

PILOT STUDY ON A-HORIZON SOIL EXPLORATION GEOCHEMISTRY, BIRCH LAKE AREA, LAKE COUNTY, MINNESOTA



**Minnesota Department of Natural Resources
Division of Minerals
Minerals Exploration Section**

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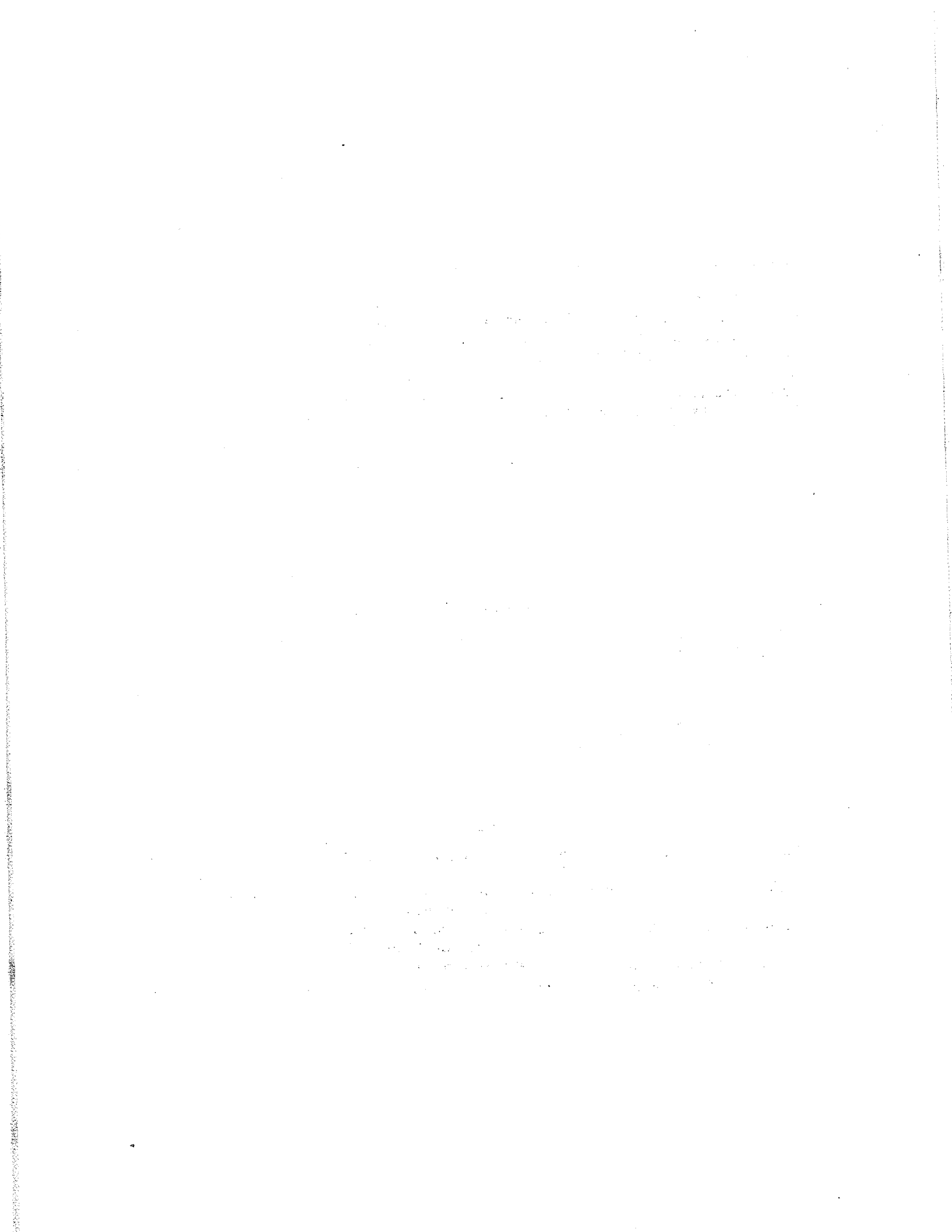
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ABSTRACT

An A-horizon geochemical exploration pilot study was conducted over copper-nickel mineralization in the Birch Lake area of the Duluth Complex. Four extraction methods were tested to determine which method gave maximum anomaly contrast. The A-horizon results were also compared to those for B-horizon samples collected at the same sites but described in another report by Meineke, Vadis and Klaysmat, 1977.

Results indicate that a 4M HNO₃/1M HCl extraction yields the maximum anomaly contrast of the four analytical methods tested. This extraction gave a multi-element (cobalt, copper, nickel and zinc) anomaly over copper-nickel mineralization. The B-horizon samples yield higher anomaly contrast than the A-horizon. Therefore, the B-horizon appears more desirable than the A-horizon as a geochemical sample media in this area.

INTRODUCTION

Yardley (1958), Alminas (1975), and Meineke, Vadis and Klaysmat (1977) have demonstrated that B-horizon soil surveys do reflect copper-nickel mineralization in the Duluth Complex of northern Lake County, Minnesota. Yardley (1961) has reported that forest duff (mainly undecomposed upper A-horizon), in this same area, also reflects copper-nickel mineralization. The trace element distribution is more erratic in the A-horizon than in the B-horizon. The more erratic anomaly patterns of the A-horizon compared to the B-horizon have been reported by many geochemists throughout the world.

The A-horizon may have advantages over the B-horizon. The A-horizon represents a composite biogeochemical sample, deriving trace elements from depths within the glacial drift through plant roots. Bradshaw (1975) reports that hydromorphic transport of trace elements or thick glacial drift may produce anomalies in the A-horizon which are not reflected in the B-horizon and C-horizon.

The Division of Minerals of the Minnesota Department of Natural Resources, as part of a program to develop exploration geochemical methods for evaluation of Minnesota's mineral potential, conducted a survey to examine the usefulness of the A-horizon as a geochemical sample media. This survey was conducted in the Birch Lake area. Four extraction methods were tested to determine which method yielded maximum contrast over background. A comparison was made between the results of this A-horizon study and a B-horizon survey (Meineke, Vadis and Klaysmat, 1977) conducted in the same area. Further reference to this B-horizon survey in this report will be identified by "Report 108-2".

GEOLOGY

The general Precambrian geology of the Birch Lake area is illustrated on Figure 1. Disseminated copper-nickel mineralization occurs in a basal troctolite unit (Figure 1). The Giants Range Granite is barren of copper-nickel mineralization except in very close proximity to the Duluth Complex.

The last glaciation of this region took place during the Wisconsin Stage when the Rainy Lobe advanced in a southwesterly direction over the area (Wright, 1972). The resulting glacial drift probably does not exceed fifty feet. Outcrops of bedrock do occur in the area surveyed. Both the angularity and lithology of the clasts in the drift indicate local derivation (Matsch).

SAMPLE COLLECTION

The soil in this region is generally a moderately well developed podzol. The A-horizon consists of undecomposed to fully decomposed, brown to black, organic material usually three inches thick. The organic material does not contain significant mineral matter and, therefore, the Ah (or A₁) horizon is absent. Occasionally, a bleached (eluviated) Ae (or A₂) horizon, less than 1/2 inch, is observed.

Partially decomposed to decomposed (FH or A₀ horizon) organic material was sampled with a shovel usually at a depth interval of 1-3 inches. Boulders commonly were encountered at each sample site.

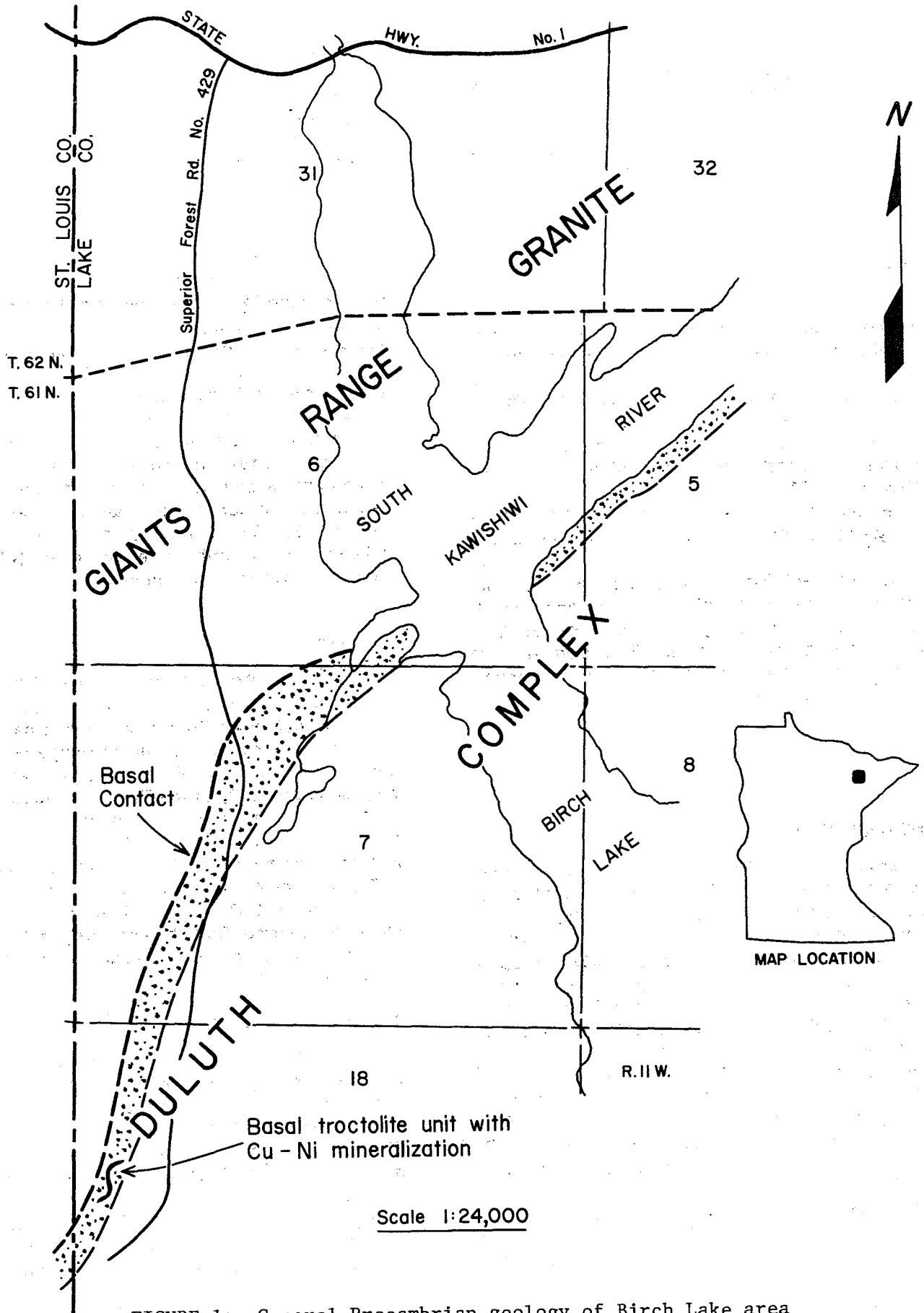


FIGURE 1: General Precambrian geology of Birch Lake area (from Phinney, 1967 and Sims, 1973)

Seven samples were collected (Figure 2); four over granite and three over copper-nickel mineralization. The sample sites shown on Figure 2 are the same as those for the B-horizon survey described in Report 108-2.

SAMPLE PREPARATION AND ANALYTICAL METHODS

The samples were dried at 80°C, broken up with a rolling pin and sieved. Ignition of the samples was not considered due to reduction of copper values resulting from ashing (Peachey, 1976; Meineke, Vadis and Klaysmat, 1976). The -80 mesh fraction was analyzed using four extraction methods. These methods are as follows with details given in the Appendix:

- AN-1: Concentrated HCl, HNO₃ & HF
- AN-15: 4M HNO₃/1M HCl
- AN-17: 0.1M EDTA
- AN-18: Ammonium Citrate/Hydrogen Peroxide

The "AN" numbers above will be used to identify the extraction methods throughout this report. The extraction methods were chosen for their selective extraction of sample components (i.e. organics, etc.) based on Meineke and Klaysmat (1976), other surveys conducted by the Minerals Exploration Section, and numerous other references. LOI (loss-on-ignition) was determined as an estimate of organic content for each sample according to AN-14 described in the Appendix. Arsenic was analyzed by AN-3.

Following dissolution of the samples by the above methods, the sample solutions were analyzed on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer for silver, arsenic, cobalt, copper, nickel, lead, zinc, iron and manganese. Lead and zinc were determined by the Perkin-Elmer electrodeless discharge lamps (EDL) and power supply. Arsenic was analyzed using the EDL system, deuterium background corrector and arsine generator.

RESULTS AND DISCUSSION

The element concentrations of the A-horizon samples for the various analytical methods tested are given in Tables 1-4. The samples located over granite are given at the top of each table, and the

samples over the Duluth Complex at the bottom. See also Figure 2 for sample locations.

Silver, arsenic, cobalt, copper, nickel, lead and zinc were analyzed primarily as indicators of mineralization. Iron, manganese and LOI were analyzed to determine if relationships existed between the trace element concentrations and the iron-manganese hydroxides or organic material in the A-horizon. False anomalies may result from excessive amounts of iron-manganese hydroxides or organics, if their concentrations demonstrate a close correlation to trace element concentrations.

In order to compare the element concentrations and the extractability of the various analytical methods, the mean values for each element in Tables 1-4 are given in Table 5. AN-1 is a near total digestion and obviously extracts significantly more metal from the samples than the other methods tested (Table 5).

Part of the purpose of this survey was to determine which analytical method yielded maximum contrast over background values for the A-horizon. Most analytical methods tested did give a definite anomaly or contrast for cobalt, copper, nickel and zinc over the Duluth Complex. Calculations (Table 6) were made which quantify the contrast for the various analytical methods. From Table 6, it is evident that AN-15 gives the best contrast for cobalt and nickel, and AN-1 and AN-15 for copper and zinc. Based on Table 6, it appears that AN-15 would be the preferred method for exploration geochemical surveys in this region as it gives maximum contrast and a multi-element anomaly for cobalt, copper, nickel and zinc.

Several comments can be made on apparent relationships between the trace elements, iron, manganese and LOI. The samples over the Duluth Complex will not be considered because of their anomalous values. Sample 2785 (Tables 1-4) suggests that copper may be enriched in the organic fraction of the sample (LOI = 37.4%, Table 1), or in the iron hydroxides as evidenced by the higher iron values in 2785 (Tables 1-4). Sample 2785 (Tables 3 & 4) may indicate that lead and zinc are enriched in the organics or iron hydroxides. Manganese does not appear to be related to any of the trace metals analyzed. These comments are by no means conclusive. A survey with considerably more samples is necessary in order to evaluate these relationships. Such a survey should include correlation analysis to determine if ratios are necessary to normalize the effect of organics or iron-manganese hydroxides.

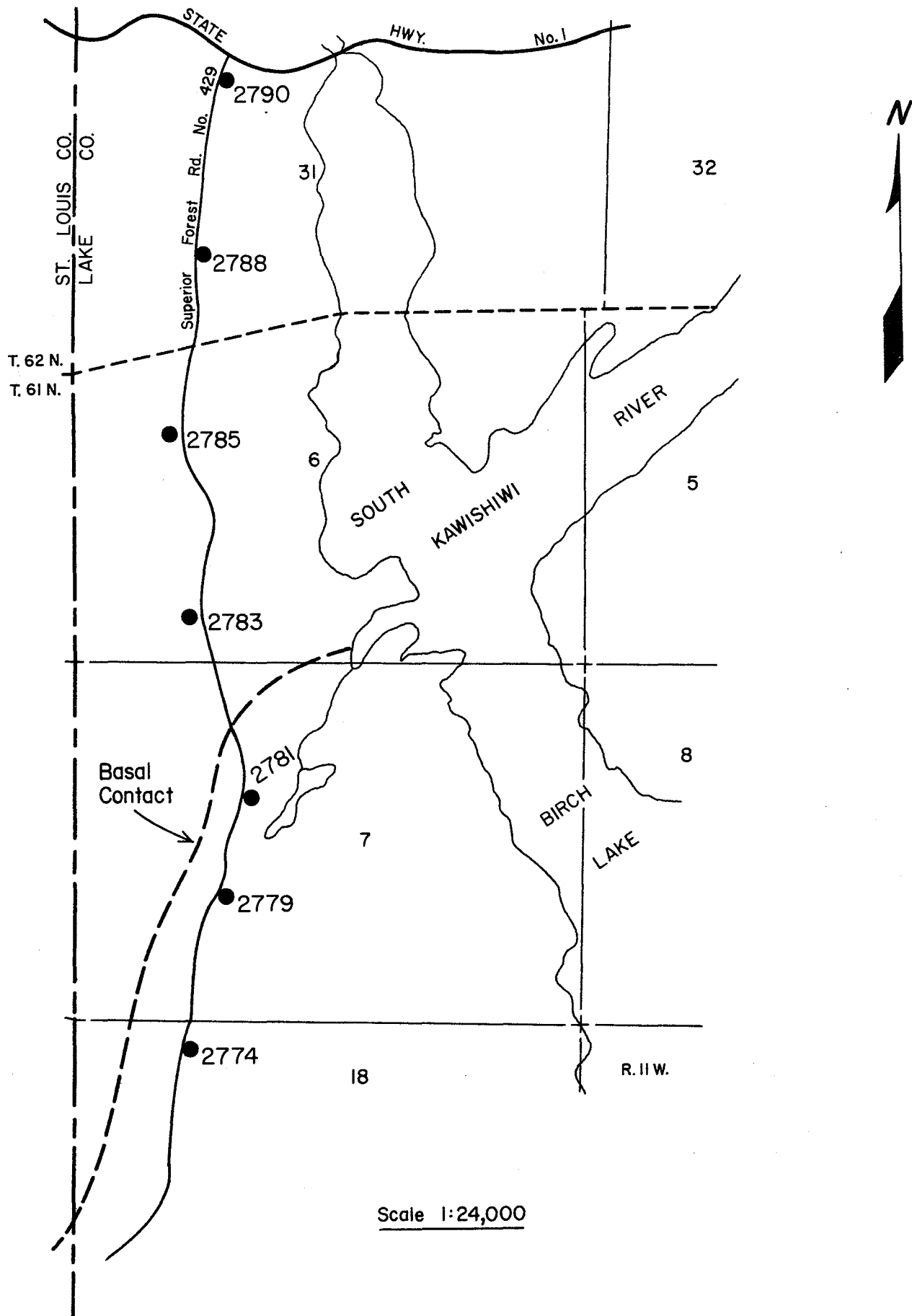


FIGURE 2: A-horizon sample sites with sample numbers

COMPARISON OF A AND B-HORIZONS

The sample sites on Figure 2 are the same as those for the B-horizon survey described in Report 108-2. A comparison will be made between the results of the A-horizon and B-horizon surveys.

A-horizon soils often have higher trace metal concentrations than the B-horizon. Alminas (1975) found the copper content of the B-horizon to be consistently higher than the A-horizon and a correlation of 0.96 between the horizons in the Birch Lake region. Comparison of the total digestion on the -80 mesh fraction for the A-horizon (Table 1) and B-horizon (Report 108-2, Table 2) indicates: 1) cobalt, zinc, iron and manganese do not demonstrate a definite preferential accumulation in either horizon; 2) copper and nickel are higher in the B-horizon, and arsenic and lead are higher in the A-horizon. Visual observation of the data from the A-horizon and B-horizon does indicate a good correlation between the two horizons, especially for copper, nickel and zinc.

For both the A-horizon and B-horizon, the AN-15 extraction gives maximum anomaly contrast. This contrast is significantly higher for the B-horizon. Ex-

amination of the AN-15 results for each horizon, over granite, does indicate that the A-horizon is somewhat more erratic than the B-horizon.

CONCLUSIONS

The AN-15 extraction gives maximum contrast and a multi-element anomaly for cobalt, copper, nickel and zinc and, therefore, is the preferred analytical method for the A-horizon in the Birch Lake region.

Comparison of the trace metal concentrations to iron, manganese and LOI does suggest that iron hydroxides and organic material may influence the concentration of the trace metals and, therefore, create false anomalies. However, additional samples are necessary before any firm conclusions can be reached.

Comparing this A-horizon survey with a B-horizon survey conducted in the same area indicates that the B-horizon gives higher anomaly contrast and the metal values are somewhat less erratic than the A-horizon. Therefore, the B-horizon appears to be more desirable than the A-horizon as a geochemical sample media in this area.

TABLE 1: A-horizon (-80 mesh fraction) analyzed by AN-1, 3 & 14

Sample Number	Ag (ppm)	As (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	LOI (%)
2790	0	1.2	70	10	66	60	74	2.76	424	12.3
2788	0	0	64	28	62	80	98	2.84	360	10.6
2785	0	0	64	60	68	30	66	3.68	220	37.4
2783	0	0	38	26	50	40	44	1.54	348	22.8
2781	.01	1.4	98	612	354	40	260	4.94	940	20.1
2779	0	0.8	78	320	204	20	110	3.74	1068	17.7
2774	0	0	60	88	96	0	50	1.44	144	12.8

TABLE 2: A-horizon (-80 mesh fraction) analyzed by AN-15

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2790	0	8	8	14	20	42	1.14	236
2788	0	8	18	20	20	52	1.82	176
2785	0	4	38	18	20	42	2.32	130
2783	0	0	14	14	20	24	.42	218
2781	0	24	350	224	20	154	3.12	820
2779	0	22	180	110	20	70	2.20	940
2774	0	0	56	26	0	26	.66	28

TABLE 3: A-horizon (-80 mesh fraction) analyzed by AN-17

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2790	0	3	1	4	20	3	.10	56
2788	0	2	4	4	20	4	.24	27
2785	0	6	18	8	40	10	.73	25
2783	0	4	5	1	0	6	.09	143
2781	0	10	74	11	0	16	.22	326
2779	0	7	23	4	20	6	.10	537
2774	0	4	25	6	0	5	.15	9

TABLE 4: A-horizon (-80 mesh fraction) analyzed by AN-18

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2790	0	4	4	3	20	7	.12	79
2788	0	2	7	4	40	7	.37	45
2785	0	5	17	7	40	12	.94	42
2783	0	4	5	6	20	8	.16	166
2781	0	10	106	24	20	28	.58	579
2779	0	5	31	6	0	7	.30	772
2774	0	1	23	5	0	6	.17	12

TABLE 5: Mean element concentrations for seven A-horizon samples for each analytical method from Tables 1-4

Analytical Method	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
AN-1	67	163	129	39	100	2.99	501
AN-15	9	95	61	17	59	1.67	364
AN-17	5	21	5	14	7	.23	160
AN-18	4	28	8	20	11	.38	242

TABLE 6: Anomaly contrast comparison for A-horizon samples for each analytical method

Analytical Method	D/G							
	As	Co	Cu	Ni	Pb	Zn	Fe	MN
AN-1 & 3	2.3	1.3	11.0	3.5	0.4	2.0	1.2	2.1
AN-15		3.0	10.8	7.1	0.7	2.1	1.4	3.1
AN-17		1.8	5.9	1.8	0.4	1.5	.6	5.0
AN-18		1.3	6.6	2.4	0.2	1.6	1.5	5.5

D = Mean of element values for samples 2781, 2779 and 2774 over the Duluth Complex

G = Mean of element values for samples 2790, 2788, 2785 and 2783 over granite

D/G = Geochemical anomaly contrast

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APPENDIX: DESCRIPTION OF ANALYTICAL METHODS

AN-1: Concentrated HCl, HNO₃ and HF

1.0000 gm sample digested in 25 mls of concentrated hydrochloric acid for 20 minutes. Next, 10 mls of concentrated nitric acid was added and allowed to digest for 30 minutes. Finally, 5 mls of concentrated hydrofluoric acid was added and allowed to digest for 15 minutes. All digestions were done at 90°C. After digestion, the sample-acid solution was diluted to 100 mls with deionized water and filtered with #40 Whatman filter paper.

AN-3: Arsenic by Arsine Generator

1.0000 gm sample was digested in 40 mls of concentrated HCl for one hour at 90°C. After 50 minutes, 1 gm of KI is added to the solution so that the arsenic (III) is oxidized to arsenic (V). After digestion, the solution was diluted with deionized water to 100 mls and filtered with #40 Whatman filter paper. The filtered solution is then analyzed using the arsine generator.

AN-14: LOI

1.0000 gm sample was ashed in a porcelain crucible at 800°C for 40 minutes in a muffle furnace.

AN-15: 4M HNO₃/1M HCl

1.0000 gm sample was digested in 10 mls of 4M HNO₃ and 10 mls of 1M HCl at 90°C for two hours. After digestion, sample-acid solution was diluted to 100 mls with deionized water and filtered with #40 Whatman filter paper.

AN-17: 0.1M EDTA

Dissolve 37.22 gms of EDTA disodium salt in 500 mls of deionized water, adjust pH to 4.8 with ammonium hydroxide, and then dilute with deionized water to 1000 mls (0.1M EDTA solution).

1.0000 gm sample was digested for 18 hours in 15 mls of EDTA solution with occasional stirring. After digestion, the solution was diluted with deionized water to 100 mls and filtered with #40 Whatman filter paper.

AN-18: Ammonium Citrate/Hydrogen Peroxide

1.0000 gm sample was digested in a solution containing 40 mls of 10% ammonium citrate and 20 mls of 30% hydrogen peroxide for 18 hours with occasional stirring. After extraction, solution was filtered with #40 Whatman filter paper and 5 mls of concentrated HCl was added and boiled for one half hour until hydrogen peroxide was gone, resulting in a slight color change. The remaining solution was diluted with deionized water to 100 mls.