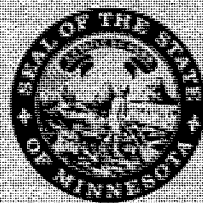# PILOT STUDY ON SOIL EXPLORATION GEOCHEMISTRY, BIRCH LAKE AREA, LAKE COUNTY, MINNESOTA

Minnesota Department of Natural Resources
Division of Minerals
Minerals Exploration Section

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

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MINNESOTA DEPARTMENT OF NATURAL RESOURCES
DIVISION OF MINERALS
MINERALS EXPLORATION SECTION

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

ABSTRACT

A B-horizon and seepage soil geochemical exploration pilot study was conducted over copper-nickel mineralization in the Birch Lake area of northern Minnesota. Seven extraction methods and three size fractions were tested to determine which size fraction and analytical methods gave the best contrast of anomalous samples over background.

Results indicate that the extraction method which yields maximum contrast varies between the various metals considered. However, the 4M HNO_3/1M HCl method appears to give the best contrast when exploring for copper, nickel and zinc.

INTRODUCTION

Yardley (1958) and Alminas (1975) have demonstrated that soil exploration geochemical surveys do reflect copper-nickel mineralization in the Duluth Complex of northern Lake County, Minnesota. The Division of Minerals of the Minnesota Department of Natural Resources, as part of a program to develop exploration geochemical methods for evaluation of mineral potential, decided to conduct further tests on the use of soil as a geochemical sample media in this region.

During 1975-76 a pilot study on soil exploration geochemistry was conducted in the Duluth Complex. B-horizon and seepage soil samples were collected over both copper-nickel mineralization and barren granite. Seven extraction methods were tested on various size fractions of the soil to determine which size fraction and extraction method yielded maximum contrast over background. Also, a dithiazone field analytical method was tested.

GEOLOGY

The general Precambrian geology of the Birch Lake area is illustrated on Figure 1. Disseminated copper-nickel mineralization occurs in a basal troc-tolite 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

Three types of soil samples were collected: A-horizon, B-horizon and seepage soil. Seepage soil, for this study, is a name given to soils which occur at the toe of hills where the water table nearly comes to the surface or actually reaches the surface. The seepage soils collected are generally oxidized and contain relatively large amounts of iron. Seepage soils may occur beneath humus.

The soil in this region of Minnesota is a moderately well developed podzol. The humus of the A-horizon in the area surveyed was generally three inches thick. The B-horizon was sampled in the range of 6-18 inches in the iron rich portion. The B-horizon sampled is generally medium to dark brown-red in color, and a fine to coarse grained silty-sand or sandy-silt. Boulders commonly were found at sample sites.

A-horizon samples were collected along with the B-horizon but were not analyzed for this study. The A-horizon trace element concentrations are usually very erratic compared to the B-horizon and, therefore, more difficult to interpret. The A-horizon samples will be tested by various extraction methods in the future.

Ten B-horizon and twelve seepage soil samples were collected. Sample sites were selected over both the granite and copper-nickel mineralization (Figures 2 and 3). Two of the seepage soil samples were collected over the basal troctolite unit near Filson Creek six miles northeast of the area shown on Figure 3. The B-horizon samples were taken with
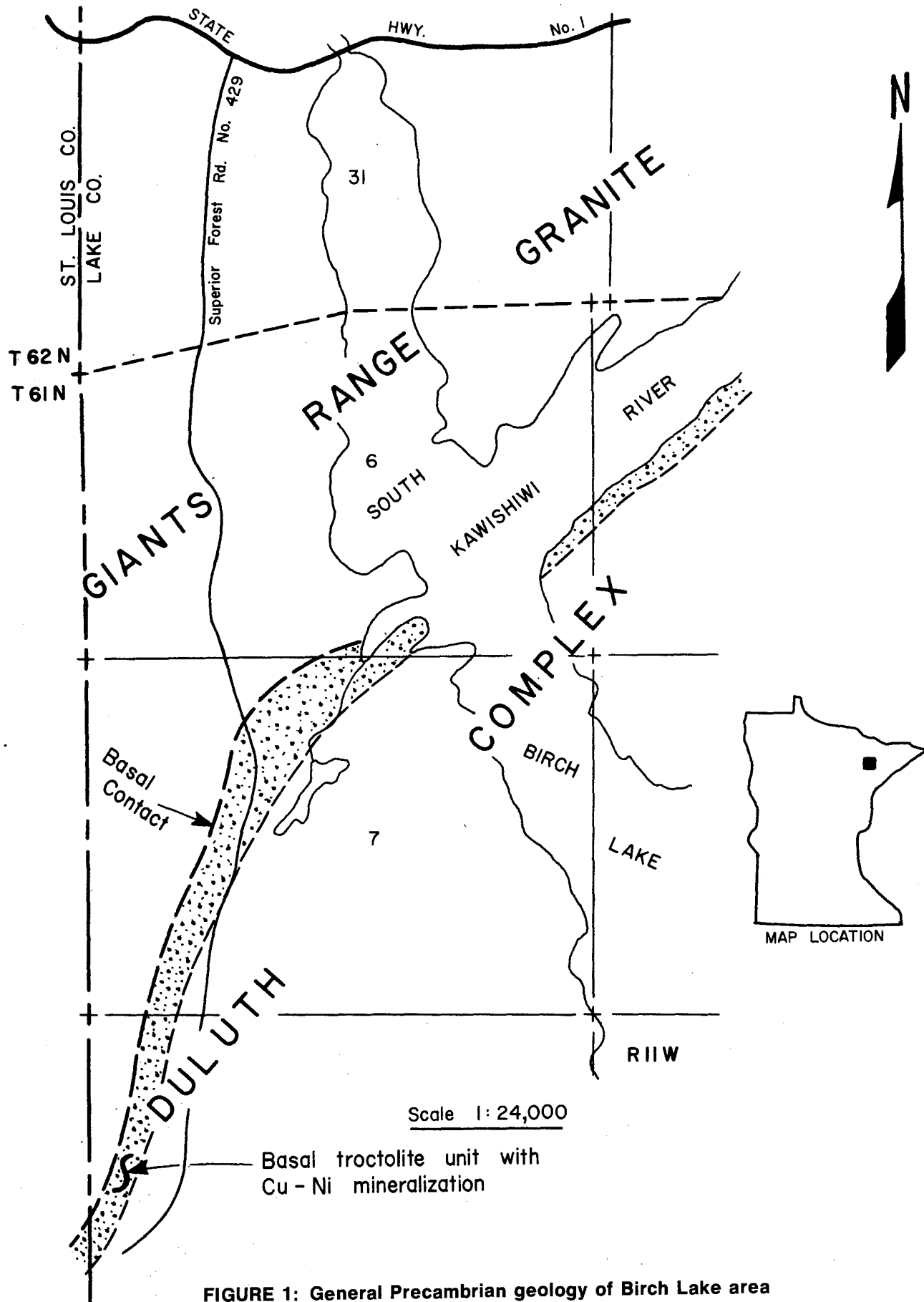
FIGURE 1: General Precambrian geology of Birch Lake area
(From Phinney, 1967 and Sims, 1973)

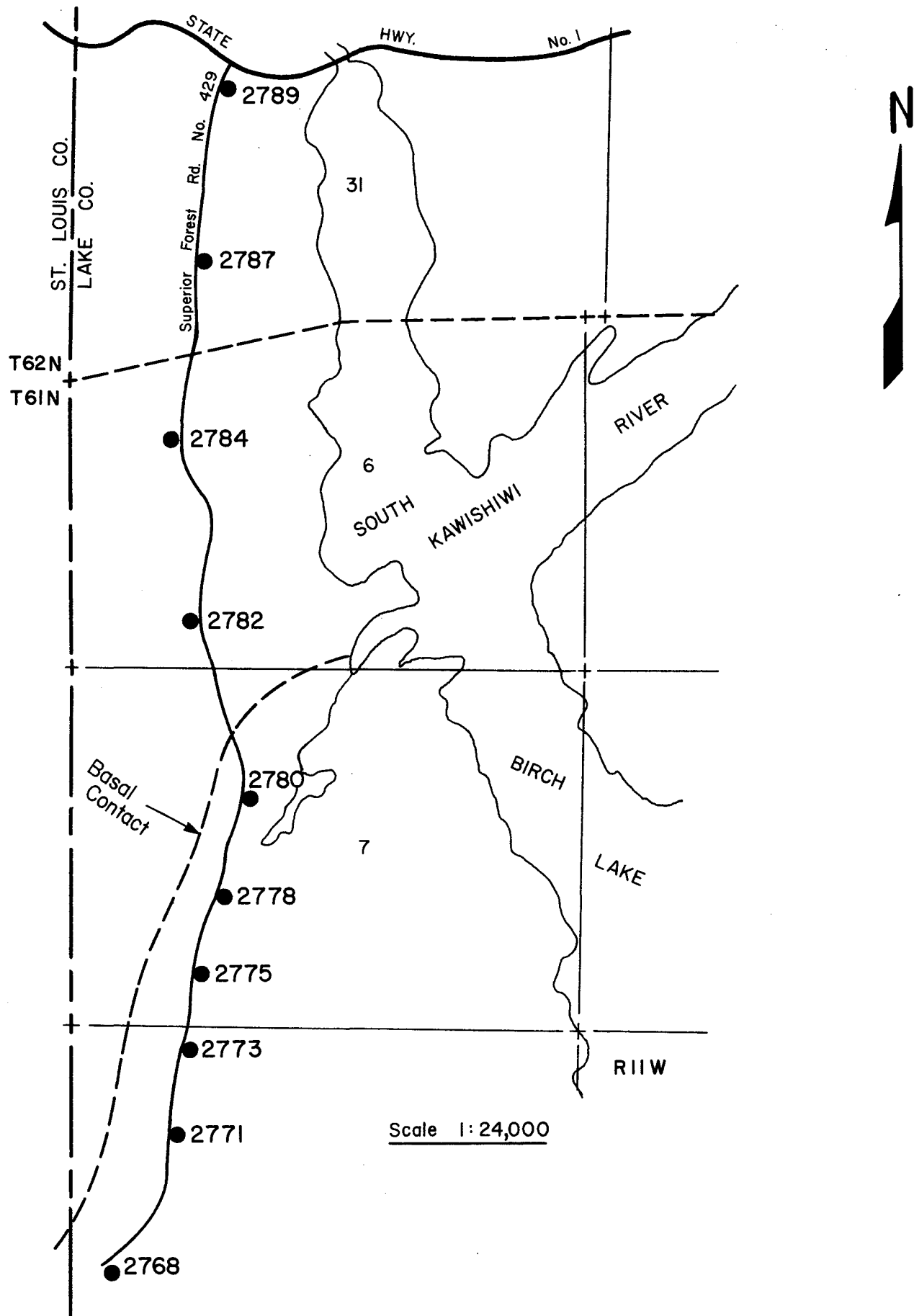Scale 1: 24,000

Basal troctolite unit with
Cu – Ni mineralization

FIGURE 2: B-horizon sample sites with sample numbers
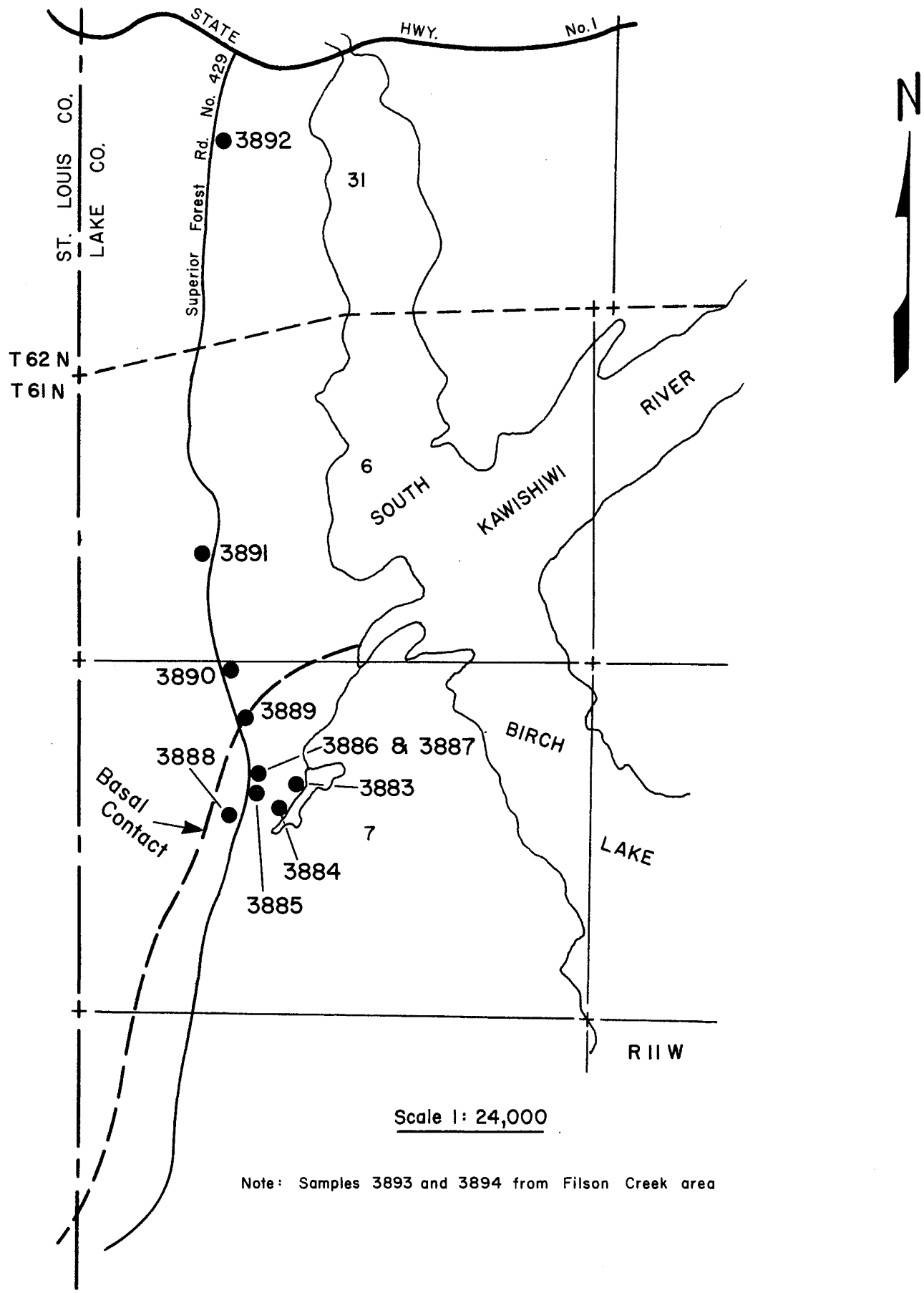
FIGURE 3: Seepage soil sample sites with sample numbers

Note: Samples 3893 and 3894 from Filson Creek area

Scale 1: 24,000

a two inch diameter flight auger and the seepage soils with a shovel.

SAMPLE PREPARATION AND ANALYTICAL METHODS

The soil samples were dried at 80°C, broken up with a rolling pin, and sieved to three size fractions: 1) −35+80 mesh (−500+177 micron), 2) −80 mesh, and 3) −230 mesh (−63 micron).

The B-horizon samples were tested by seven extraction methods to determine which method yielded maximum contrast between samples over mineralization and those over granite. These methods are as follows with details given in the Appendix.

AN-10: Concentrated HCl, HNO_3 & HF in an acid digestion bomb

AN-8: Ascorbic Acid & Hydrogen Peroxide

AN-15: 4M HNO_3 & 1M HCl

AN-17: o.1M EDTA

AN-18: Ammonium Citrate & Hydrogen Peroxide

AN-19A & AN-19B Ammonium Citrate & Hydroxylamine Hydrochloride

AN-21: Ammonium Oxalate & Oxalic Acid

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 references. The seepage soils only were analyzed by AN-10.

Arsenic and sulfur were analyzed by AN-3 and AN-11, respectively. See Appendix for details of these methods.

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, chromium, copper, molybdenum, nickel, lead, titanium, zinc, iron, magnesium and manganese. Lead and zinc were determined by the Perkin-Elmer electrodeless discharge lamps (EDL) and power supply. Arsenic was analyzed on the Perkin-Elmer 303 using the EDL system, deuterium background corrector and arsine generator.

A dithiazone titration method (see AN-20 in Appendix) was tested in the laboratory on the B-horizon samples for possible application as a field method.

RESULTS AND DISCUSSION

The element concentrations for the various size fractions and analytical methods tested are given in Tables 1 through 12. 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 Figures 2 and 3 for sample locations and Figure 1 for relation to geology. Table 2 gives the soil type encountered at each B-horizon sample site.

Silver, arsenic, cobalt, copper, nickel, lead, sulfur and zinc were analyzed primarily as indicators of mineralization. Chromium, titanium, iron and magnesium were analyzed to determine if the bedrock chemistry was reflected in the B-horizon.

Iron and manganese were also analyzed to determine if relationships existed between the trace elements and the iron-manganese hydroxides, which could result in false anomalies if excessive amounts of this sample component occurred in some samples.

In order to compare the element concentrations of the various size fractions and the extractability of the various analytical methods for the B-horizon, the mean values for each element in Tables 1-9 and 11 are given in Table 13. AN-10 is a near total digestion and obviously extracts significantly more metal from the samples than the other analytical methods tested (Table 13). Cobalt, chromium, copper, nickel and lead are clearly concentrated in the coarse fraction (−35+80 mesh) as opposed to the finer fractions (−80 and −230 mesh). The −35+80 mesh fraction contains a large amount of mineral and rock fragments. Therefore, it appears that a higher proportion of these elements are contained in the fragments. The finer fractions generally contain a higher proportion of secondary minerals and hydroxides, which more readily break down into finer sizes. For some elements, the −230 mesh fraction has higher concentrations than the −80 mesh fraction.

Comparing Figures 1 and 2 with chromium, titanium, iron and magnesium in Table 1 clearly indicates that these elements do reflect the chemical composition of the bedrock (granite and gabbro). Also, comparison of these figures with Table 2 reveals that the higher sulfur content of the Duluth Complex is also reflected in the −80 mesh fraction.

The purpose of this survey was mainly to determine which analytical method yielded maximum contrast over background values for the B-horizon. Most of the size fractions and analytical methods tested did give a definite anomaly or contrast for copper and nickel over the Duluth Complex. Table 14 gives the percent coefficients of variation for each element size fraction and analytical method. Often, the coefficients of variation will indicate the method which yields the maximum contrast between background and mineralization. However, high variations are possible which will not yield the best contrast. Therefore, another calculation was made as described in Table 15. Generally, the maximum contrast values in Table 15 correspond to the maximum coefficients of variation for each element, size fraction and analytical method in Table 14.

From Table 15, it is evident that AN-15 gives the best contrast for both copper and nickel. Table 15 further suggests that AN-8 is more desirable if only searching for copper and AN-10 for zinc. If copper, nickel and zinc, or copper and zinc were mainly of interest in a B-horizon survey, then AN-15 appears to be the best analytical method.

At least for AN-10, the −80 and −230 mesh fractions generally give higher contrast than the −35+80 mesh fraction. The contrast is not significantly different for the −80 and −230 mesh fraction. Therefore, the −80 mesh fraction is preferred as it is more easily sieved.

The field dithiazone method (AN-20) (Tables 10 and 15) did not reflect mineralization very well. Furthermore, the color changes were difficult to determine because the B-horizon samples clouded the solution. Use of this method, based on these results, appears difficult to apply in the field.

The seepage soils were only analyzed by AN-10 on the −80 mesh fraction (Table 12). The copper-nickel mineralization is definitely reflected by comparing Figures 1 and 3 with Table 12. As described previously, these samples were collected near the toe of hills, often below the humus layer. Often seepage soil samples would be collected in the normal course of B-horizon sampling on a grid. The element concentrations for the seepage soils are significantly higher than the B-horizon samples. The B-horizon samples were not collected at the toes of hills.

Samples 3886 and 3887 (Table 12) indicate that significantly different element concentrations can be obtained only twenty feet apart when collecting a gleyed (reduced) sample as compared to an oxidized sample. This suggests that gleyed samples should not be compared to oxidized seepage or B-horizon samples in geochemical surveys. All seepage samples collected for this survey, except 3887, were oxidized.

The seepage soils may have application in detailed location of mineralization, especially in areas where B-horizon sampling does not reflect mineralization due to excessively thick glacial drift. The seepage soils should be collected in an area where the groundwater at least occasionally reaches the surface. The metal ions are transported in the groundwater and precipitated in the seepage soil.

Although only AN-10 was tested on the seepage soils, the similar nature of these samples to the B-horizon soil would suggest that the analytical methods which yield maximum contrast for the B-horizon soil should also be applied to seepage soils.

Coefficients of determination (r^2) for the B-horizon samples analyzed by AN-15 are given in Table 16.

An insufficient number of samples (10) were collected to give a high degree of confidence to the r^2 values. However, Table 16 does give a general indication of the element relationships.

Examination of Table 16 reveals that cobalt, copper, nickel and zinc all demonstrate a strong relation to iron and manganese. This suggests that these metals are contained in the iron-manganese oxides of the B-horizon, as would be expected. Copper and nickel demonstrate a strong positive relation. Although not shown in Table 16, copper and nickel have even a stronger positive relation (.84) for the samples over the Duluth Complex. This strong relation for copper and nickel indicates that the B-horizon is reflecting the chemical nature of the underlying bedrock.

If a survey were conducted where at least 30 B-horizon or seepage soil samples were collected, it would be desirable to further examine the element relationships. Evaluation of the trace element relations with iron and manganese may reveal that ratios of the trace elements with iron or manganese would be necessary to suppress high trace element values resulting from high concentrations of iron-manganese oxides.

Ratios of trace elements and iron were calculated for the B-horizon samples analyzed by AN-15 for this survey. These ratios did tend to smooth the data; however, anomaly contrast was also significantly reduced.

CONCLUSIONS

Chromium, titanium, iron and magnesium of the −35 + 80 mesh fraction of the B-horizon does reflect the bedrock composition.

For the B-horizon, AN-15 gives the best contrast over background for both copper and nickel. For copper only, AN-8 gives the best contrast. If copper, nickel and zinc or copper and zinc are mainly of interest in a B-horizon survey, then AN-15 appears to be the best analytical method. The −80 and −230 mesh fractions both yield approximately the same contrast. However, for ease of sieving, the −80 mesh fraction is more desirable.

The field dithiazone method (AN-20) did not reflect mineralization as well as other methods and appears difficult to apply to B-horizon soils.

Seepage soils do reflect mineralization. Their main application should probably be limited to the detailed follow-up stage of geochemical exploration. Although only AN-10 was tested on these samples, the analytical methods which yield the best contrasts for the B-horizon should give similar results for the seepage soil.

TABLE 1: B-horizon (−35+80 mesh fraction)
analyzed by AN-10 & 11

Sample Number	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Ti (%)	Zn (ppm)	Fe (%)	Mg (%)	Mn (ppm)
2789	Not analyzed										
2787	100	40	20	60	33	.03	.24	60	1.23	0.53	253
2784	87	123	73	313	67	.04	.22	50	1.67	0.67	280
2782	97	97	23	197	67	.07	.27	80	1.63	0.73	383
2780	120	173	767	523	67	.06	.85	180	1.63	1.33	607
2778	120	200	337	343	67	.03	.94	123	6.00	2.23	680
2775	133	133	237	317	67	.05	.91	187	6.03	2.03	587
2773	90	337	190	383	33	.04	.32	43	2.60	2.10	417
2771	100	457	130	1183	67	.03	.28	50	2.10	1.93	483
2768	103	127	153	197	33	.01	.60	97	3.80	1.23	583

TABLE 2: B-horizon (−80 mesh fraction)
analyzed by AN-3, 10 & 11

Sample Number	Soil Type	Ag (ppm)	As (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Ti (%)	Zn (ppm)	Fe (%)	Mg (%)	Mn (ppm)
2789	P	0	0	73	23	20	<20	67	20	.04	.62	67	2.53	.96	400
2787	PP	0	0	53	27	30	<20	70	13	.04	.47	50	2.47	1.03	353
2784	PP	0	0	83	83	37	<20	113	17	.05	.47	57	3.40	1.07	377
2782	P	0	0	63	43	27	<20	83	23	.03	.56	73	2.60	1.27	487
2780	P	0	0	70	63	860	<20	463	27	.07	.60	240	4.93	.97	447
2778	P	0	0.4	83	83	330	<20	263	17	.05	.61	123	4.43	1.33	480
2775	P	0	0.2	93	110	233	<20	223	13	.09	.50	123	4.63	1.27	373
2773	P	0	0	77	223	110	<20	177	13	.06	.57	57	3.23	1.90	383
2771	HG	0	0	77	333	60	<20	170	20	.05	.63	57	3.10	2.40	520
2768	P	0	0.4	67	80	230	<20	23	13	.21	.77	87	4.33	1.33	503

P = Podzol
PP = Peaty podzol
HG = Humic gley

TABLE 3: B-horizon (−230 mesh fraction)
analyzed by AN-10 & 11

Sample Number	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Ti (%)	Zn (ppm)	Fe (%)	Mg (%)	Mn (ppm)
2789	77	27	23	67	33	.02	.51	77	1.67	.80	340
2787	73	27	23	67	133	.02	.56	60	2.33	1.03	363
2784	93	157	57	147	33	.03	.48	57	3.47	1.17	393
2782	83	60	23	93	67	.02	.55	77	2.30	1.20	433
2780	107	47	750	463	33	.03	.43	243	4.47	.60	397
2778	100	53	317	250	33	.03	.47	133	4.20	.93	423
2775	113	107	220	243	33	.03	.40	143	3.77	.93	297
2773	87	193	137	160	33	.02	.51	66	2.70	1.10	263
2771	93	380	83	200	33	.02	.69	30	3.13	2.33	443
2768	97	90	233	233	67	.03	.55	33	3.90	1.33	533

TABLE 4: B-horizon (−80 mesh fraction) analyzed by AN-8

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	6	0	3	8	.47	45
2787	3	0	3	9	.57	40
2784	5	2	2	8	.64	40
2782	6	3	4	12	.51	66
2780	7	81	24	9	.66	115
2778	6	26	8	5	.50	89
2775	7	18	5	3	.21	16
2773	6	16	6	4	.44	11
2771	8	24	22	9	.54	31
2768	3	13	6	4	.42	98

TABLE 5: B-horizon (−80 mesh fraction) analyzed by AN-15

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	9	8	10	33	.87	101
2787	11	13	13	50	1.25	88
2784	11	12	11	27	1.49	89
2782	11	10	13	33	1.04	122
2780	21	495	267	111	3.26	256
2778	21	197	132	72	3.11	265
2775	28	128	115	65	3.15	170
2773	12	68	50	27	1.82	58
2771	12	36	49	20	1.05	77
2768	18	149	107	50	2.41	249

TABLE 6: B-horizon (−80 mesh fraction) analyzed by AN-17

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	1	3	3	3	.04	15
2787	0	3	3	3	.06	9
2784	0	4	0	3	.13	9
2782	0	4	0	3	.04	16
2780	2	50	1	7	.14	72
2778	2	14	0	3	0	50
2775	0	12	5	3	0	11
2773	2	10	1	3	.05	6
2771	0	17	12	5	.07	10
2768	3	9	5	3	0	68

TABLE 7: B-horizon (−80 mesh fraction) analyzed by AN-18

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	1	7	6	9	.22	19
2787	1	6	6	7	.23	11
2784	2	6	4	7	.27	9
2782	2	7	5	8	.16	25
2780	7	104	26	14	.76	125
2778	3	28	8	7	.31	90
2775	5	22	5	7	.25	15
2773	2	14	4	9	.23	5
2771	2	18	7	8	.21	9
2768	6	17	7	10	.34	89

TABLE 8: B-horizon (−80 mesh fraction) analyzed by AN-19A

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	0	22	1	3	.14	19
2787	0	22	0	3	.07	23
2784	0	23	1	3	.20	11
2782	0	23	0	3	.14	9
2780	0	54	9	5	.38	95
2778	0	29	2	3	.08	75
2775	0	25	0	3	.04	14
2773	0	24	4	2	.18	7
2771	0	18	4	3	.20	10
2768	0	17	0	3	.13	90

TABLE 9: B-horizon (−80 mesh fraction) analyzed by AN-19B

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	6	4	2	4	.15	19
2787	5	4	0	5	.18	12
2784	8	6	2	14	.71	245
2782	2	5	2	6	.22	42
2780	4	44	10	9	.50	110
2778	3	120	2	4	.18	22
2775	5	110	4	5	.16	22
2773	0	8	2	4	.15	5
2771	2	6	2	5	.24	12
2768	8	6	0	4	.13	105

TABLE 10: B-horizon (−80 mesh fraction) analyzed by AN-20

Sample Number	Dz (mls)
2789	1.5
2787	1
2784	9
2782	1
2780	7.5
2778	3
2775	3
2773	1.5
2771	1.5
2768	3

TABLE 11: B-horizon (−80 mesh fraction) analyzed by AN-21

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
2789	7	5	4	10	.59	33
2787	7	7	9	9	.72	14
2784	6	38	17	17	.73	144
2782	7	5	11	9	.36	31
2780	20	139	82	35	2.11	172
2778	15	51	36	14	1.51	142
2775	12	42	30	15	1.33	58
2773	0	20	10	8	.57	10
2771	8	21	13	9	.32	9
2768	12	28	26	14	1.24	115

TABLE 12: Seepage soil (−80 mesh fraction)
analyzed by AN-10

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	Remarks
3892	0	80	67	250	33	—	4.00	510	
3891	0	73	30	283	33	93	4.17	417	
3890	0	73	27	247	0	80	3.50	307	
3889	0	70	23	253	33	110	4.47	393	
3886	0	100	400	527	33	173	5.17	400	
3887	0	60	110	310	33	80	2.73	273	Gleyed (reduced) soil 20' down drainage from 3886
3885	0	100	643	493	33	97	4.90	623	
3888	0	90	1300	753	33	117	6.27	413	
3883	0	87	953	480	33	100	4.90	340	
3884	0	83	233	340	67	73	4.53	400	
3893	3	110	6000	793	33	120	5.67	343	Sample from Filson Creek area
3894	3	147	9200	1067	0	123	8.17	361	Sample from Filson Creek area

TABLE 13: Mean element concentrations for ten B-horizon samples for each analytical method and size fraction

Analytical Method	Ag (ppm)	As (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Ti (%)	Zn (ppm)	Fe (%)	Mg (%)	Mn (ppm)
AN-10 & 11 (−35+80)			106	187	214	391	56	.04	.51	97	2.97	1.42	475
AN-3, 10 & 11 (−80)	0	0.1	74	107	194	165	18	.07	.58	93	3.57	1.35	432
AN-10 & 11 (−230)			92	114	187	192	50	.03	.52	92	3.19	1.14	389
AN-8			6		18	8	-			7	.50		55
AN-15			15		112	77				49	1.95		148
AN-17			1		13	3				4	.05		27
AN-18			3		23	8				9	.30		40
AN-19A			0		26	2				3	.16		35
AN-19B			4		31	3				6	.26		59
AN-21			9		36	24				14	.95		73

TABLE 14: Percent coefficients of variation $(100\%(S/\bar{X}))$ for ten B-horizon samples for each analytical method and size fraction

Analytical Method	As	Co	Cr	Cu	Ni	Pb	S	Ti	Zn	Fe	Mg	Mn
AN-10 & 11 (−35+80)		15	70	108	83	30	45	61	57	63	47	32
AN-3, 10 & 11 (−80)	170	15	91	133	78	27	75	15	62	26	34	14
AN-10 & 11 (−230)		14	95	119	61	65	18	16	70	29	41	20
AN-8		27		134	99				42	26		64
AN-15		42		135	106				57	49		55
AN-17		115		108	124				34	100		97
AN-18		71		128	82				24	57		110
AN-19A				40	144				25	60		103
AN-19B		66		148	95				53	73		128
AN-21		59		110	95				57	61		87

TABLE 15: Anomaly contrast comparison for B-horizon samples for each analytical method and size fraction

Analytical Method	D/G												THM
	As	Co	Cr	Cu	Ni	Pb	S	Ti	Zn	Fe	Mg	Mn	
AN-10 & 11 (−35+80)		1.2	2.7	7.7	2.6	1.0	.8	2.7	1.8	2.4	2.8	1.8	
AN-3, 10 & 11 (−80)	2	1.2	3.4	10.5	2.7	.9	2.3	1.2	1.9	1.5	1.4	1.1	
AN-10 & 11 (−230)		1.2	2.1	9.1	2.7	.6	1.5	1.0	1.6	1.5	1.1	1.0	
AN-8		1.2		30.0	4.0				.7	.8		1.3	
AN-15		1.7		16.3	10.0				1.6	2.1		1.8	
AN-17		6.0		4.8	2.0				1.3	.6		3.1	
AN-18		2.7		4.9	2.0				1.1	1.6		3.5	
AN-19A				1.2	6.0				1.0	1.2		3.1	
AN-19B		.8		9.8	.7				.7	.7		.6	
AN-20													1.1
AN-21		1.6		3.6	3.3				1.5	2.0		1.5	

D = Mean of element values for samples 2768, 2771, 2773, 2775, 2778 and 2780 over the Duluth Complex

G = Mean of element values for samples 2782, 2784, 2787 and 2789 over granite

D/G = Contrast

TABLE 16: Coefficients of determination (r^2) for −80 mesh B-horizon samples analyzed by AN-15

	Co	Cu	Ni	Zn	Mn
Fe	.80	.56	.68	.64	.60
Mn	.53	.51	.56	.62	
Ni		.68			

r^2 determined by $\log y = a + b \log x$

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APPENDIX: DESCRIPTION OF ANALYTICAL METHODS

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-8: Ascorbic Acid & Hydrogen Peroxide

Ascorbic acid-hydrogen peroxide solution was prepared by adding 5 gm of ascorbic acid to 500 mls of deionized water, followed by the addition of 200 mls of 30% hydrogen peroxide.

1.0000 gm sample was digested in 20 mls of the above solution for 18 hours with occasional stirring. After digestion, the solution was diluted with deionized water to 100 mls and filtered with #40 Whatman filter paper.

AN-10: Concentrated HCl, HNO_3 & HF in Acid Digestion Bomb

1.0000 gm sample was placed in a teflon crucible and wetted with 0.5 ml of aqua regia. Next, 3.0 ml of HF was added to the sample. The crucible was inserted in a stainless steel bomb and placed in an oven for 30 to 40 minutes at 110°C. After the bomb has cooled to ambient temperature, 3.0 gm of boric acid is added to dissolve any precipitates which have for-

med. Finally, sample solution is diluted with deionized water to 100 mls. Filtering is not required.

AN-11: Sulfur

1.0000 gm sample was placed in crucible with a tin-copper accelerator strip. Crucible is placed in tube furnace at 3000°F. As sulfur dioxide evolves from sample, the sulfur concentration of the sample is measured with a Leco titrator.

AN-15: 4M HNO_3 & 1M HCl

1.0000 gm sample was digested in 10 mls of 4M HNO_3 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.

AN-19A: Ammonium Citrate & Hydroxylamine Hydrochloride

Test solution was prepared by dissolving 50 gm of ammonium citrate and 20 gm of hydroxylamine hydrochloride in 300 mls of deionized water. The pH was adjusted to 4.3 with ammonium hydroxide and the solution was diluted with deionized water to 1000 mls.

1.0000 gm sample was digested in 50 mls of the above solution for 18 hours with occasional stirring. After digestion, the sample solution was diluted with deionized water to 100 mls and filtered with #40 Whatman filter paper.

AN-19B: Ammonium Citrate & Hydroxylamine Hydrochloride

Test solution was prepared by dissolving 50 gm of ammonium citrate and 20 gm of hydroxylamine hydrochloride in 300 mls of deionized water. The pH was adjusted to 2.0 with concentrated hydrochloric acid and the solution diluted with deionized water to 1000 mls. The pH in 1000 ml solution is 2.4.

1.0000 gm sample was digested in 50 mls of the above solution for 18 hours with occasional stirring. After digestion, sample solution was diluted with deionized water to 100 mls and filtered with #40 Whatman filter paper.

AN-20: Dithiazone

100 mg sample was added to 5 mls of total heavy metal (THM) buffer solution and titrated with dithiazone solution. Values recorded as mls of dithiazone to reach end point. THM buffer and dithiazone capsules supplied by GISCO.

AN-21: Ammonium Oxalate & Oxalic Acid

24.87 gm of ammonium oxalate and 12.6 gm of oxalic acid was dissolved in 1000 mls of deionized water (0.1M oxalic acid).

1.0000 gm sample was digested in 50 mls of the above solution for 18 hours with occasional stirring. After digestion, the sample solution was diluted with deionized water to 100 mls and filtered with #40 Whatman filter paper.