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



Minnesota Department of Natural Resources
Division of Minerals
Minerals Exploration Section

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

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Division of Minerals
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ABSTRACT

A peat geochemical exploration pilot study was conducted over copper-nickel mineralization in the Birch Lake area of northern Minnesota. Four extraction methods were tested to determine which method gave the maximum contrast over mineralization compared to areas barren of copper-nickel mineralization.

Results indicate that peat does reflect known copper-nickel mineralization. 0.1M EDTA gives the maximum contrast over background for the extraction methods tested. The survey suggests that peat samples for geochemical exploration surveys should be taken at approximately the same depth or at the base of the peat formation due to variations in element concentrations resulting from various degrees of humification.

Ore deposits often occur below swamps in glaciated terrain, and many of the areas' potential for base metal deposits in northern Minnesota are covered by swamps. Therefore, peat geochemical surveys can be an added tool in the search for mineral deposits and the evaluation of mineral potential if glacial drift conditions are not prohibitive.

Introduction

Peat as a geochemical exploration sample media has been shown to reflect mineralization in Canada, Ireland, Norway, Sweden and other areas of the world (Hawkes and Salmon, 1960; Morrissey and Romer, 1973; Salmi, 1959; Band, 1976; Larsson, 1976). Also, ore deposits often occur below swamps in glaciated terrain due to relatively easily erodible associated rocks (Morrissey and Romer, 1973; Nieminen and Yliruokanen, 1976).

Many of the areas' potential for base metal deposits in northern Minnesota are covered by swamp deposits. 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 test the use of peat as a geochemical sample media.

During 1975-76 a pilot study was conducted on the use of peat as a geochemical exploration sample media over copper-nickel mineralization in the Duluth Complex. Peat samples were collected over both copper-nickel mineralization and barren

granite. The peat samples were tested with four extraction methods to determine a method which yielded the maximum contrast over background.

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 50 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

Eleven peat samples were collected with a Davis peat coring sampler. The peat cores obtained are 7/8 inch diameter. Samples were taken from various depths. Sample sites (Figure 2) were selected over both the granite and copper-nickel mineralization. One sample was collected over the basal troctolite unit near Filson Creek six miles northeast of the area shown on Figure 2.

Sample Preparation and Analytical Methods

The peat samples were dried at 80°C, broken up in a blender and sieved to -80 mesh (177 micron). Ignition of the samples prior to analysis was not considered due to reduction of copper values resulting from ashing (Peachey, 1976; Meineke, Vadis and Klaysmat, 1976).

The -80 mesh sample was tested by four extraction methods to determine which method yielded maximum contrast between samples over copper-nickel mineralization and those over granite. These methods are as follows with descriptions of methods given in the Appendix.

AN-1: Concentrated HCl, HNO₃ and HF

AN-15: 4M HNO₃ and 1M HCl

AN-17A & AN-17B: 0.1M EDTA

AN-18: Ammonium Citrate and Hydrogen Peroxide
The "AN" numbers above will be used to identify the extraction methods throughout this report. The ex-

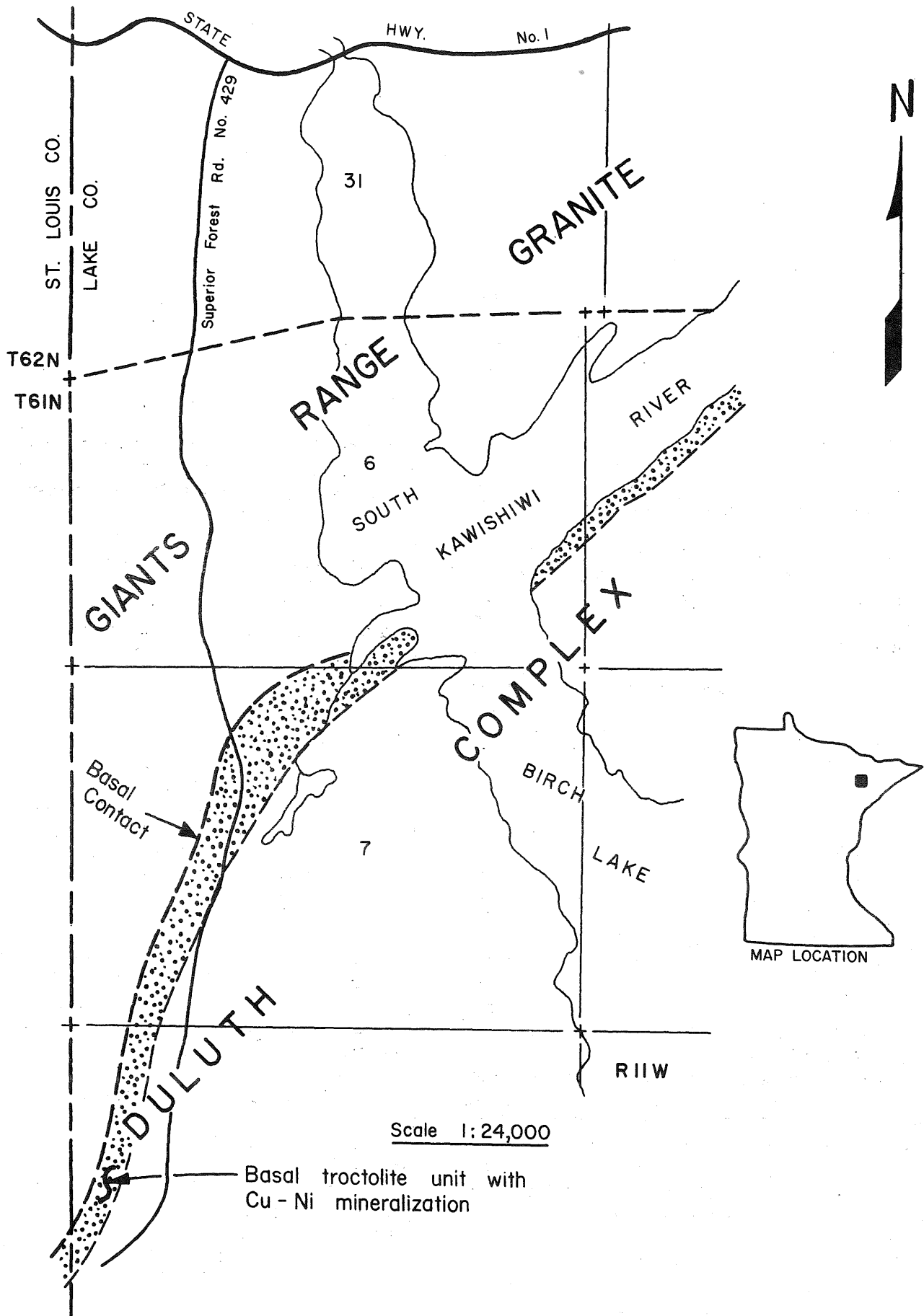


FIGURE 1: General Precambrian geology of Birch Lake area
 (From Phinney, 1967 and Sims, 1973)

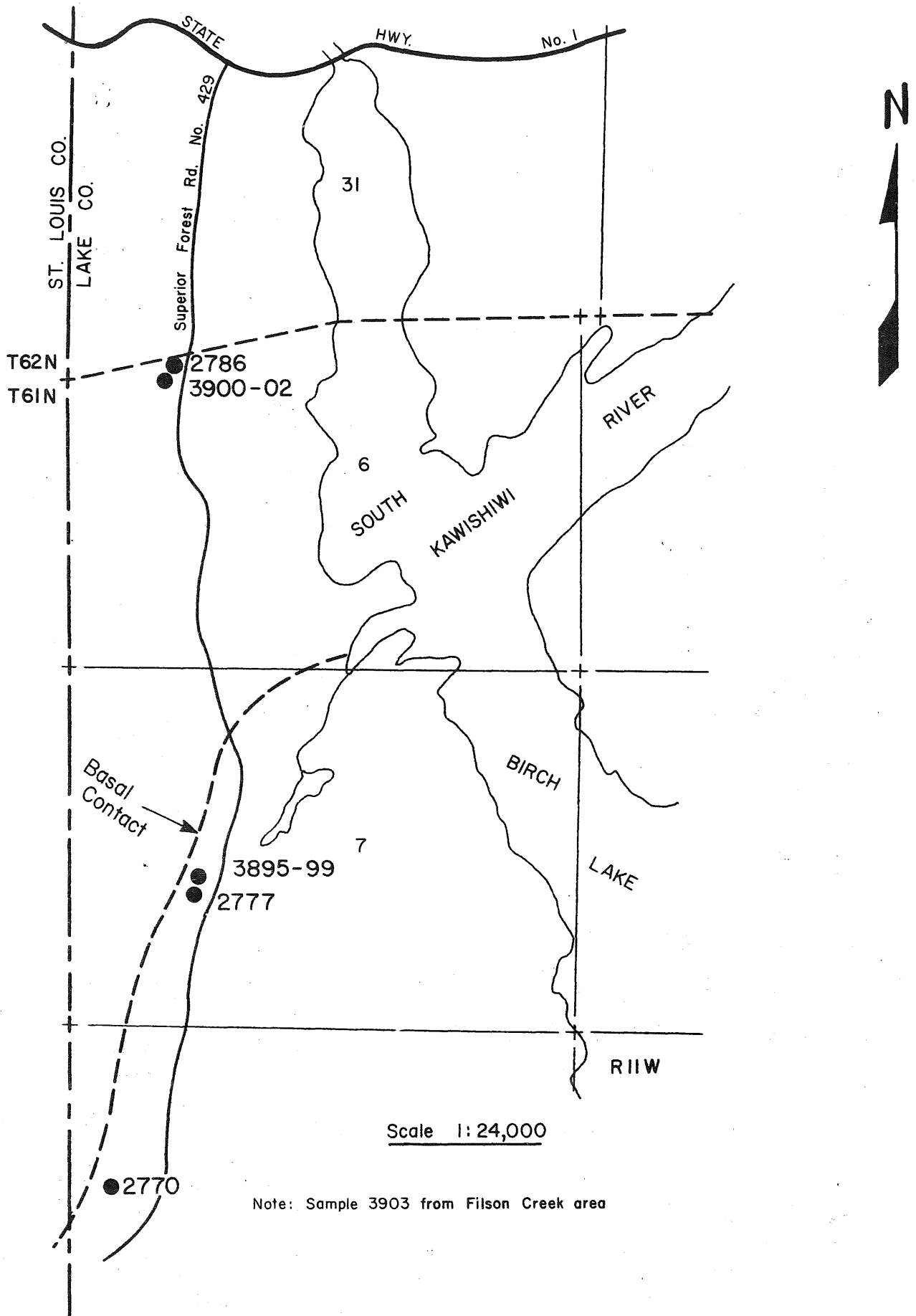


FIGURE 2: Sample sites with sample numbers

traction 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. LOI (loss-on-ignition) was determined as an estimate of organic content for each sample according to the method (AN-14) described in the Appendix.

Following dissolution of the samples by the above extraction methods, the sample solutions were analyzed on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer for silver, cobalt, copper, nickel, lead, zinc, iron and manganese. Lead and zinc were determined by using the Perkin-Elmer electrodeless discharge lamps and power supply.

Results and Discussion

The element concentrations for the four extraction methods tested are given in Tables 1-5. The samples located over the granite are given at the top of each table and the samples over copper-nickel mineralization at the bottom. See also Figure 2 for sample locations and Figure 1 for relation to mineralization.

All samples collected are peat, except 3900 (only listed in Table 1), which is a clay sample collected directly below peat sample 3901.

Sample 2786 was taken at a depth of 18-24 inches. The thickness of the peat is unknown at this site, but probably less than six feet. Samples 3902 and 3901 represent a section from a depth of 54 inches to the base of the peat formation (69"). Sample 2777 was collected at a depth of 28-36 inches. The thickness of the peat at this site is probably seven feet. Samples 3895-3899 represent a section from 12 inches of depth to the base of the peat formation (86"). At sample sites 2770 (24-30") and 3903 (60-70") the thickness of the peat is unknown.

Table 1, in addition to element concentrations for AN-1, gives the LOI for all peat samples. Iron, manganese and LOI were analyzed to determine if relationships existed between the trace elements and the iron-manganese hydroxides or the organics which could result in false anomalies if excessive amounts of these sample components occurred in some samples.

Table 1 indicates that the LOI and, therefore, the organic content of the peat decreases with depth. This decrease in LOI with depth is a result of increased humification with depth and is typical of peat bogs.

Tables 1-5 suggest that the concentrations of the elements also increase with depth and degree of humification. However, when mineralization occurs beneath the bogs, as is the case for samples over the Duluth Complex, increases in element concentrations would also be expected.

As described previously, the objectives of this pilot study were to determine if peat reflected mineralization and, if so, which extraction method yielded maximum contrast over background values. Examination of Tables 1-5 indicates that copper and nickel do reflect mineralization by all extraction methods tested as compared to the samples over the granite. However, from examination of the tables, it appears desirable to collect samples with approximately the same degree of humification (approximately equal LOI). This could practicably be accomplished by taking all samples at the same depth from surface or only collecting basal peat samples. This may not be absolutely necessary, but should result in less element variation due to organic variation from sample to sample and, therefore, make interpretation less difficult.

In order to compare the degree of extraction of each analytical method, the mean concentration of the eleven peat samples for each method are given in Table 6. AN-1, which is a near total digestion, extracts significantly more metals than the other methods. However, to obtain maximum geochemical contrast between background and mineralization, a strong digestion such as AN-1 is not desirable. This method extracts metal from components of the peat (i.e. clays and igneous and metamorphic, rock-forming silicates) whose metal content are of either remote origin or not as directly related to mineralization as is the case of the organic fraction of the peat. Metal fixation in peat largely results from sequestration of the metals from groundwater by formation of organo-metallic complexes and chelation (Maynard and Fletcher, 1973). The other three methods tested (AN-15, 17 and 18) are more specific for extraction of metal from the organic fraction of the peat and, therefore, more desirable for the purposes of geochemical exploration. AN-1 was only tested and reported for comparison purposes.

Table 7 gives the percent coefficients of variation for each element and analytical method. Often the coefficients of variation will indicate the analytical 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 8. The maximum contrast values in Table 8, except iron and manganese, correspond to the maximum coefficients of variation for each element and analytical method in Table 7. From Table 8, it is evident that AN-17A (0.1M EDTA) gives the maximum contrast for cobalt, copper and nickel and, therefore, is recommended for peat geochemical surveys in this region of Minnesota. Table 8 also suggests that iron and manganese are reflecting the mafic composition of the mineralized troctolite as compared to the granite.

Coefficients of determination (r^2) for the peat samples analyzed by AN-17A are given in Table 9. An insufficient number of samples (11) were collected to give a high degree of confidence to the r^2 values. However, Table 9 does give a general indication of the relationships.

Several observations can be made from Table 9. Cobalt, copper, nickel and zinc all have a negative relation with LOI, which appears to result from the degree of humification of the peat, previously described. Copper and nickel have a strong positive (.81) relation. Although not shown in Table 9, copper and nickel have an even stronger positive relation (.87) for the samples over the Duluth Complex. This strong relation for copper and nickel indicates that the peat is reflecting the chemical nature of the underlying bedrock.

If a survey were conducted where at least 30 peat samples were collected, it would be desirable to further examine the element and LOI relationships. Evaluation of the element-LOI relationships may indicate, for example, that the element concentrations should be based on the unignitable weight of the sample (element concentration/(1-LOI/100)). Such a manipulation may smooth erratic values resulting

from varying LOI, even if samples are collected with approximately the same LOI.

Conclusions

Although only eleven peat samples were collected for this pilot study, the trace element concentrations of the peat does reflect known mineralization. For the extraction methods tested, 0.1M EDTA (AN-17A) gives the best contrast over background and, therefore, is the suggested method for peat geochemical exploration surveys in this region of Minnesota.

Results from this survey suggest that peat samples for geochemical exploration surveys should all be taken from the same depth or at the base of the peat formation.

Ore deposits often occur below swamps in glaciated terrain, and many of the areas' potential for base metal deposits in northern Minnesota are covered by swamps. Therefore, peat geochemical surveys can be an added tool in the search for mineral deposits and the evaluation of mineral potential, if glacial drift conditions are not prohibitive.

TABLE 1: Peat and one clay sample analyzed by AN-1

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	*LOI (%)	Remarks
2786	0	8	46	40	0	44	0.24	48	89.25	Sample interval 18-24"
3900 (clay)	0	83	53	343	33	90	3.23	367		Clay below sample 3901
3902	0	0	40	60	20	10	0.92	92	89.36	Same Site [54-64" 64-69"
3901	0	28	72	112	40	110	1.60	164	52.43	
2777	0	26	128	66	40	38	1.04	118	78.57	28-36"
3895	0	10	120	62	0	20	0.80	90	81.63	Same Site [12-38" 40-64" 56-70" 66-76" 76-86"
3896	0	12	286	136	0	34	0.92	168	82.05	
3897	0	10	474	282	0	42	1.32	192	69.17	
3898	0	38	276	206	80	192	1.52	170	47.51	
3899	0	36	402	252	40	84	1.36	168	52.68	
2770	0	20	298	104	60	134	1.04	164	58.45	24-30"
3903	0	54	280	202	20	70	1.36	242	40.26	60-70" from Filson Creek area

*LOI determined by AN-14

TABLE 2: Peat samples analyzed by AN-15

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	Remarks	
2786	6	12	12	42	.28	47	Sample interval 18-24"	
3902	7	13	9	3	.88	76	Same Site [54-64"	
3901	13	29	29	54	.92	88		64-69"
2777	8	60	24	21	.80	126	28-36"	
3895	7	50	24	12	.58	94	Same Site [12-38"	
3896	7	140	78	21	.84	181		40-64"
3897	19	240	198	37	.82	219		56-70"
3898	24	145	199	52	1.04	134		66-76"
3899	29	218	231	48	1.08	113		76-86"
2770	6	95	47	27	.56	131	24-30"	
3903	42	132	125	58	.88	128	60-70" from Filson Creek area	

TABLE 3: Peat samples analyzed by AN-17A

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	Remarks	
2786	1	2	3	25	.02	34	Sample interval 18-24"	
3902	2	5	3	4	.27	43	Same Site [54-64"	
3901	5	25	10	27	.25	43		64-69"
2777	3	50	12	7	.38	96	28-36"	
3895	3	28	11	6	.16	52	Same Site [12-38"	
3896	3	73	24	5	.18	90		40-64"
3897	10	103	51	16	.19	96		56-70"
3898	16	179	129	40	.33	113		66-76"
3899	13	237	148	30	.23	80		76-86"
2770	3	108	9	14	.32	109	24-30"	
3903	20	113	55	27	.16	66	60-70" from Filson Creek area	

TABLE 4: Peat samples analyzed by AN-17B

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	Remarks	
2786	5	6	10	40	.18	34	Sample interval 18-24"	
3902	0	8	7	7	.64	58	Same Site [54-64"	
3901	6	29	15	36	.38	42		64-69"
2777	7	59	18	17	.56	98	28-36"	
3895	6	42	17	10	.37	68	Same Site [12-38"	
3896	4	147	63	14	.62	144		40-64"
3897	11	210	127	31	.58	159		56-70"
3898	13	176	158	41	.43	112		66-76"
3899	14	227	170	30	.33	73		76-86"
2770	7	100	36	24	.38	100	24-30"	
3903	26	152	96	43	.54	81	60-70" from Filson Creek area	

TABLE 5: Peat samples analyzed by AN-18

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	Remarks	
2786	4	7	9	36	.18	30	Sample interval 18-24"	
3902	7	17	10	8	.47	46	Same Site [54-64"	
3901	14	32	24	37	.40	40		64-69"
2777	9	53	23	22	.60	101	28-36"	
3895	7	44	24	11	.49	79	Same Site [12-38"	
3896	6	153	90	23	.68	140		40-64"
3897	27	248	220	32	.78	158		56-70"
3898	36	158	239	46	.81	109		66-76"
3899	29	244	268	37	.70	75		76-86"
2770	8	95	57	24	.40	107	24-30"	
3903	48	180	139	41	.50	81	60-70" from Filson Creek area	

TABLE 6: Mean element concentrations for eleven peat samples for each analytical method

Analytical Method	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	LOI (%)
*AN-1 & 14	0	22	220	138	27	71	1.10	147	67.40
AN-15		6	95	47		27	.56	131	
AN-17A		7	84	41		18	.23	75	
AN-17B		9	105	65		27	.46	88	
AN-18		18	112	100		29	.55	88	

*Sample 3900 (clay) not included in mean values.

TABLE 7: Percent coefficients of variation ($100\%(S/\bar{X})$) for eleven peat samples for each analytical method

Analytical Method	Co	Cu	Ni	Pb	Zn	Fe	Mn	LOI
AN-1 & 14	73	67	61	101	78	35	37	26
AN-15	80	77	95		54	29	39	
AN-17A	93	88	125		68	43	38	
AN-17B	77	77	96		48	31	45	
AN-18	82	79	100		42	34	46	

TABLE 8: Anomaly contrast comparison for each analytical method

Analytical Method	Co	Cu	M/B Ni	Pb	Zn	Fe	Mn
AN-1	2.2	5.3	2.3	1.5	1.4	1.3	1.6
AN-15	2.0	7.5	6.8		1.1	1.2	3.1
AN-17A	3.0	10.1	11.0		1.0	1.3	2.2
AN-17B	2.8	9.9	7.8		.9	1.2	2.3
AN-18	2.6	7.7	9.5		1.1	1.8	2.7

M = mean of element values for samples 2777, 3895, 3896, 3897, 3898, 3899, 2770 and 3903 over Cu-Ni mineralization.

B = mean of element values for samples 2786, 3901 and 3902 over granite (background) M/B = contrast

**TABLE 9: Coefficients of determination (r^2)
for peat samples analyzed by AN-17A**

	Co	Cu	Ni	Zn	Fe	Mn
LOI	*.71	*.43	*.35	*.55	*.05	*.09
Mn	.14	.45	.22	.00	.37	
Fe	.00	.13	.06	*.02		
Ni		.81				

*negative relation

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

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-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 and 1M HCl

1.0000 gm sample was digested in 10 mls 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-17A: 0.1M EDTA

37.22 gms of EDTA disodium salt was dissolved in 500 mls of deionized water, the pH adjusted to 4.8 with ammonium hydroxide, and then diluted to 1,000 mls (0.1M EDTA solution) with deionized water.

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

AN-17B: 0.1M EDTA

37.22 gms of EDTA disodium salt was dissolved in 500 mls of deionized water and then diluted to 1,000 mls (0.1M EDTA solution) with deionized water.

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

AN-18: Ammonium Citrate and 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 the solution was filtered with #40 Whatman filter paper, 5 mls of concentrated hydrochloric acid added and boiled for 1/2 hour until hydrogen peroxide was gone, resulting in a slight color change. The remaining solution was diluted with deionized water to 100 mls.

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