PILOT STUDY ON STREAM SEDIMENT EXPLORATION GEOCHEMISTRY, FILSON CREEK, LAKE COUNTY, MINNESOTA

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PILOT STUDY ON STREAM SEDIMENT EXPLORATION GEOCHEMISTRY, FILSON CREEK, LAKE COUNTY, MINNESOTA

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ABSTRACT

Northern Minnesota is typified by low relief, extensive swampy conditions and sluggish streams. Under these conditions, clastic stream sediment infrequently occurs and, for geochemical exploration purposes, is problematical because of drastic variations in the stream water chemistry.

A stream sediment pilot study was conducted over copper-nickel mineralization in the Duluth Complex. The purpose of this study was to determine which sample media (clastic sediments, organic bank sediments or Fe-Mn oxide precipitates) best reflected copper-nickel mineralization and to determine which size fraction and extraction methods, prior to atomic absorption analysis, yielded maximum contrast between background and mineralization.

The results of this study indicate that organic stream bank sediments are more prevalent than clastic sediments and Fe-Mn oxides — they yield a multi-element anomaly as opposed to generally a bi-element anomaly for clastic sediments and Fe-Mn oxides — and appear to be less affected by drastic variations in the stream water chemistry than clastic sediments.

All three sample medias reflect the mineralization both directly over and downstream from mineralization using partial extraction techniques. The downstream dispersion provides a larger target which enables a lower sample density for reconnaissance exploration. For the partial extraction methods tested, ammonium citrate/hydrogen peroxide method on the −80 mesh fraction gave maximum contrast for both the clastic and organic sediments, and ammonium citrate/hydroxylamine hydrochloride for the Fe-Mn oxides.

INTRODUCTION

Traditionally, clastic (active) stream sediments have been used as a sample media for stream geochemical exploration surveys. Numerous papers have been published on this subject. Yardley (1958) has described a clastic stream sediment study he conducted on Filson Creek.

Often in glaciated low relief areas, clastic stream sediment is difficult to locate and sample. Therefore, other sample medias which occur more frequently are more desirable. Furthermore, other sample medias may be more successful in locating mineralization.

Other stream sample medias include organic stream sediments and Fe-Mn oxide coatings on boulders. The application of organic stream materials has recently been reported by Brundin and Nairis (1972), Closs (1976), Peacock and Michie (1975), Kauranne (1975), Ek (1976), Lestinen (1976), and Larsson (1976). The use of Fe-Mn oxide coatings has been reported by Whitney (1975), and Carpenter, et al. (1975).

Many of the areas' potential for base metal deposits in northern Minnesota are of low relief, swampy and do not have abundant clastic stream sediment. Therefore, it is desirable to develop a stream geochemical method which is readily applicable to northern 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 a study on three types of stream sediment sample medias.

During 1975-76 a pilot study was conducted using clastic stream sediments, organic stream bank samples and Fe-Mn oxide coatings on stream boulders. This pilot study was done over and surrounding copper-nickel mineralization in the Duluth Complex. For each type of sample media, several extraction methods were tested to determine a method which yielded the maximum contrast over background.

GEOLOGY

The general Precambrian geology of the Filson Creek area is illustrated on Figure 1. Disseminated copper-nickel mineralization occurs in the area outlined. 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 is thin and discontinuous. Both the angularity and lithology of the clasts in the drift indicate local derivation (Matsch).

SAMPLE COLLECTION

The pH of stream water was measured at every sample site. The values ranged from 5.8 to 6.4, with a median value of 6.2.

The clastic (active) stream sediments were collected either by hand or with a trenching shovel from the center of the stream. The samples are a composite of sediment collected from at least six sites over a stream length of about 100 feet. The samples are composed of mainly mineral and rock fragments, with some Fe-Mn oxide coating, ranging from

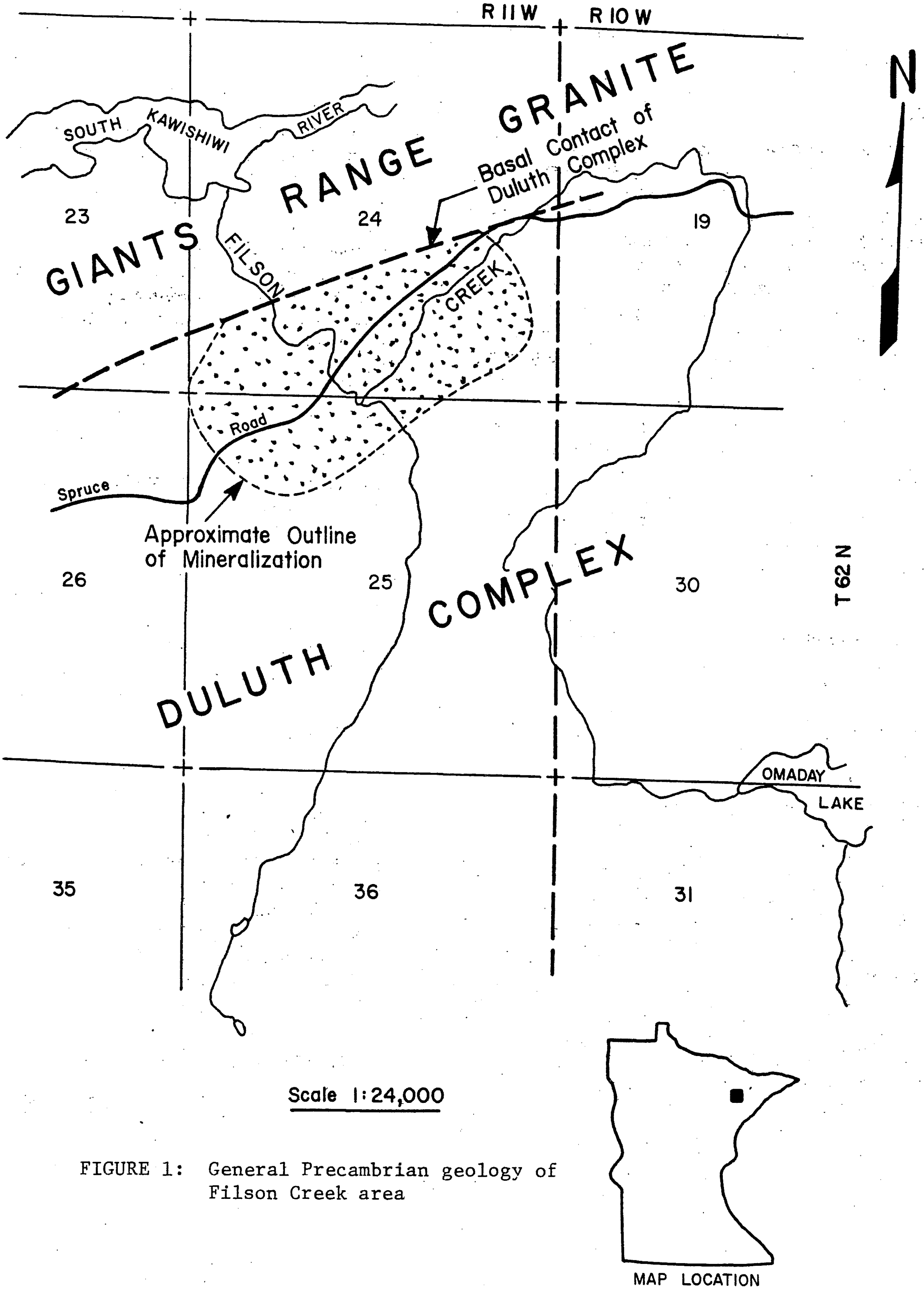

FIGURE 1: General Precambrian geology of Filson Creek area

pebble to very fine sand size. Clay and organic sediments were avoided as much as possible. The sample sites are shown on Figure 2. Clastic stream sediments were difficult to impossible to find in many areas of the creek.

The organic stream bank samples were collected either by hand or with a trenching shovel. These samples were collected below the normal water level from the stream bank. The samples are a composite of material collected from both banks of the stream from at least four sites over a stream length of about 100 feet. The samples are composed mainly of organic material with lesser amounts of clay, silt and sand. The organics range from decomposed to undecomposed material. Minor live roots were included. The sample sites are shown on Figure 3. This material was easy to locate and sample.

The Fe-Mn oxide samples were scraped with a pocket knife onto a sheet of paper. This material occurs as a thin (< .5 mm) dark grey to black coating on rocks within the stream. The samples were collected from rock lying within the active portion of the creek. Each sample was a composite from approximately twenty rocks over a stream length of about fifty feet. The rocks ranged in size from four inches to three feet. The smaller sized rocks lying in the stream bed had more oxide coating than larger rocks. The oxide flaked off dry rocks more easily than when wet. Little or no oxide coating occurred for a short interval downstream from a swamp through which the stream flowed. The sample sites are shown on Figure 4. Oxide coated rocks were, at least, as difficult to find as the clastic sediments.

SAMPLE PREPARATION AND ANALYTICAL METHODS

The clastic sediments 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 organic stream bank samples were dried at 80°C, broken up in a blender, and sieved to two size fractions: −80 mesh and −230 mesh. 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). 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.

The oxide samples were ground up in a mortar and pestle and sieved to a −80 mesh.

Several extraction methods were applied to the three sample types to determine which method yielded maximum contrast between mineralization and background. These extraction methods are as follows. The "AN" numbers will be used to identify these methods throughout the report and are further described in the Appendix.

AN-1: Concentrated HCl, HNO_3 & HF
AN-8: Ascorbic Acid & Hydrogen Peroxide
AN-10: Concentrated HCl, HNO_3 & HF in acid digestion bomb
AN-15: 4M HNO_3 & 1M HCl
AN-17: 0.1M EDTA
AN-18: Ammonium Citrate & Hydrogen Peroxide
AN-19A & AN-19B: Ammonium Citrate & Hydroxylamine Hydrochloride

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. Arsenic and sulfur were analyzed by AN-3 and AN-11 respectively.

The clastic sediments were analyzed by AN-3, 8, 10, 11, 15, 17, 18 and 19A. The organic bank samples were analyzed by AN-1, 3, 15, 17, 18, 19A and 19B. The oxide samples were analyzed by AN-1, 18 and 19B.

Following dissolution of the samples by the above methods, the sample solutions were analyzed on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. 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.

Cobalt, copper, nickel, zinc, iron and manganese were analyzed on all three sample types. Silver, arsenic and lead were analyzed on the organic and clastic samples. Chromium, sulfur, titanium, molybdenum and magnesium were analyzed only on the clastic samples.

A dithiazone titration method (AN-20) was tested in the laboratory on the clastic sediments for possible application as a field method.

RESULTS AND DISCUSSION

Iron and manganese were analyzed for all samples and LOI for the organic samples to determine if relationships existed between the trace elements and the Fe-Mn oxides or the organics, which could result in false anomalies if excessive amounts of these sample components occurred in some samples. For the Fe-Mn oxide samples, varying amounts of iron or manganese could also result in false anomalies.

Clastic Stream Sediments

The element concentrations for the various size fractions and analytical methods tested on the clastic stream sediments are given in Tables 1-9. 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 location, and Figure 1 for relation to geology.

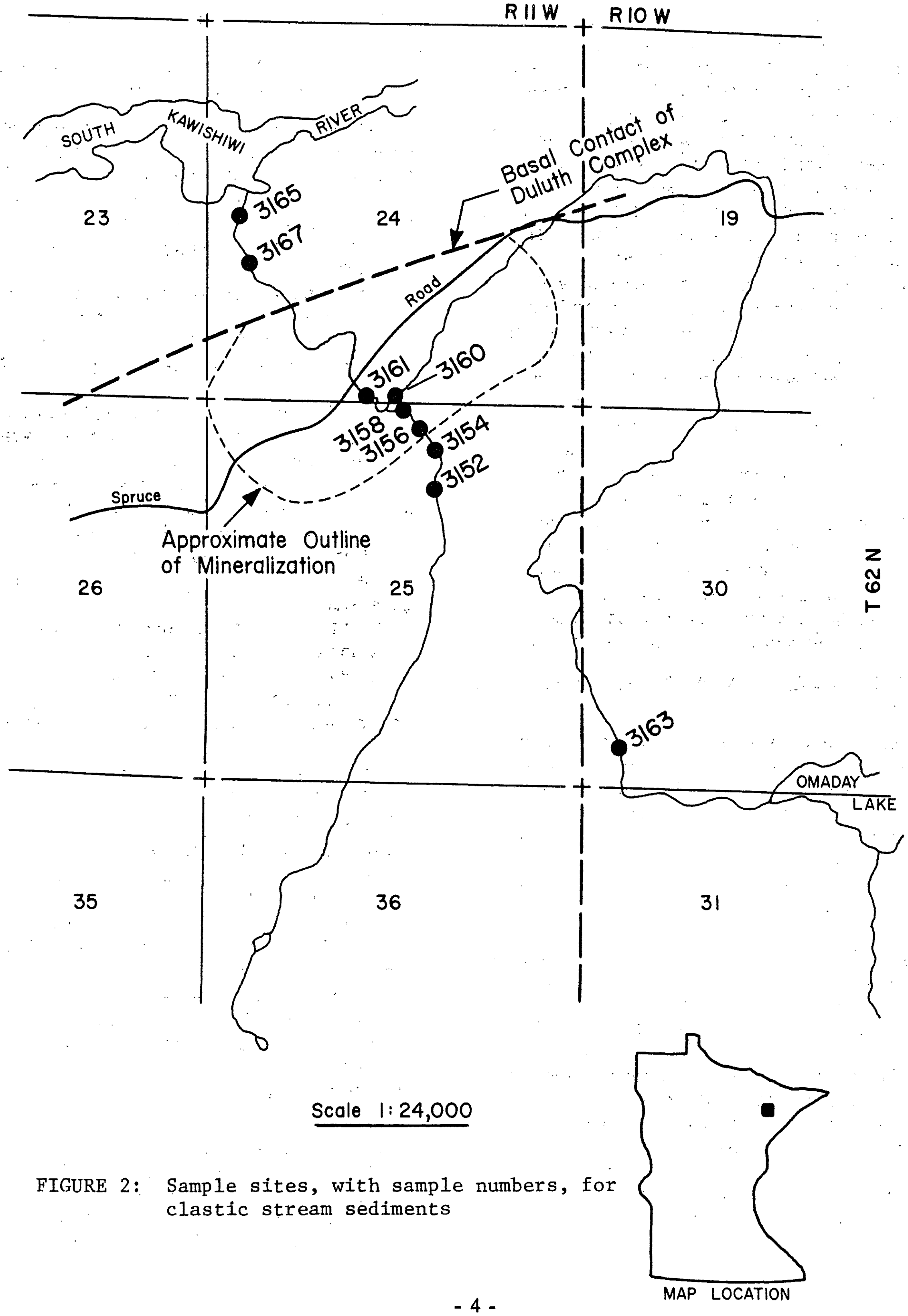

FIGURE 2: Sample sites, with sample numbers, for clastic stream sediments

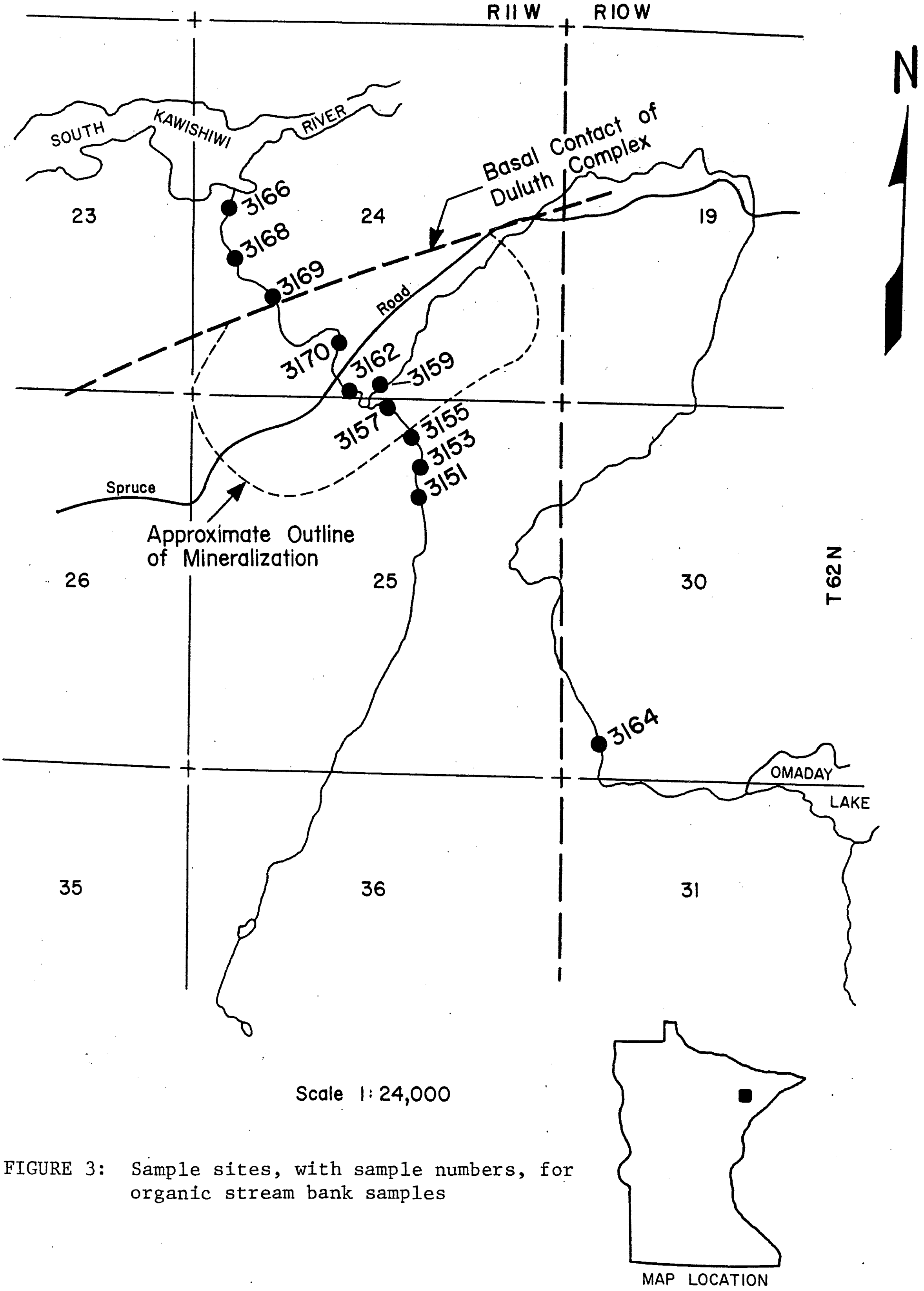

FIGURE 3: Sample sites, with sample numbers, for organic stream bank samples

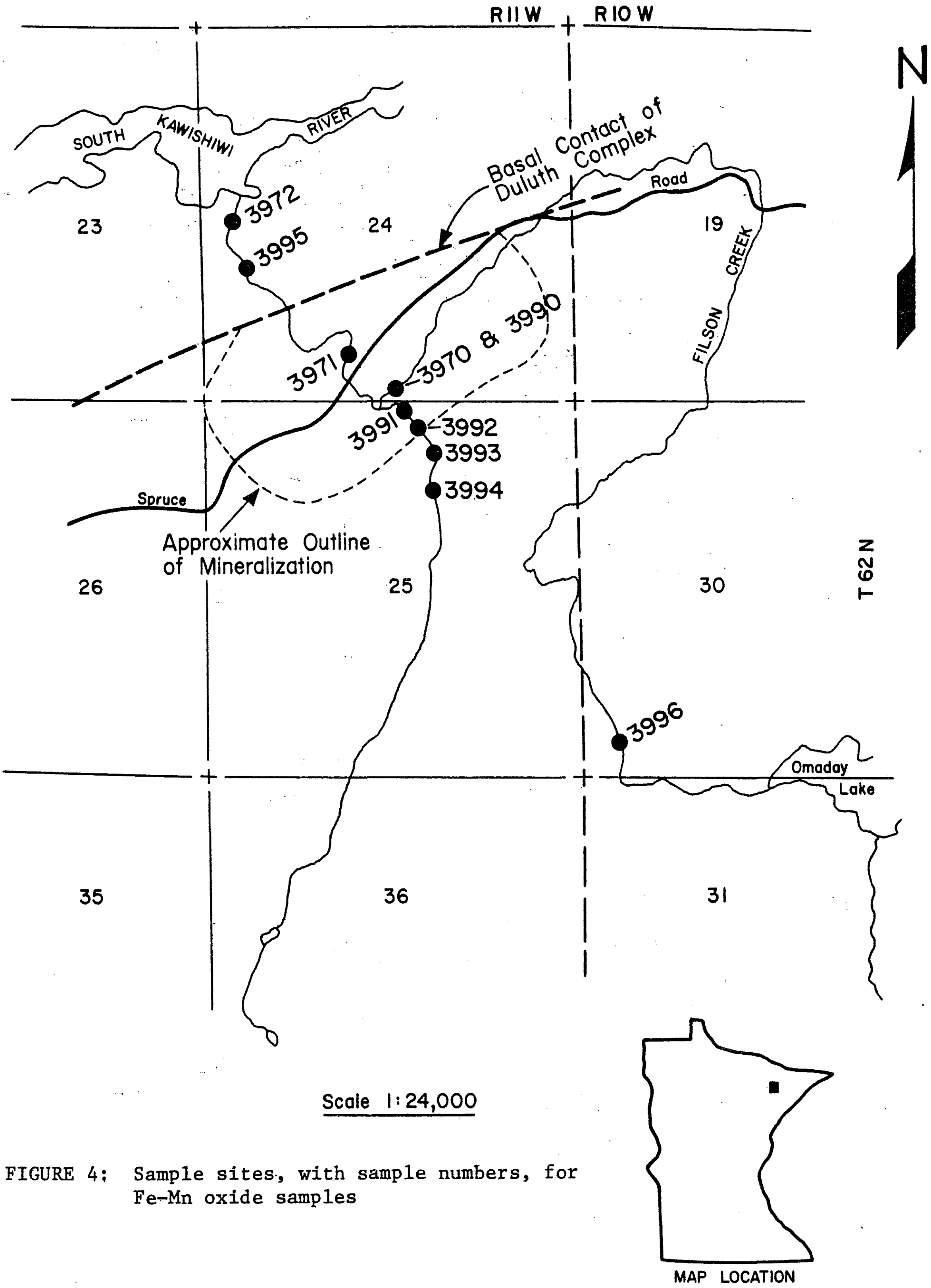

FIGURE 4: Sample sites, with sample numbers, for Fe-Mn oxide samples

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 clastic stream sediment.

Table 1 indicates that chromium, titanium and iron in the −35+80 mesh fraction of the clastic stream sediments analyzed by AN-10, clearly reflects the bedrock chemistry. The finer fraction, −80 mesh, (Table 2) also analyzed by AN-10, reflects the bedrock chemistry for chromium, titanium and, to a lesser degree, iron. The −80 mesh fraction clearly reflects the copper-nickel mineralization, especially for copper, whereas the −35+80 mesh fraction (Table 1) does not.

In order to compare the element concentrations of the various size fractions and the extractability of the various analytical methods, the mean values for each element in Tables 1-8 are given in Table 10. AN-10 is a near total digestion and obviously extracts significantly more metal from the samples than the other analytical methods tested (Table 10). Silver, arsenic, chromium, copper, nickel, sulfur, zinc, iron and manganese are clearly concentrated in the fine fraction (−80 mesh) as opposed to the coarser fraction (−35+80 mesh). In the B-horizon soil of this region, chromium, copper and nickel were found to have higher concentrations in the −35+80 mesh fraction (Meineke, Vadis and Klaysmat, 1977) which is opposite to that described for the clastic stream sediments.

The objective was to determine if the clastic stream sediments reflected mineralization and, if so, which size fraction and analytical method yielded maximum contrast over background values. Examination of Tables 2-9 indicates that copper and nickel do reflect mineralization, but in varying degrees. Table 11 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 12. Generally, the maximum contrast values in Table 12 correspond to the maximum coefficients of variation for each element, size fraction and analytical method in Table 11.

The M/UPS (Table 12) is a quantitative measure of the contrast between samples upstream from mineralization (UPS) and those over mineralization (M). The DS/UPS is a measure both of downstream dispersion of metals from the mineralized area and contrast between UPS and downstream (DS) samples. It is desirable to use an analytical method which gives both high contrast over mineralization (M/UPS) and downstream dispersion (DS/UPS), because mineralization can be located more easily with wider spaced sampling.

From Table 12, it is evident that AN-18 (−80 mesh fraction) gives the maximum contrast and downstream dispersion for copper and nickel of any method considered. Table 12 also indicates that AN-18 (−230 mesh fraction) gives a lower contrast than AN-18 (−80 mesh fraction), which suggests that AN-18 on the −80+230 mesh fraction may yield even better contrast.

The field dithiazone method (AN-20) (Tables 9 and 12) mainly reflected downstream dispersion of the mineralization. The AN-20 method appears to produce sufficient contrast to be applicable to clastic stream sediment surveys. However, based on sample 3154 (Tables 6 and 9), it appears that AN-20 results are seriously affected by high concentrations of manganese and iron.

Organic Stream Bank Sediments

The element concentrations for the various size fractions and analytical methods tested on the organic stream bank sediments are given in Tables 13-20. The location of these samples is shown on Figure 3.

In order to compare the element concentrations of the two size fractions and the extractability of the various analytical methods, the mean values for each element in Tables 13-20 are given in Table 21. AN-1 is a near total digestion and obviously extracts significantly more metal from the samples than the other analytical methods tested (Table 21). For AN-1 (Table 21), cobalt, copper, nickel, lead, zinc and iron are clearly concentrated in the finer fraction (−230 mesh) as compared to the −80 mesh fraction. The LOI (Table 21) is considerably less in the −230 mesh as compared to the −80 mesh fraction. This reduction in LOI probably results from a lesser proportion of coarse undecomposed organic material in the −230 mesh fraction.

The objective was to determine if the organic stream bank sediments reflected mineralization and, if so, which size fraction and analytical method yielded maximum contrast over background values. Examination of Tables 13-20 indicates that copper and, to a lesser degree, arsenic, cobalt, nickel, lead and zinc do reflect mineralization.

To determine which size fraction and analytical method gives maximum contrast over background, Table 22 gives the percent coefficients of variation and Table 23 contrast calculations. See section on "Clastic Stream Sediments" for explanation of these tables.

The maximum values in Table 23 generally correspond to the maximum coefficients of variation in Table 22. Also, the variation of LOI (Table 22) is relatively low considering the variable nature of this type of sample.

From Table 23, it is evident that AN-18 (−80 mesh fraction) gives the maximum contrast and downstream dispersion for copper and nickel of any method considered. Both contrast and downstream dispersion for the organic stream bank sediments (OSBS) (Table 23) are similar to the clastic stream sediments (Table 12) for copper and nickel; however, the OSBS appears to give better contrast and downstream dispersion for arsenic, cobalt, lead and zinc. A multi-element response of this type definitely aids in the interpretation of geochemical surveys.

Zinc has a generally higher or equal DS/UPS compared to the M/UPS (Table 23). Copper, on the other hand, has a higher M/UPS compared to DS/UPS. Nickel dispersion falls between copper and zinc. This indicates that the downstream dispersion (mobility) of these metals increases from copper to nickel to zinc. A similar conclusion can be reached for the clastic stream sediments (Table 12). However, for the clastic stream sediments (Table 12), the nickel appears to have a mobility approximately the same as zinc.

Fe-Mn Oxide Precipitates

The element concentrations for the various analytical methods tested on the Fe-Mn oxides are given in Tables 24-26. The location of these samples is shown on Figure 4.

For comparison of the extractability of the analytical methods, the mean values for each element in Tables 24-26 are given in Table 27. AN-1 is a near total digestion and obviously extracts more metal from the samples than the other methods; however, the difference is much less than that observed for the clastic (Table 10) and organic sediments (Table 21). All methods (Table 27) extract approximately the same amount of manganese, but a lesser amount of iron for AN-18 and 19B. Therefore, it appears that AN-18 and 19B will extract nearly all trace elements from the manganese oxides and, to a lesser extent, iron oxides. Based on this observation, it would be expected that AN-18 and 19B would extract the trace elements from most of the secondary manganese oxides in any type of geochemical sample.

The objective was to determine if the Fe-Mn oxides reflected mineralization and, if so, which analytical method yielded maximum contrast over background values. Examination of Tables 24-26 indicates that copper, nickel and, to a lesser degree, zinc do reflect mineralization.

To determine which analytical method gives maximum contrast over background, Table 28 gives the percent coefficients of variation and Table 29 contrast calculations. See section on "Clastic Stream Sediments" for explanation of these tables. The maximum values in Table 29 generally correspond to the maximum coefficients of variation in Table 28.

From Table 29, it is evident that AN-19B gives the maximum contrast and downstream dispersion of any extraction method considered. The contrast and downstream dispersion for the Fe-Mn oxide (Table 29) is similar to or better than that for the clastic sediments (Table 12) and the organic stream bank samples (Table 23).

Even though the Fe-Mn oxides yield similar or better contrast than the clastic sediment and organic bank samples, they do have disadvantages compared to the other medias. The Fe-Mn oxide is, at least, as difficult to locate in the stream as clastic sediment. The oxide is not precipitated until the stream water pH is neutralized which results in the absence of the oxide considerable distances downstream from swamps. Also, dark, hard coatings of organic-clay material on stream boulders are difficult to differentiate from Fe-Mn coating. As a result, samples are obtained, at least in the area surveyed, which are low in Fe-Mn and, therefore, not comparable to the Fe-Mn oxide precipitates. This is the suggested explanation for the low iron and manganese values in samples 3970, 3972 and 3990 (Tables 24, 25 and 26). These samples were not used in the calculations of Tables 27, 28 and 29. In areas of steep stream gradients, with usually lesser swampy conditions, organic-clay coatings on stream boulders may not be a problem.

Coefficients of Determination

The coefficients of determination (r^2) for the three stream sample types and the analytical method for each sample type which yielded maximum contrast are given in Tables 30-32. An insufficient number of samples were collected for each of the three sample types to give a high degree of confidence to the r^2 values. However, Tables 30-32 do give a general indication of the element relationships.

Table 30 (clastic sediments) indicates a varying relation between the trace elements and iron and manganese. Copper and nickel from samples over the Duluth Complex (not shown in Table 30) has an $r^2 = .71$.

High iron and manganese values appear to have an effect on trace element values of the clastic sediments. Sample 3154 in Table 6 and other tables, especially Table 7, has high trace element values and very high iron and manganese. This sample is not over known copper-nickel mineralization.

Table 31 (organic bank samples) indicates that cobalt, nickel and zinc have a negative relation to the organic content (LOI) and a positive relation to iron and manganese. Copper, on the other hand, does not have a significant relation to LOI, iron or manganese. Copper and nickel from samples over the Duluth Complex (not shown in Table 31) has a $r^2 = .79$, and for all samples $r^2 = .73$ (Table 31). This is interesting, as copper and nickel do not display similar relations in Table 31. The r^2 values in Table 31 are similar to coefficients of determination for an organic stream sediment survey conducted by Closs (1976) in the Geraldton area of Ontario, except that the Ontario survey indicated a positive relation for copper and LOI ($r^2 = .12$) and no significant relation between zinc and LOI.

Generally, a metal will display a similar r^2 value for both iron and manganese (Tables 30 and 31). However, for the Fe-Mn oxide samples (Table 32) this is not observed. It is also unusual that iron and manganese do not have any relation. The unusual relationships in Table 32 may be the result of the very high concentrations of iron and manganese in these samples. Not enough samples were collected to fully examine the relationships; however, surveys with lake sediments have indicated that high concentrations of iron and manganese do not yield a consistent relation to trace metals (Garrett and Hornbrook, 1976; Meineke, Vadis and Klaysmat, 1976). For the lake sediments, it has been suggested that the scavenging and coprecipitation capacity of the iron and manganese oxides, at high concentrations, exceeds the amount of available trace metals in the environment, therefore, resulting in weak or no relationships between iron and manganese and the trace metals. If this is the case, metal to iron or manganese ratios are neither necessary nor justified.

If a survey were conducted where at least thirty samples of the same stream sample type were collected, it would be desirable to further examine the element relationships. Evaluation of the trace element relations with iron, manganese and LOI may reveal that ratios are necessary to normalize high trace element values resulting from high concentrations of iron, manganese or organics.

CONCLUSIONS

The three stream sample medias tested (clastic sediment, organic bank samples, and Fe-Mn oxide precipitates) in Filson Creek all reflect known copper-nickel mineralization. All three sample medias reflect the mineralization both directly over and downstream from mineralization using partial extraction techniques. The downstream dispersion provides a larger target which enables a lower sample density for reconnaissance exploration. The total digestion methods (AN-1 and AN-10) appear to restrict the anomalies to the mineralized areas for the clastic sediments and organic stream bank samples with lesser downstream dispersion than the partial extractions and, therefore, may be more useful for follow-up surveys.

For the clastic sediments (−80 mesh fraction), AN-18 yields the maximum contrast and downstream dispersion of all extraction methods considered. It does appear that Fe-Mn scavenging or coprecipitation of trace metals does create false anomalies. Therefore, ratios may be necessary to normalize this effect.

The field dithiazone method (AN-20) does reflect mineralization using the clastic sediments, but it must be applied with caution as it also appears to give false anomalies in sediments with high iron and manganese oxides.

For the organic stream bank samples (OSBS), the −80 mesh fraction analyzed by AN-18 yields the maximum contrast and downstream dispersion of all extraction methods tested. The contrast and downstream dispersion for the OSBS is similar to the clastic sediment for copper and nickel; however, the OSBS appears to give better contrast and downstream dispersion for arsenic, cobalt, lead and zinc. A multi-element response definitely is advantageous in geochemical surveys. Based on this survey, it does not appear that relationships exist between the trace metals and iron, manganese or LOI for the OSBS which require normalization of the data; however, this should be further examined in a survey with more samples.

The Fe-Mn oxides yielded maximum contrast and downstream dispersion using the AN-19B extraction. The contrast and downstream dispersion for the Fe-Mn oxide is equal to or better than that for the clastic sediments and OSBS. Variations in normal levels of iron and manganese do not appear to create false anomalies and, therefore, normalization of trace metals does not appear necessary or justified.

The area surveyed, and most of northern Minnesota, is typified by low relief, extensive swampy conditions and sluggish streams. Under these conditions, both clastic stream sediments and Fe-Mn oxides are difficult to locate and sample. Their infrequent occurrence in comparison to OSBS also results in less sample coverage. The OSBS are generally abundant in most streams and also appear to yield a better multi-element response than the other sample medias. Therefore, based on this survey, it is concluded that the OSBS is the best stream sample media for this region.

In higher relief areas of northern Minnesota, OSBS may not be as abundant below the normal water level, and clastic sediments and Fe-Mn oxides may necessarily have to be used as a stream sample media; although this remains to be examined. Also, the clastic sediments and Fe-Mn oxides may be better than OSBS in higher relief and less swampy areas, where sudden changes in stream water pH should be less frequent due to lesser swampy conditions.

To further test these conclusions, the Minerals Division, during 1977-78, will conduct pilot studies on several streams with various environmental conditions.

TABLE 1: Clastic stream sediment (−35+80 mesh fraction) analyzed by AN-3, 10 and 11

Sample Number	Ag (ppm)	As (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	S (%)	Ti (%)	Zn (ppm)	Fe (%)	Mg (%)	Mn (ppm)
3165	0	0	103	30	20	67	0	.032	0.42	63	2.23	1.10	530
3167	0	0	110	43	17	63	0	.024	0.51	67	2.83	1.27	483
3161	0	0	120	287	100	120	0	.030	1.47	67	4.00	1.47	567
3160	0	0	100	207	60	103	0	.024	0.86	63	3.30	1.43	523
3158	0	0	103	277	67	143	0	.018	1.28	73	3.27	1.23	640
3156	0	0	100	93	27	80	0	.019	0.78	67	3.06	1.13	513
3154	0	0.8	107	357	257	173	0	.018	1.53	117	4.87	1.63	1043
3152	0	0.3	93	173	50	100	0	.017	1.41	80	4.53	1.86	733
3163	0	1.1	107	137	20	90	0	.026	4.48	70	6.50	1.00	740

TABLE 2: Clastic stream sediment (−80 mesh fraction) analyzed by AN-3, 10 and 11

Sample Number	Ag (ppm)	As (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Ti (%)	Zn (ppm)	S (%)	Fe (%)	Mg (%)	Mn (ppm)	Mo (ppm)
3165	1	0.4	80	93	67	87	0	0.66	97	.076	3.64	0.84	753	< 20
3167	3	1.3	87	83	73	127	1	0.57	100	.080	4.44	0.80	1323	< 20
3161	0	1.0	90	330	247	170	0	1.92	160	.074	5.14	0.82	690	< 20
3160	0	1.3	93	357	220	167	0	1.62	173	.078	5.04	0.73	790	< 20
3158	1	1.8	80	150	140	177	1	1.25	110	.044	6.24	0.92	880	< 20
3156	0	0.7	77	133	57	130	0	1.28	110	.046	4.44	0.65	693	< 20
3154	1	2.9	103	187	57	147	3	1.56	113	.044	7.24	0.85	2327	< 20
3152	0	0.7	73	160	80	150	3	0.90	90	.040	4.87	0.85	873	< 20
3163	3	2.1	80	227	40	103	1	2.72	97	.090	8.09	0.87	1060	< 20

TABLE 3: Clastic stream sediment (−80 mesh fraction) analyzed by AN-8

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3165	5	44	12	24	.32	126
3167	13	40	13	22	.68	683
3161	3	152	13	20	.36	90
3160	10	158	20	25	.82	301
3158	6	105	14	17	.69	170
3156	4	22	7	16	.24	90
3154	35	48	10	38	1.69	2000
3152	6	54	8	16	.48	253
3163	4	14	8	20	.62	231

TABLE 4: Clastic stream sediment (−80 mesh fraction) analyzed by AN-15

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3165	8	46	22	34	.47	152
3167	18	41	20	31	.82	691
3161	8	61	28	30	.58	126
3160	14	40	37	54	1.12	341
3158	9	58	35	52	1.16	226
3156	6	16	12	34	.35	107
3154	34	36	20	49	1.94	1559
3152	10	24	20	27	.69	288
3163	10	21	12	34	.93	276

TABLE 5: Clastic stream sediment (−80 mesh fraction) analyzed by AN-17

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3165	7	33	10	11	.10	106
3167	13	29	15	13	.27	540
3161	5	33	7	9	.09	79
3160	8	17	8	11	.23	230
3158	5	24	5	6	.12	120
3156	3	10	5	6	.05	70
3154	24	31	8	26	.30	1248
3152	6	11	4	6	.14	185
3163	7	9	8	10	.20	172

TABLE 6: Clastic stream sediment (−80 mesh fraction) analyzed by AN-18

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3165	4	46	17	17	.21	115
3167	14	62	22	31	.71	751
3161	5	148	21	15	.19	74
3160	8	105	12	17	.46	290
3158	4	75	7	14	.29	128
3156	0	15	4	13	.12	71
3154	24	45	13	37	.71	1452
3152	4	30	3	11	.22	198
3163	4	16	2	17	.35	186

TABLE 7: Clastic stream sediment (−230 mesh fraction) analyzed by AN-18

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3165	9	18	10	5	20	.74	350
3167	9	65	22	7	21	.29	168
3161	7	167	33	7	23	.38	168
3160	Not Analyzed						
3158	8	100	19	2	21	.63	265
3156	8	29	12	4	18	.37	211
3154	80	213	23	12	127	2.01	4850
3152	10	30	10	4	12	.53	500
3163	26	63	23	12	24	.75	1300

TABLE 8: Clastic stream sediment (−80 mesh fraction) analyzed by AN-19A

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3165	4	22	10	12	.16	110
3167	12	24	11	14	.39	646
3161	4	24	8	13	.12	74
3160	5	22	7	17	.34	273
3158	2	26	6	8	.24	133
3156	0	17	6	7	.09	75
3154	25	21	9	24	.52	1516
3152	3	18	7	7	.22	211
3163	4	21	4	12	.26	192

TABLE 9: Clastic stream sediment (−80 mesh fraction) analyzed by AN-20

Sample Number	mls
3165	7.5
3167	10.5
3161	6
3160	3.0
3158	3.5
3156	3.5
3154	6
3152	3.5
3163	4

TABLE 10: Mean element concentrations for nine clastic stream sediment 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-3, 10 & 11(−80)	1	1.4	85	191	109	140	1	.06	1.39	117	5.46	.81	1043
AN-3, 10 & 11(−35+80)	0	.2	105	178	69	104	0	.02	1.42	74	3.84	1.35	526
AN-8			10		71	12				22	.66		438
AN-15			13		38	23				38	.90		418
AN-17			9		22	8				11	.17		306
AN-18(−80)			7		60	11				19	.36		363
AN-18(−230)			20		86	19	7			33	.71		977
AN-19A			7		22	8				13	.26		359

TABLE 11: Percent coefficients of variation (100%(S/$\overline{X}$)) for nine clastic stream sediment samples for each analytical method and size fraction

Analytical Method	Ag	As	Co	Cr	Cu	Ni	Pb	S	Ti	Zn	Fe	Mg	Mn
AN-3, 10 & 11(−80)	122	57	11	51	70	22	122	33	48	25	26	9	50
AN-3, 10 & 11(−35+80)		174	7	64	110	35		50	86	23	34	21	41
AN-8			101		76	34				31	66		140
AN-15			67		41	39				27	53		111
AN-17			71		46	41				56	51		125
An-18(−80)			104		73	73				46	61		126
AN-18(−230)			126		82	42	53			115	78		165
AN-13A			109		13	27				42	53		130

TABLE 12: Anomaly contrast comparison for nine clastic stream sediment samples for each analytical method and size fraction

Analytical Method	Cu		Ni		Zn		Mls - THM	
	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS
AN-10(−80)	3.4	1.2	1.3	.8	1.4	1.0		
AN-8	3.9	1.2	2.0	1.6	.9	1.0		
AN-15	2.2	1.8	2.1	1.3	1.3	.9		
AN-17	1.7	2.1	1.2	2.2	.8	1.0		
AN-18(−80)	4.0	2.0	2.2	3.3	.8	1.2		
AN-18(−230)	1.6	.5	1.5	.9	.5	.5		
AN-19A	1.3	1.2	1.0	1.6	1.0	1.0		
AN-20							.7	2.1

UPS = mean of element concentrations for samples 3152, 3154, 3156 and 3163, which are *upstream* from copper-nickel mineralization.

M = mean of element concentrations for samples 3158, 3160 and 3161, which are *over* copper-nickel mineralization.

DS = mean of element concentrations for samples 3165 and 3167, which are *downstream* from copper-nickel mineralization.

M/UPS = upstream contrast

DS/UPS = downstream dispersion

TABLE 13: Organic stream bank sediment (−80 mesh fraction) analyzed by AN-1, 3 and 14

Sample Number	Ag (ppm)	As (ppm)	Co (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	LOI (%)
3166	0.3	0.8	66	137	< 20	130	37	80	1.83	605	71.16
3168	0.3	1.4	66	179	< 20	138	44	89	1.79	652	62.70
3169	0	2.4	40	308	< 20	108	30	74	1.20	302	38.26
3170	0.3	0.7	60	203	< 20	122	40	79	1.55	373	63.62
3162	0	0.4	61	213	< 20	131	27	75	2.09	470	73.38
3159	0.3	0.7	73	328	< 20	166	117	90	2.12	494	79.78
3157	0	0.7	86	249	< 20	188	47	108	2.23	460	75.92
3155	0	0.6	63	77	< 20	107	38	78	1.94	479	67.80
3153	0.3	0.5	49	87	< 20	111	44	69	1.73	465	70.84
3151	0.3	0.6	61	167	< 20	131	27	86	1.58	296	78.20
3164	0.3	0.5	40	59	< 20	78	37	58	1.25	290	54.70

TABLE 14: Organic stream bank sediment (−230 mesh fraction) analyzed by AN-1 and 14

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	LOI (%)
3166	0	92	192	144	26	96	2.00	438	36.60
3168	0	120	260	178	76	110	2.44	690	43.24
3169	0	100	336	136	52	76	1.76	306	58.25
3170	0	90	248	130	40	106	1.88	346	44.11
3162	0	104	286	166	52	108	2.80	474	30.34
3159	0	100	398	200	48	102	2.40	452	28.26
3157	0	100	402	214	48	120	2.80	488	28.06
3155	0	86	116	136	60	102	2.20	434	41.55
3153	0	80	118	146	44	82	2.00	465	40.28
3151	Not analyzed for −230 mesh fraction								
3164	0	86	82	88	62	76	1.60	452	49.46

Table 15: Organic stream bank sediment (−80 mesh fraction) analyzed by AN-15

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3166	18	107	38	30	.71	311
3168	23	128	43	41	.89	412
3169	15	229	49	41	.79	211
3170	17	125	42	43	.60	172
3162	16	134	39	30	.82	240
3159	17	139	47	33	.59	150
3157	14	174	40	29	.77	195
3155	15	49	24	26	.74	214
3153	13	47	27	15	.70	262
3151	10	95	31	11	.45	91
3164	7	39	21	21	.59	138

TABLE 16: Organic stream bank sediment (−80 mesh fraction) analyzed by AN-17

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3166	8	66	8	17	.35	257
3168	10	82	16	24	.49	344
3169	9	124	22	21	.46	169
3170	5	75	30	13	.30	123
3162	7	95	16	13	.41	191
3159	7	82	23	13	.27	116
3157	9	119	12	14	.43	169
3155	8	32	12	16	.46	182
3153	7	34	16	13	.40	232
3151	5	84	8	5	.27	76
3164	5	21	20	11	.32	104

TABLE 17: Organic stream bank sediment (−80 mesh fraction) analyzed by AN-18

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3166	14	96	24	30	.56	262
3168	18	117	28	40	.62	362
3169	13	212	48	42	.69	184
3170	9	127	31	33	.46	140
3162	9	108	22	23	.49	193
3159	7	200	25	26	.34	114
3157	9	153	22	27	.51	158
3155	8	40	9	26	.54	171
3153	7	42	9	22	.49	225
3151	6	70	16	12	.25	66
3164	7	34	13	25	.47	111

TABLE 18: Organic stream bank sediment (−230 mesh fraction) analyzed by AN-18

Sample Number	Ag (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3166	0	8	108	44	0	46	.28	336
3168	0	16	132	48	4	48	.48	454
3169	0	12	242	72	0	54	.46	196
3170	0	10	132	54	2	38	.24	170
3162	0	8	120	32	0	24	.24	254
3159	0	10	190	38	0	32	.18	178
3157	0	6	190	36	2	38	.42	208
3155	0	10	46	36	2	32	.56	246
3153	0	8	48	30	0	22	.36	304
3151	0	0	90	26	0	14	.12	76
3164	0	6	32	24	0	26	.30	158

TABLE 19: Organic stream bank sediments (−80 mesh fraction) analyzed by AN-19A

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3166	5	17	18	17	.38	250
3168	8	18	24	25	.46	354
3169	6	18	28	22	.46	177
3170	2	17	17	17	.28	130
3162	5	18	20	15	.38	200
3159	4	19	18	16	.23	120
3157	3	19	21	18	.37	168
3155	7	16	11	17	.27	188
3153	4	16	12	13	.34	230
3151	3	18	16	7	.27	74
3164	2	16	10	14	.32	109

TABLE 20: Organic stream bank sediments (−80 mesh fraction) analyzed by AN-19B

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)
3166	12	7	19	22	.46	277
3168	18	7	23	32	.58	405
3169	12	11	32	31	.57	209
3170	9	7	19	23	.35	152
3162	10	11	19	20	.49	218
3159	4	11	21	21	.31	127
3157	10	17	26	22	.52	182
3155	7	3	9	23	.53	208
3153	5	3	10	19	.46	254
3151	7	10	20	11	.32	86
3164	9	2	9	19	.43	130

TABLE 21: Mean element concentrations for eleven organic stream bank sediment samples for each analytical method and size fraction

Analytical Method	Ag (ppm)	As (ppm)	Co (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Mn (ppm)	LOI (%)
AN-1, 3 & 14(−80)	0.2	.9	60	182	128	44	81	1.76	444	66.94
AN-1 & 14(−230)	0		96	244	154	51	98	2.19	455	40.02
AN-15			15	115	36		29	.70	218	
AN-17			7	74	17		15	.38	178	
AN-18(−80)			10	109	22		28	.49	181	
AN-18(−230)	0		9	121	40	1	34	.33	235	
AN-19A			4	17	18		16	.34	182	
AN-19B			9	8	19		22	.46	204	

TABLE 22: Percent coefficients of variation (100%(S/$\overline{X}$)) for eleven organic stream bank sediment samples for each analytical method and size fraction

Analytical Method	Ag	As	Co	Cu	Ni	Pb	Zn	Fe	Mn	LOI
AN-1, 3 & 14(−80)	76	64	23	49	23	57	16	19	27	18
AN-1 & 14(−230)			12	47	24	22	15	19	22	24
AN-15			28	50	26		36	18	41	
AN-17			25	46	40		34	21	43	
AN-18(−80)			37	56	51		30	25	45	
AN-18(−230)			45	55	35	138	36	41	43	
AN-19A			49	7	31		29	23	43	
AN-19B			43	56	38		26	21	43	

TABLE 23: Anomaly contrast comparison for eleven organic stream bank sediment samples for each analytical method and size fraction

Analytical Method	As		Co		Cu		Ni		Pb		Zn	
	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS
AN-1 & 3(−80)	1.7	1.8	1.2	1.3	2.7	1.6	1.3	1.3	1.4	1.1	1.2	1.2
AN-1(−230)			1.2	1.3	3.2	2.2	1.4	1.3	.9	.9	1.2	1.2
AN-15			1.5	1.9	2.8	2.0	1.7	1.6			1.9	1.9
AN-17			1.2	1.5	2.3	1.7	1.5	.9			1.4	1.9
AN-18(−80)			1.4	2.3	3.4	2.3	2.5	2.2			1.4	1.7
AN-18(−230)			1.5	2.0	3.2	2.2	1.6	1.6	1.6	4.0	1.5	2.0
AN-19A			1.0	1.8	1.1	1.1	1.8	1.8			1.4	1.6
AN-19B			1.3	2.1	2.2	1.4	1.9	1.8			1.3	1.5

UPS = mean of element concentrations for samples 3155, 3151, 3153 and 3164, which are *upstream* from copper-nickel mineralization.

M = mean of element concentrations for samples 3157, 3159, 3162, 3169 and 3170, which are *over* copper-nickel mineralization.

DS = mean of element concentrations for samples 3166 and 3168, which are *downstream* from copper-nickel mineralization.

M/UPS = upstream contrast DS/UPS = downstream dispersion

TABLE 24: Fe-Mn oxide (−80 mesh fraction) analyzed by AN-1

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (%)
3972	90	60	50	130	2.64	.51
3995	1939	304	1700	3100	17.39	18.67
3971	2960	250	640	730	9.32	19.00
3990	81	73	122	77	2.63	.04
3970	40	90	40	110	1.59	.40
3991	1491	56	426	1600	18.88	15.61
3992	1886	53	760	2400	9.93	24.98
3993	1929	68	664	1900	11.53	24.83
3994	1826	40	485	1600	13.20	20.65
3996	1730	59	482	1100	9.44	21.20

TABLE 25: Fe-Mn oxide (−80 mesh fraction) analyzed by AN-18

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (%)
3972	70	40	65	60	.45	.45
3995	2302	294	1666	3000	5.32	22.26
3971	3200	215	615	700	6.66	15.19
3990	30	50	22	42	.16	near 0
3970	20	65	35	70	.44	.36
3991	1550	38	338	1400	5.08	15.22
3992	2000	48	706	2200	5.16	24.88
3993	2200	68	660	1800	5.92	25.80
3994	2180	40	444	1400	5.86	21.40
3996	1954	52	436	1200	5.84	19.10

TABLE 26: Fe-Mn oxide (−80 mesh fraction) analyzed by AN-19B

Sample Number	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (%)
3972	80	25	60	90	.45	.50
3995	1861	231	1477	2800	5.26	20.18
3971	3200	200	595	750	8.00	16.82
3990	23	23	10	40	.15	near 0
3970	50	20	20	75	.43	.39
3991	1273	19	299	1200	4.73	13.82
3992	1777	33	637	2100	5.45	22.73
3993	1817	46	560	1500	5.76	22.37
3994	1630	21	379	1300	5.31	18.49
3996	1588	35	381	900	5.53	16.81

TABLE 27: Mean element concentrations for seven Fe-Mn oxide samples for each analytical method

Analytical Method	Co (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)	Fe (%)	Mn (%)
AN-1	1966	119	737	1776	12.81	20.71
AN-18	2198	108	695	1671	5.69	20.55
AN-19B	1878	84	618	1507	5.72	18.75

Does not include samples 3970, 3972 and 3990 because of low iron and manganese

TABLE 28: Percent coefficients of variation (100%(S/$\overline{X}$)) for seven Fe-Mn oxide samples for each analytical method

Analytical Method	Co	Cu	Ni	Zn	Fe	Mn
AN-1	24	92	60	45	30	16
AN-18	23	96	65	45	10	21
AN-19B	33	108	65	48	18	17

Does not include samples 3970, 3972 and 3990 because of low iron and manganese

TABLE 29: Anomaly contrast comparison for seven Fe-Mn oxide samples for each analytical method

Analytical Method	Co		Cu		Ni		Zn	
	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS	M/UPS	DS/UPS
AN-1	1.2	1.1	2.8	5.5	.9	2.8	.7	1.8
AN-18	1.1	1.1	2.4	5.7	.9	3.0	.6	1.8
AN-19B	1.3	1.1	3.2	6.8	.9	3.0	.7	1.9

UPS = mean of element concentrations for samples 3992, 3993, 3994 and 3996, which are *upstream* from copper-nickel mineralization.

M = mean of element concentrations for samples 3971 and 3991 which are *over* copper-nickel mineralization. Samples 3970 and 3990 not included because of low iron and manganese.

DS = element concentration for sample 3995, which is *downstream* from copper-nickel mineralization. Sample 3972 not included because of low iron and manganese.

M/UPS = upstream contrast

DS/UPS = downstream dispersion

TABLE 30: Coefficients of determination (r^2) for −80 mesh clastic stream sediments analyzed by AN-18

	Co	Cu	Ni	Zn	Mn
Fe	.71	.01	.11	.68	.92
Mn	.87	*.02	.06	.80	
Ni		.45			

* Negative relation

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

TABLE 31: Coefficients of determination (r^2) for −80 mesh organic stream bank samples analyzed by AN-18

	Co	Cu	Ni	Zn	Fe	MN
LOI	*.14	*.07	*.39	*.45	*.45	*.02
Mn	.62	.00	.04	.42	.64	
Fe	.47	.02	.15	.65		
Ni		.73				

* Negative relation

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

TABLE 32: Coefficients of determination (r^2) for −80 mesh Fe-Mn oxide samples analyzed by AN-19B

	Co	Cu	Ni	Zn	Mn
Fe	.94	.28	.00	*.17	.00
Mn	.00	.01	.19	.35	

* Negative relation

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

Does not include samples 3970, 3972 and 3990 because of low iron and manganese.

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APPENDIX: DESCRIPTION OF ANALYTICAL METHODS

AN-1: Concentrated HCl, HNO_3 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-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 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 of 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 100°C. After the bomb has cooled to ambient temperature, 3.0 gm of boric acid is added to dissolve any precipitates which have formed. 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. The crucible is placed in a tube furnace at 3000°F. As sulfur dioxide evolves from the sample, the sulfur concentration of the sample is measured with a Leco titrator.

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 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 #40Whatman 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.