

E. M. Cameron and J. J. Lynch
Resource Geophysics and Geochemistry Division

In the 1973 field season extensive base metal anomalies were identified in the drainage systems of this area (Cameron and Durham, 1974a, 1974b). These anomalies have their origin in massive sulphide type

mineralization in the volcanics of the area. It was apparent from these data that the most mobile elements (e.g. Zn) travelled several miles in the drainage system before being precipitated in lake sediments. The

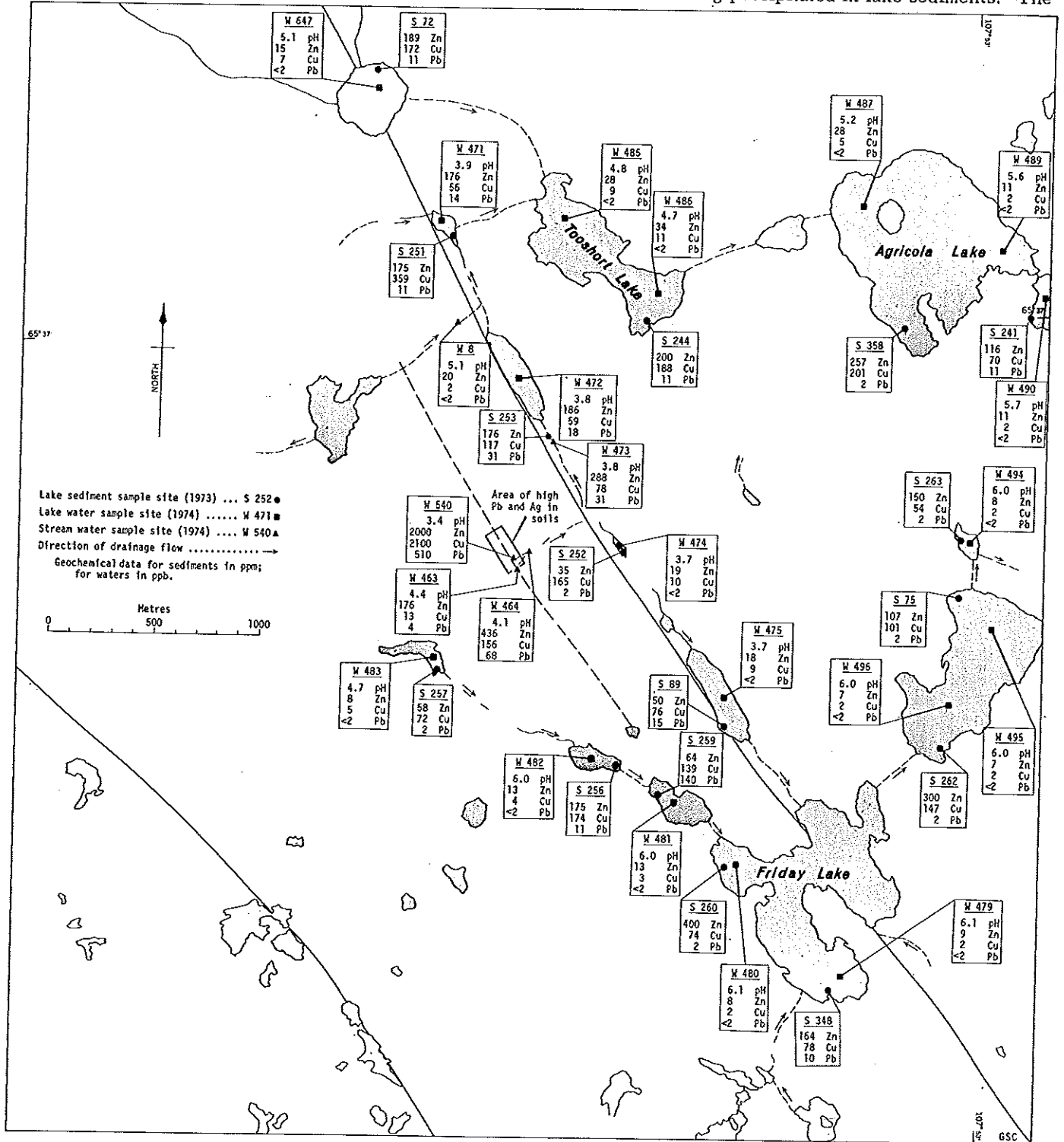


Figure 1. Selected analyses for Zn, Cu and Pb in lake waters and lake sediments, Agricola Lake area, N.W.T.

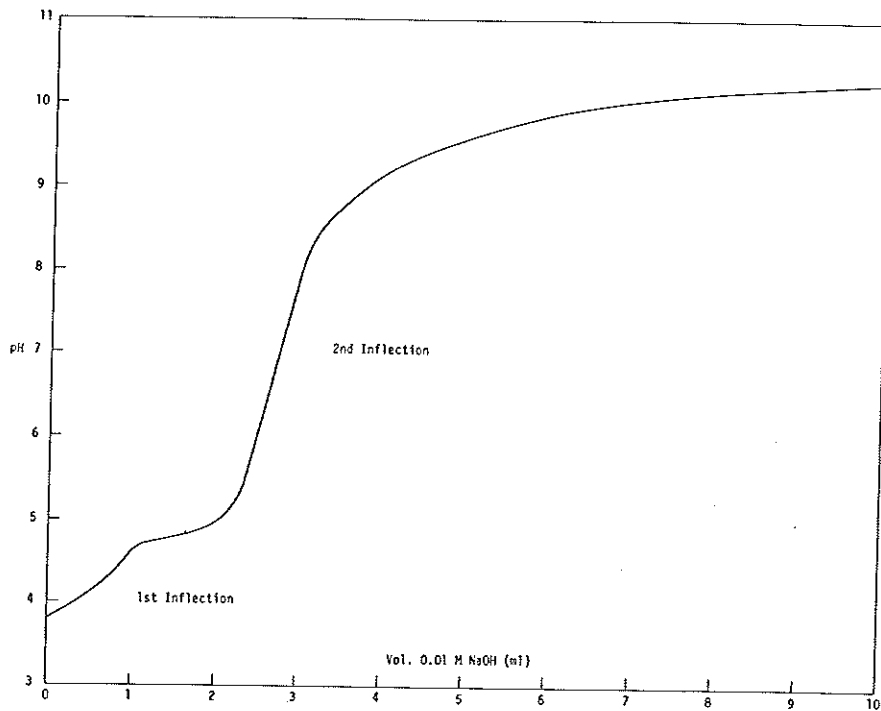


Figure 2.
Titration curve for sample 9
(50 ml sample).

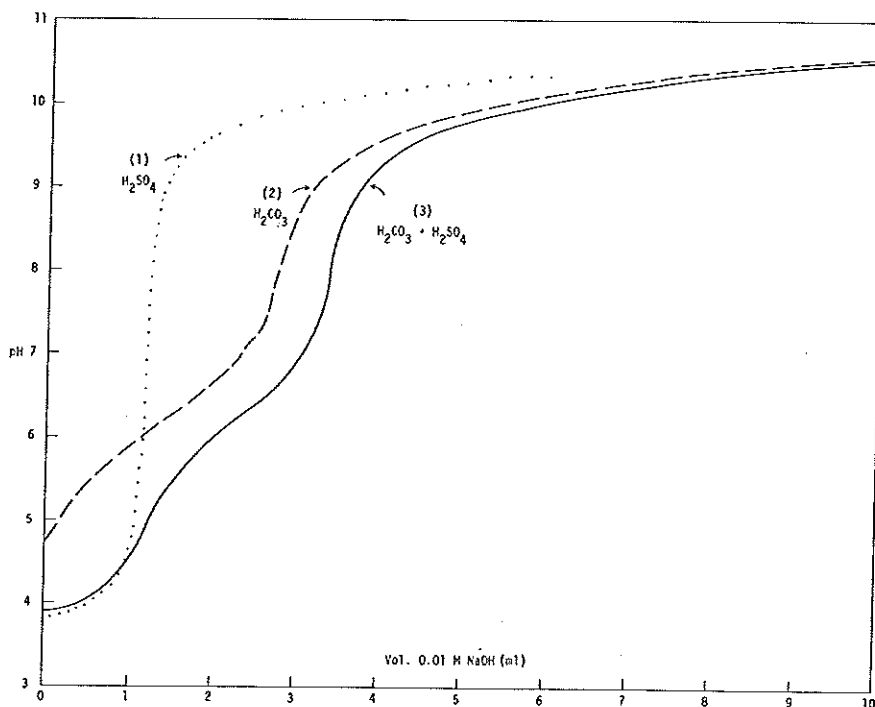


Figure 3.
Titration curves for (1) H_2SO_4 , (2) H_2CO_3 , (3) mixture
of H_2SO_4 and H_2CO_3 .

primary object of the 1974 hydrogeochemical studies was to more fully explain these processes of secondary dispersion. However, the results of the work, based on field analyses, were so favourable that the program was enlarged to consider the use of hydrogeochemical methods as a primary exploration method.

Boyle *et al.* (1971) have provided an excellent summary of the application of hydrogeochemical methods

of exploration in the Canadian Shield. These methods have been infrequently used for a variety of reasons which they discuss. The features of the Shield that have discouraged such use include the relatively impermeable nature of Shield rocks, the low topographic relief, and the various effects of glaciation. In areas of permafrost, such as at Agricola Lake, the disadvantages may appear to be even more serious. Groundwater circula-

tion and the oxidation of sulphides would, at first sight, appear to be severely restricted in this environment. Present-day oxidation is, of course, essential to any scheme of hydrogeochemical prospecting. Many geologists and geochemists have assumed that present-day oxidation is largely lacking in northern Canada and other permafrost areas. However, Boyle *et al.* (1971) have listed a number of examples of oxidized sulphide bodies in the Shield. While they suggest that this may be largely of Tertiary age, they feel that oxidation has continued in many places to the present. The most extensive work on this problem has been carried out in the Soviet Union. Here modern oxidation of sulphide bodies in permafrost areas has been demonstrated (Shvartsev and Lukin, 1965). Also, the migration of solutions along thin films of water at mineral/ice or ice/air interfaces has been demonstrated (Tyutynova, 1960, 1961). This work has been briefly reviewed by Cameron (1974).

Water samples were collected in 500 ml plastic bottles. They were analyzed in the field within two or three days of collection by procedures described elsewhere (see Horton and Lynch, this section). All samples were analyzed for Zn and Cu and some also for Pb. Almost without exception the samples were clear and colourless. They were not filtered prior to analyses. Several hundred samples were returned to Ottawa and analyzed for a more extensive suite of elements approximately two months after collection. No acid or other preservative was added prior to shipping. Contrary to the experience of other workers, there was no decrease in the Zn and Cu content of the waters as a result of this storage. This applied to waters of neutral as well as of acidic pH and of varying trace element composition. However, some samples gave higher Zn and Cu values by later laboratory analyses, compared to the field determinations. This is provisionally explained on the basis of the Zn and Cu of these waters being organically bonded. Organically bonded metals may extract less rapidly into M. I. B. K. when chelated with APDC than these metals in the ionic form. Field extractions were performed by hand shaking; in Ottawa shaking was done by mechanical means for a longer period of time. These various comparative data will be given in a later report.

In Figure 1 a selection of the water data are given for the Agricola Lake area. Sediment, soil and water analyses for the same area are shown in Cameron and Durham (1974b, Fig. 2). By far the highest concentrations of Zn, Cu and Pb are found in ponds, streams, and springs near the massive sulphide prospect (identified as the area of high soil Pb and Ag in Fig. 1). Several water samples were collected near the prospect with pH values in the 3.2 - 4.0 range and with Zn and/or Cu values near 1000 ppb and Pb values near 500 ppb. Samples collected before and after the start of drilling operations showed no marked differences in base metal content.

Downstream these waters are diluted as they mix with waters of lower trace element content. However, they remain noticeably anomalous as far as Agricola Lake. Approximately 1½ miles to the east of Agricola

Lake this drainage system enters a large unnamed lake. Here the mean value of three water samples was 3 ppb Zn, 2 ppb Cu and 2 ppb Pb. These may be considered as background values. It is of interest that in the Agricola Lake drainage system the most anomalous lake sediment samples for zinc are from Agricola Lake itself, several miles from the principal source of this metal. By contrast, the content of Zn in the waters of this lake is rather low, as a result of dilution and precipitation. These features will be discussed in detail in a later report, but the significance to geochemical reconnaissance of this observation should be noted. If anomalous levels of indicator elements can be detected at a greater distance from the source for lake sediments than for waters, then the former can be sampled at wider intervals.

The downstream dispersion of Zn, Cu and Pb in this drainage chain may be examined in more detail by reference to Table 1. Near the massive sulphide prospect there are a number of waters of varied metal ratios, reflecting perhaps metal zoning within the sulphide body and variable leaching conditions. Two such waters are samples 540 and 463. After mixing of these and other waters (sample 464) they travel mainly underground (at least in summer) north-eastwards to the main northwest-trending valley. Here they are mixed with waters of low pH and low trace element content (sample 474, Fig. 1). These valley waters may owe their low pH to the oxidation of the pyritic, carbonaceous slates underlying the valley. The changes in Zn/Pb and Cu/Pb between samples 464 and 471 indicate that Pb is fairly rapidly precipitated. The Zn/Cu ratio does not change substantially from samples 464 until Agricola Lake is reached. Zn is clearly the more mobile of the elements.

Table 1
Metal Ratios and pH values for selected waters from the Agricola Lake drainage chain

Sample	Zn/Cu	Zn/Pb	Cu/Pb	pH
540	0.95	3.9	4.1	3.4
463	13.5	19.0	3.2	4.4
464	2.8	6.4	2.3	4.1
473	3.7	9.3	2.5	3.8
472	3.2	10.3	3.3	3.8
471	3.1	12.6	4.0	3.9
485	3.1	>14	>4.5	4.8
486	3.1	>17	>5.5	4.7
487	5.6	>14	>2.5	5.2
489	5.5	-	-	5.6
490	5.5	-	-	5.7

The Friday Lake drainage chain (Fig. 1) presents an entirely different picture. These waters have only weakly anomalous levels of Zn and Cu and no detectable Pb. By contrast, many of the lake sediments of this drainage are noticeably anomalous with respect to

Table 2
Major and Trace Constituents of selected waters, Agricola Lake area

Sample (1)	2	9	6	14	19	M-52
Na, ppm	1.56	1.00	0.52	0.68	0.46	1.4
K, ppm	0.94	0.58	0.68	0.32	0.18	0.7
Mg, ppm	2.38	1.42	0.90	1.26	0.30	1.3
Ca, ppm	5.58	2.50	1.72	1.00	1.44	4.6
Fe, ppb	875	74	<10	80	58	10
Mn, ppb	92	76	25	41	< 5	< 1
Zn, ppb	1080	179	43	22	11	2
Cu, ppb	867	39	8	10	2	< 1
Pb, ppb	341	15	2	< 2	< 2	-
Cl, ppm	0.6	0.3	0.6	0.3	0.4	1.2
SO ₄ , ppm	76.7	40.6	13.6	41.5	7.3	2.4
Mineral Acidity as ppm CaCO ₃	22.8	8.5	0.9	16.1	n.d.	-
Total Acidity as ppm CaCO ₃	48.6	26.5	4.3	33.1	n.d.	-
pH	3.2	3.5	4.1	3.5	5.3	7.2
Conductivity as μ mhos/cm	230	112	31	155	15	<55

(1) Sample Locations: Sample 2 near 540 (Fig. 1); 9 near 472; 6 near 485; 14 near 474; 19 near 480; M-52, Yellowknife River, Reeder *et al.*, 1972.

n. d. = not determined

regional background (for background values see Cameron and Durham, 1974b). Our observations have revealed no large, actively oxidizing, base metal sulphide bodies along this chain, hence the low trace element content of the waters. In view of this, the anomalous nature of many of the sediments requires some explanation. Whatever the cause, it provides further evidence that anomalous base metal values are more widely distributed in the lake sediments of mineralized areas than in the waters.

For some other samples from the area the major constituents have been determined (Table 2). The waters shown in Table 2 are relatively pure. Only sulphate is notably abundant. In comparison with the sample from the Yellowknife River (also in the Slave Province), the samples are variably enriched in sulphate, base metals, Fe and Mn. Also these waters are markedly more acidic. It is the excess H ion that enhances the conductivity of the waters from the Agricola Lake drainage chain. The high sulphate, representing free sulphuric acid, is related to the oxidizing sulphides in the area. The source is sulphides enriched in base metals in the case of sample 2 and base metal-poor sulphides in the case of Sample 14. The low salt content of the waters allows the wide dispersion of H₂SO₄ before neutralization. This, in turn, facilitates the dispersion of base metals. The weak solutions of sulphuric acid associated with the massive sulphide body is a potent agent for the leaching of sulphides.

Samples 2, 9, 6 and 14 were titrated with 0.01 M NaOH. These samples showed a pronounced inflection in the titration curve between pH 4 and 5 caused by free sulphuric acid (Fig. 2). A second inflection, believed to be caused by weak acid(s) occurs between

pH 7 and 8. Artificial mixtures of sulphuric and carbonic acids gave titration curves similar to Fig. 2 (Fig. 3). In order to determine whether the second (weak acid) was carbonic acid, samples were aerated with CO₂-free air and titrated. Aeration removes any free carbonic acid. In all cases, the aerated sample titration curves were slightly displaced to the left. However, the general shape of the second inflection was not changed, thus indicating the continued presence of a non-volatile weak acid or hydrolysis (e. g. Al).

To summarize the above data, the most significant finding is that the massive sulphide body and other sulphides in this area are undergoing active oxidation at the present day. Oxidation of the sulphides produces groundwater that is a weak solution of sulphuric acid which further leaches the body. The sulphuric acid solution is not quickly neutralized in the drainage system. This has obviously facilitated the wide dispersion of base metals, particularly Zn, in the drainage waters. Anomalous levels of base metals appear to be more broadly dispersed in lake sediments than in waters, with consequent advantages to their utilization in geochemical reconnaissance.

These favourable results for lake waters plus their ease of sampling and analysis suggested that they might be a very useful medium for semi-reconnaissance and detailed exploration in the northern Shield. To test this further, a 750-square-mile area around Agricola Lake was sampled at an approximate density of 1 sample per 3 square miles. An area of approximately 900 square miles was similarly sampled at High Lake, N.W.T. Most lakes in the Hackett River camp that contains a number of massive sulphide bodies were

sampled. These data will be published in detail in a later report. The pH of waters from the latter two areas are approximately neutral, in contrast to the acidic waters of the Agricola Lake area. This undoubtedly reflects the abundance of exhalative-type limestones at High Lake and at Hackett River. Lead could not be detected at all in these neutral waters and it is possible that the mobility of Cu is reduced. Highly anomalous values for Zn were, however, found in lake waters from both areas near known massive sulphide mineralization. This very mobile element may be very useful for hydrogeochemical surveys in the northern Shield.

Mr. Bruce Ballantyne was responsible for most of the water sampling; both he and Mr. Robert Benson completed the High Lake regional sampling in the remarkably short time of 2 days. The skill and enthusiasm of our helicopter pilot, Mr. Bob Watson, contributed greatly to the efficiency of the water sampling. Mr. Ronald Horton, Miss Elizabeth Ruzgaitis and Miss Sue Costaschuk analyzed the water samples in the field, and Mr. Gilles Gauthier and Mr. W. Nelson carried out most of the determinations in Ottawa. We are most grateful to all these persons for their hard work and enthusiasm.

References

Boyle, R.W., Hornbrook, E.H.W., Allan, R.J., Dyck, W., and Smith, A.Y.

1971: Hydrogeochemical methods - application in the Canadian Shield; *Bull. Can. Inst. Mining Met.*, v. 64 (715), p. 60-71.

Cameron, E.M.

1974: Geochemical methods of exploration for massive sulphide mineralization in the Canadian Shield; *Proc. Fifth Int. Geochem. Explor. Symp.*, Vancouver, 1974. Elsevier.

Cameron, E.M. and Durham, C.C.

1974a: Follow-up investigations on the Bear-Slave Geochemical Operation; in *Report of Activities, April to October 1973*, *Geol. Surv. Can.*, Paper 74-1, Pt. A, p. 53-60.

1974b: Geochemical studies on the eastern part of the Slave Province, 1973; *Geol. Surv. Can.*, Paper 74-27, 20 p.

Reeder, S.W., Hitchon, Brian, and Levinson, A.A.

1972: Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada - 1. Factors controlling inorganic composition; *Geochim. et Cosmochim. Acta*, v. 36, p. 825-865.

Shvartsev, S.L. and Lukin, A.A.

1965: Hydrogeochemical zonality of groundwaters of some sulphide ore deposits in deep frozen ground; in *Cryogenic Processes in Soils and Rocks*, *Publ. Nauka, Moscow*, p. 141-148.

Tyutyunov, I.A.

1960: The processes leading to alteration and reconstruction of soils and rocks at negative temperatures; *Izd-vu AN SSSR, Moscow*.

1961: Introduction to the theory of the formation of cryogenic rocks; *Izd-vu AN SSSR, Moscow*.