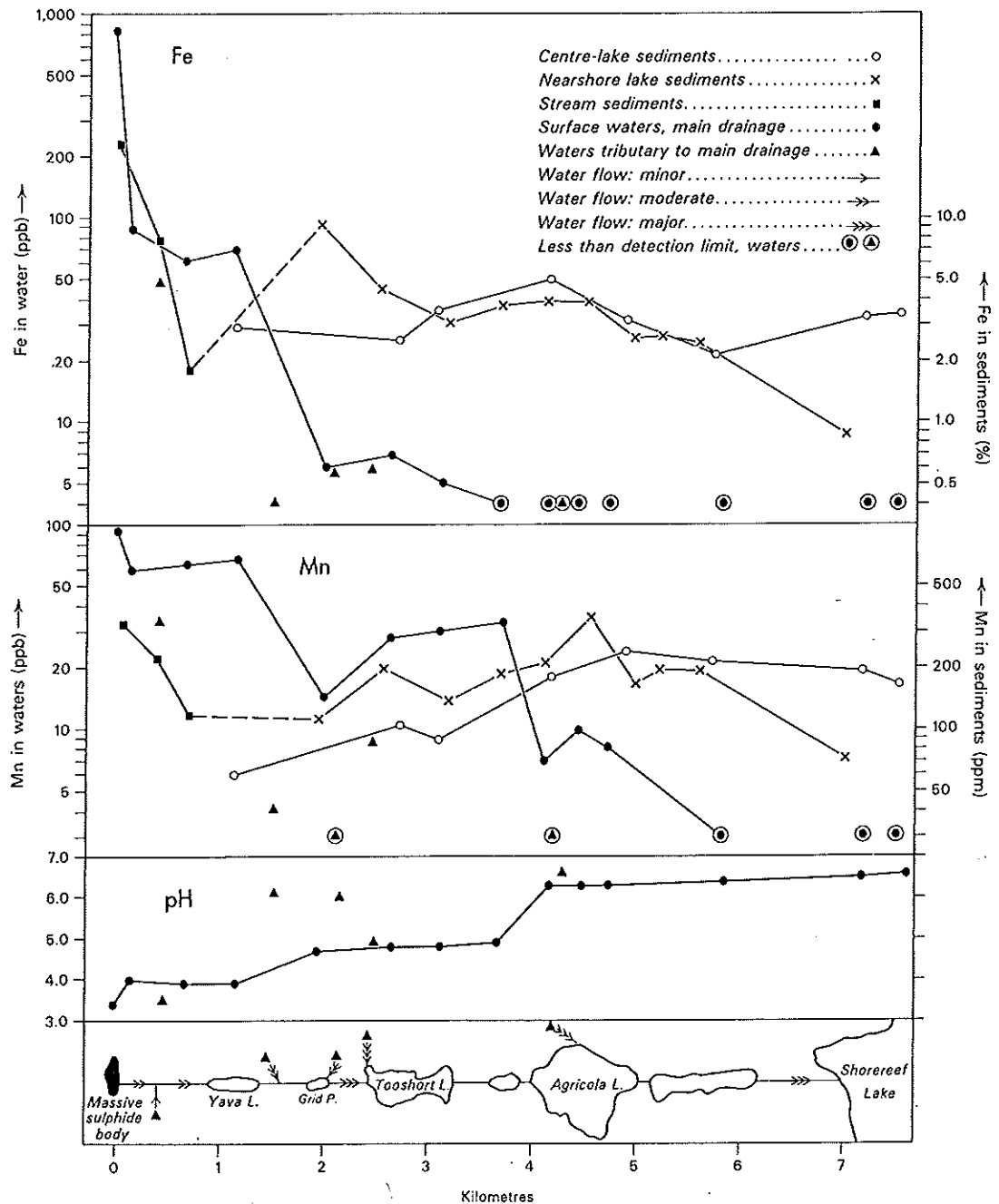


Fig.2. Distribution of Fe and Mn lake and stream sediments and waters, Agricola Lake system.

In many respects, the distribution of Zn in sediments and waters is similar to that of Cu. The major difference is that there is no intensive precipitation of Zn along the proximal portion of the drainage system. Thus the Zn content of the iron-rich stream sediment (741199) closest to the massive sulphide body is only one-fifth the content of Cu, while the Grid Pond sediments contain less than half the Cu content. Both nearshore and centre-lake sediments

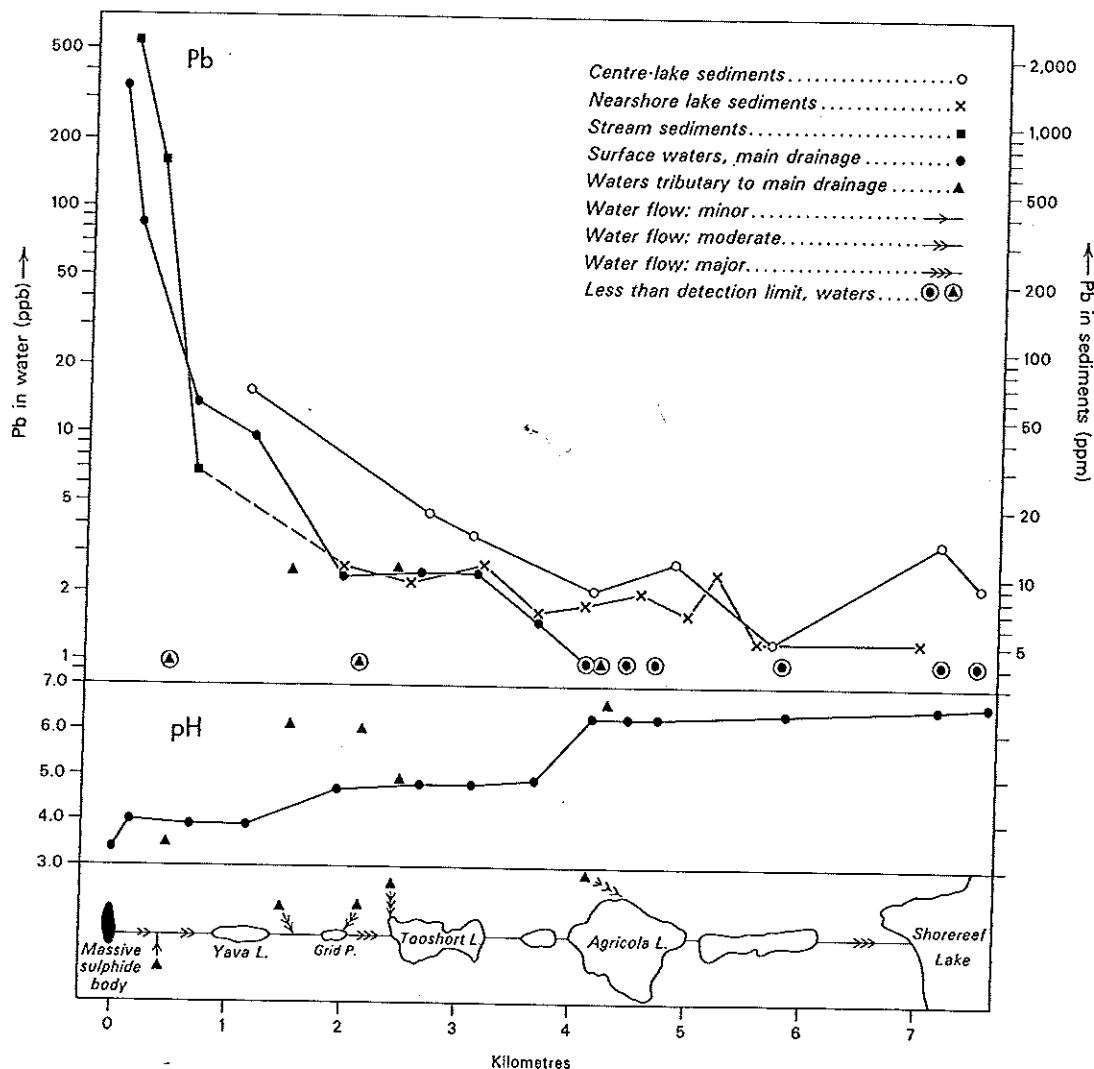


Fig.3. Distribution of Pb in lake and stream sediments and waters, Agricola Lake system.

reach maximum values of Zn in Agricola Lake. Concentrations in nearshore sediments then fall off rapidly down-drainage, sympathetically with the declining Zn content of the waters. Centre-lake samples continue to be highly anomalous to the end of the sampled drainage.

Cd was not measured in the lake water or nearshore sediments. In the centre-lake sediments Cd behaves similarly to Zn. There is 0.6 ppm in Yava Lake. The maximum content is in west Agricola Lake with 4.7 ppm (Zn/Cd ratio of 250), declining to 1.0 ppm in Shorereef Lake.

Note that Cu is precipitated over a wider range of pH than Zn or Cd. This varies from pH \sim 4.0 for stream waters at the site of high-Cu sediment sample 741199 near the proximal end of the drainage (Fig. 4), to pH \sim 6.3 in Agricola Lake. The Zn and Cd contents of sediments rise in Tooshort Lake with a pH of 4.8 and continue to Agricola Lake. Too much reliance must not be placed on these data as absolute values for precipitation pH, since

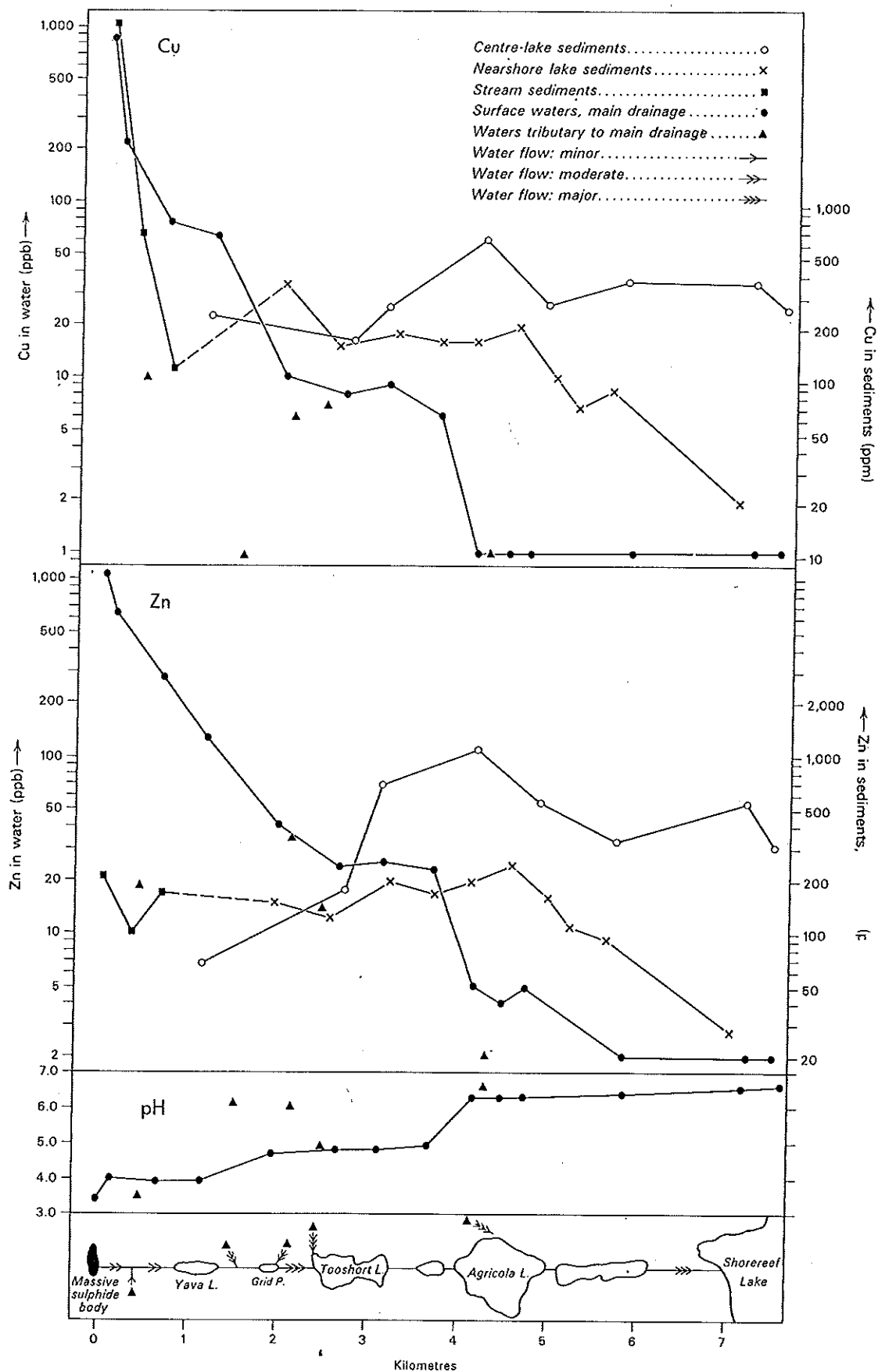


Fig.4. Distribution of Cu and Zn in lake and stream sediments and waters, Agricola Lake system.

they may vary from year to year within given lakes. However, the tendency for Cu to precipitate at lower pH values, along with Fe, is clear. This behaviour of Cu relative to Zn is consistent with previous data from acidic stream systems (e.g., central Norway: Mehrrens and Tooms, 1973; Wales: Foster and Hunt, 1975; Yukon: Boyle and Gleeson, 1975).

One further feature to note in Fig. 4 is that all the streams flowing into the Agricola Lake system that drain volcanic or carbonaceous slate terrain are anomalous in Zn. All but one are also anomalous in Cu. This is important for reconnaissance-level exploration, since the mineralized "target" is much larger than the massive sulphide body itself.

Arsenic

There are two principal sources for this element: the massive sulphide mineralization and the metasedimentary rocks, principally the carbonaceous slates. Soils developed over the massive sulphide contain up to 6200 ppm As, while those developed on the slates may contain several hundred parts per million (Cameron and Durham, 1974, fig. 2). The iron-rich nearshore sediments of Grid Pond, which is floored by slates, contain 614 ppm As. Immediately down-drainage, in Tooshort Lake, there is 74 ppm, and this general level persists to mid-Agricola Lake, at 50 ppm. The content then rapidly declines to 3 ppm in Shorereef Lake.

Of the indicator elements measured in this drainage, As is unique in that it is more abundant in the nearshore sediments than in the corresponding centre-lake sediments. Centre-lake sediment from Yava Lake contains 135 ppm As. Then, from Tooshort Lake downstream, the content is rather uniform, from 25 ppm in Tooshort Lake to 23 ppm in Shorereef Lake. The exception to this uniformity is 99 ppm in the sample from the western part of Agricola Lake.

Since the nearshore sediments are the subaqueous equivalents of soils, their As content is considered to be mainly derived from the underlying bed-rock. The distribution of As in the nearshore samples indicates that a considerable stratigraphic thickness of metasedimentary rocks are enriched in this element, the highest content being in the slates above the volcanic contact, and then decreasing stratigraphically upwards. Thus anomalous levels of As, presumably of exhalative origin, have a particularly wide primary distribution. This interpretation is supported by previous soil analyses (Cameron and Durham, 1974).

The lower content of As in centre-lake sediments, compared to soils and nearshore sediments, testifies to its low mobility. The higher value in the sediment from west Agricola Lake, which also contains the maximum content of Fe for these materials (Fig. 2), may indicate that As has travelled on iron-rich particulates, which have settled at this point.

In the 1972 nearshore sediment reconnaissance, As was the most anomalous element in the Agricola Lake samples, relative to its regional concentration

(Table I). The 1972 As data shown in Table I are not directly comparable with the more recent data discussed elsewhere in this paper. The colorimetric method used to obtain the 1972 data gives lower results than the present method.

Nickel and cobalt

In the 1972 reconnaissance, nearshore samples from Agricola Lake were found to be strongly anomalous in Ni and Co (Table I). Subsequent studies and drilling have shown, however, that the massive sulphide body does not contain significant quantities of these elements. The highly mineralized waters derived from the body contain only minor quantities of Ni and Co in relation to other base metals (Table VI). The main source of these metals in the drainage is believed to be the metasedimentary rocks, again principally the carbonaceous slates (Fig. 1). Waters from seeps along the slate-floored valley contain up to 160 ppb Ni and 60 ppb Co. The pond that drains north into Yava Creek (Fig. 1) contained 76 ppb Ni in the 30 June 1975 water samples. Co was not measured.

Both metals are mobile in this environment and have a distribution similar to Zn. Sediments deposited in the acidic waters of the proximal portion of the drainage system contain low levels of Ni and Co (e.g., 24 ppm Ni and 4 ppm Co in the centre-lake samples from Yava Lake). These sediments reach a maximum of 409 ppm Ni and 84 ppm Co in west Agricola Lake and then decrease gradually downstream to 335 ppm Ni and 30 ppm Co in Shorereef Lake. Nearshore samples reach a maximum in Agricola Lake (126 ppm Ni and 73 ppm Co for a 1972 sample, Table I), then decrease down-drainage.

Sulphate

Acidic, sulphate-rich waters are associated with the volcanic-hosted mineralization (Table VI) and also with the carbonaceous slates. In the water samples collected on 30 June 1975, Yava Lake contained 35 ppm SO_4 , but Grid Pond only 10.3 ppm because of dilution from streams entering the main drainage. From Grid Pond, SO_4 decreases down-drainage to 3.4 ppm in Shorereef Lake.

DISCUSSION

In terms of mobility, the elements associated with the mineralization may be divided into a number of groups. The least mobile are Pb, Ag and Hg and these elements are largely retained in the soils near the massive sulphide body. Their geochemical behaviour has been discussed by Cameron (1977). Pb is retained as insoluble sulphates, plumbojarosite and anglesite. The locus of Ag is not known, but is likely present as an impurity in the lead sulphates. The immobility of Hg relates, in part at least, to the low chloride content of

the groundwaters and surface waters. Arsenic is also relatively immobile in the surface environment but has a wider distribution in the drainage system because of its abundance in metasedimentary rocks.

The most mobile elements are Zn, Cd, Ni and Co. These elements are not precipitated from the more acidic waters near the mineralization, but only down-drainage in waters when the pH is estimated to be 5–6 or greater. Cu has intermediate mobility. Cu, along with As, is co-precipitated with iron oxides in acidic waters near the mineralization. However, a portion of the total flux of Cu is carried down-drainage to be precipitated with the Zn, Cd, Ni and Co.

A major control on the fixing of the more mobile elements within the drainage is the presence of hydrous iron oxides. The adsorption of heavy metals on this material has recently been studied by a number of authors. Grimme (1968) found that Cu^{2+} , Zn^{2+} , Co^{2+} , and Mn^{2+} in dilute solution were adsorbed on goethite at different pH values. The sequence of adsorption, in order of increasing pH, is correlated with a decreasing tendency for the cations to hydrolyse in solution. Adsorption is virtually complete at pH values less than the first hydrolysis constant (p^*K_1) of the metal (Forbes et al., 1976). In Fig. 5 the adsorption of Cu^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} and Cd^{2+} on goethite is plotted, based on data by Forbes et al. (1976). The initial concentration of the metals was $3.2 \times 10^{-5}M$ in a $0.075M$ NaNO_3 solution. Note that Cu^{2+} is adsorbed at much lower pH values than Zn^{2+} , Co^{2+} and Cd^{2+} . These experimental data agree with the observations on a natural system presented in this paper. Since Co^{2+} and Ni^{2+} have similar first hydrolysis constants (Table VII), the pH for their adsorption on goethite should be similar. As noted above, the precipitation of Pb^{2+} is probably controlled by the solubility of its sulphates, rather than by adsorption on iron oxides. For As, its precipitation with iron oxides is likely by reaction with these oxide to form scorodite, FeAsO_4 (Boyle and Jonasson, 1973). The experimental data given in Fig. 5 indicate why not all of the Cu is precipitated in the acidic waters near the source, but continues to precipitate down-drainage in waters of increasing pH.

In the lake and stream sediments, Fe exceeds Mn by two to three orders of magnitude. It is therefore, reasonable to assume that hydrous iron oxides, rather than manganese oxides, provide the dominant control over heavy metal adsorption. The content of Mn reaches a maximum in the sediments of Agricola Lake (Fig. 2), along with such elements as Zn, Cd, Ni and Co. This maximum may also be determined by the adsorption of Mn^{2+} on goethite. Experimental evidence (Grimme, 1968) and the p^*K_1 values (Table VII) indicate that Mn is adsorbed on goethite at a slightly greater pH than Co^{2+} and Cd^{2+} .

Iron (and manganese) oxides commonly occur as coatings on fine-grained silicate particles (Jenne, 1968). The adsorption or coprecipitation of the various trace metals on the iron oxide coatings of suspended particulates can account for the downstream displacement of anomalies in the centre-lake

ADSORPTION OF METAL IONS ON GOETHITE

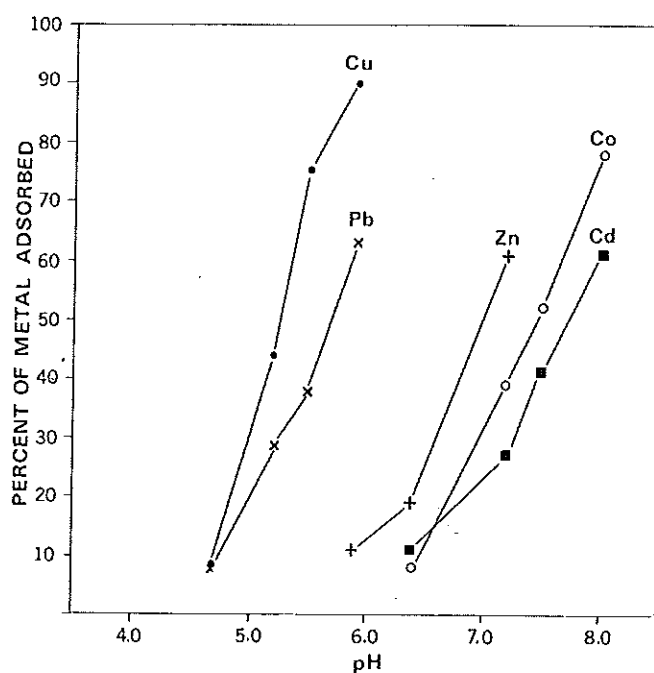


Fig.5. Adsorption of certain metal cations on goethite (data from Forbes et al., 1976).

TABLE VII

Selected first hydrolysis constants (p^*K_1) at 25°C for divalent metal cations (from Perrin, 1969)

Cation	p^*K_1	Cation	p^*K_1
Pb ²⁺	7.9	Ni ²⁺	9.9
Cu ²⁺	8.0	Cd ²⁺	10.2
Zn ²⁺	9.0	Mn ²⁺	10.6
Co ²⁺	9.85		

sediments. This requires to be confirmed by further detailed study. The clear lake waters, observed during all sampling periods to date, lack obvious suspended material.

APPLICATION TO GEOCHEMICAL EXPLORATION IN THE NORTHERN SHIELD

Lake sediments and/or waters are the most convenient sampling media for reconnaissance and intermediate-level geochemical exploration in the lake-dotted landscape of the Canadian Shield. The data given on the behaviour of elements dispersed from the Agricola Lake prospect assists in devising guidelines for exploration methods for use in the northern Shield.

The data from this acid-weathering environment should be supplemented by information from non-acidic drainage systems.

The terrain of the Canadian Shield is generally of low relief. Wide-interval, reconnaissance sampling must, therefore, depend on either extensive primary dispersion of indicator elements in host rocks, or, alternatively, extensive dispersion in solution from a more restricted source. At the Agricola Lake prospect the primary dispersion of Pb, Ag, and Hg is largely confined to the massive sulphide body and the immediately adjacent host rocks. Since these elements have poor mobility in the surface environment, they are not useful as indicators except at the most detailed levels of exploration. By contrast, Zn and Cd are highly mobile. In the Agricola Lake system, anomalous values in lake sediments are found 7 km down-drainage from the massive sulphide, and may extend further. While there is considerable precipitation of Cu near the source, sufficient quantities of this element are dispersed along the drainage for it to be a useful indicator. Arsenic has only limited mobility in the surface environment. However, its primary dispersion in the rocks of the prospect area is so extensive that it is one of the most effective guides to the exhalative mineralization. Anomalous values of Ni and Co are also found in the lake system draining the prospect. These elements, which have a mobility equivalent to Zn and Cd, are not derived from the massive sulphide, but principally from the associated metasediments.

Consideration of the above indicates the complex nature of the original discovery anomaly in Agricola Lake. This comprises mobile elements derived from potentially economic mineralization (Zn, Cd, Cu); mobile elements derived from mineralization in nearby metasediments (Ni, Co); and an immobile element with a very wide primary distribution (As). Clearly, care must be taken in interpreting reconnaissance data and in selecting appropriate indicator elements.

In the Agricola Lake drainage a major control on the fixing of elements of moderate to high mobility appears to be adsorption on hydrous iron oxides. These oxides are provided in quantity by acid-weathering sulphide mineralization. In environments where carbonate-bearing rocks host mineralization, waters are less acidic or are alkaline. This greatly reduces the quantity of soluble Fe entering the drainage and precipitating as ferric oxides. The paucity of these oxides in the drainages to fix heavy metals will tend to counterbalance the weaker mobility of many of these metals in neutral to alkaline water (Cameron and Ballantyne, 1975).

Centre-lake sediments are the most appropriate medium for wide-interval geochemical reconnaissance (i.e., 1 sample or less per 12.5 km²) in the northern Shield. They are a more uniform material than the nearshore sediments and, on the present evidence, provide a more extensive dispersion train than the latter. This feature is most likely related to adsorption of indicator elements on fine-grained particulates, which are dispersed down-drainage before settling in the lake bottoms. Adsorption on nearshore material takes place in situ, so that dispersion trains for this medium can be no greater than that

of the waters in contact with these sediments. However, since the nearshore sediments are essentially subaqueous soils, they do provide information on the composition of the underlying bedrock or overburden, as well as data for exploration purposes. These features were used in the reconnaissance survey of the area (Allan et al., 1973).

For intermediate to detail-level surveys, the sampling of waters is advantageous. The waters of northern Shield lakes are homogeneous across the lake surface (Cameron and Ballantyne, 1975). They are more readily sampled, prepared, and analysed for a number of elements than are sediments. Indicator elements in waters will always increase in quantity towards the source, unlike the same elements in sediments, which may either increase or decrease, depending on precipitation controls.

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