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Oxalic-acid leaching of rock, soil, and stream-sediment samples as an anomaly-accentuation technique

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ABSTRACT

In many instances total-rock and sieved-soil and stream-sediment samples lack the sensitivity and contrast required for reconnaissance exploration and necessary in the search for blind ore deposits. Heavy-mineral concentrates incorporate the required sensitivity and contrast but are overly expensive for two reasons: time-consuming sample preparation is required to obtain them, and they cannot be easily derived from all bulk-sample types. Trace-metal-content comparisons of the oxalic-acid-leachable portions with heavy-mineral concentrates show that the leachates are equal to the heavy-mineral concentrates in sensitivity and contrast. Simplicity of preparation and the resultant cost savings are additional advantages of this proposed method.

INTRODUCTION

As the number of undiscovered surface and near-surface deposits decreases, geochemical sample media and analytical techniques capable of detecting halos associated with blind deposits gain steadily in importance. Substantial effort has been and is being expended on improving analytical techniques. Lower sensitivity limits are being progressively decreased, to below crustal abundance for many elements. Precision at these levels has been substantially improved.

Somewhat less effort has been expended on the search for more suitable sample media. The standard sample used in geochemical exploration programs today, as well as twenty years ago, is the bulk-rock or sieved-soil or -stream-sediment sample. These sample types have been instrumental in the discovery of ore bodies outcropping at the surface, but they are less effective in the case of near-surface deposits and totally inadequate for those at any depth.

Heavy-mineral concentrates of stream sediments, or various fractions of these, have been found to be very effective in geochemical exploration situations where maximum sensitivity and contrast are required--such as in reconnaissance exploration and exploration for blind deposits. In addition to sensitivity and discrimination, concentrates provide information as to the mineralogic mode of occurrence of the metal. Concentrates are, unfortunately, not widely used in geochemical exploration as a result of three factors:

(a) the great amount of initial sample material required;

(b) the time-consuming and, therefore, expensive sample preparation required to obtain them; and

(c) The small size of the derivative sample, necessitating spectrographic rather than the more commonly used atomic absorption analytical methods.

A comparison of various sample media in southwestern New Mexico has shown that the concentrate fraction that is magnetic between 0.1 and 1.0 ampere setting on a Frantz Isodynamic Separator delineates anomalies of the greatest areal extent and is particularly effective in the detection of faint anomalies. This fraction is particularly rich in Fe oxides (exclusive of magnetite and ilmenite) and Mn oxides, as well as in the common dark-colored heavy-mineral assemblages, it will henceforth be referred to as the M-1 fraction.

The M-1 fraction is effective in the detection of faint anomalies, primarily as a result of its high content of Mn oxides and of the more reactive forms of Fe oxides.

Progressing outward from an orebody, the Fe and Mn oxides in the M-1 fraction may be derived from (1) the Mn and Fe associated with the ore, (2) the oxidized portions of a pyrite halo, (3) the remobilized Fe and Mn in the altered portions of the host rock, or (4) the Fe and Mn oxides that occur in soils or stream sediments and are enriched in trace metals as a result of surface and ground-water movement.

The authors believe that the sensitivity and discrimination of a heavy-mineral concentrate can be retained and the expensive preparation avoided by obtaining the equivalent of a M-1 mineral separate by chemical means.

[illegible]

The somewhat-selective solubilization of the more reactive forms

NO such word

of Fe and Mn oxides and of amorphous alumina and silica from limonites and clays by oxalic acid has long been recognized (Gallagher and Walsh, 1943; Goni, 1966). The combination of the ubiquitous nature of Fe and Mn oxides, their scavenging ability, and the ease of their selective extraction from various sample types (rocks, soils, stream sediments) by a simple oxalic-acid leach provides an easily obtainable sample medium that is nearly equal in effectiveness to the M-1 fraction. Oxalic acid has additional advantages in that it acts rapidly, is cheap, is readily available, and is not particularly hazardous to use.

TECHNIQUE

Five grams of the bulk sample (ground rock or sieved stream-sediment or soil) are introduced into a beaker along with 50 ml of 1.5N oxalic acid. This mixture is brought to a low boil and boiled for five minutes. The resultant oxalate solution is filtered hot through a fast (Whatman no. 41) filter and evaporated to dryness. Heating of the resultant leachate is continued until all of the free oxalic acid (a white fluffy material) is decomposed. The leachate is then transferred to a crucible and heated to 450°C in a muffle furnace to convert the oxalates to oxides and to drive off the hygroscopic water and the water of hydration. After cooling, the leachate is hand ground in an agate mortar and analyzed for 30 elements by a standard six-step semi-quantitative spectrographic method (Grimes and Marranzino, 1968).

SAMPLE TYPES

Three groups of samples, collected over and near three widely separated mineralized areas, were prepared and analyzed as described above. The resulting metal values were then compared with the corresponding metal values of M-1 fractions, <0.25-mm-sieved stream sediments and soils and ground outcrop samples.

The first group of 36 samples, consisting of 30 sieved stream sediments and 6 outcrop samples, were collected in southwestern New Mexico in the southern portion of the San Mateo Mountains. This area, covered predominantly by a Tertiary rhyolitic ash-flow tuff, is strongly altered and fractured and is intruded by numerous rhyolite-porphyry dikes and plugs. Previous geochemical work (Griffitts and others, 1971) had delineated a large area anomalous in Mn, Au, Ag, Pb, Zn, Mo, Sn, Be, Nb, La, and Y. This anomaly was not discernible in rock or stream-sediment samples and was delineated on the basis of data from stream-sediment concentrates.

The second group of 40 samples, consisting of 20 stream sediments and the same number of soils, were collected in the Copper Flat area near Hillsboro, New Mexico, over a well-known porphyry copper deposit exposed at the southern tip of the Animas uplift.

The third group of 117 samples were collected in northeastern Minnesota, over and near a Cu-Ni-Co mineral deposit in the Duluth Complex-Giants Range Granite contact zone. This group consists of sieved A-and B-horizon soils.

RESULTS

The 30 stream-sediment samples collected in the southern San Mateo Mountains were divided into 3 groups of 10 samples each. The first group or "900" series was collected immediately outside the M-1 fraction anomaly. The second group or "600" series originated from the more intense portion of the anomaly, and the third group or "400" series was collected in a background area.

The Fe and Mn contents of the various sample types are shown in figure 1. Predictably, a strong, though variable, Fe and Mn enrichment is seen in the leachates relative to the corresponding bulk samples.

Figures 2a and 2b show that Pb and Bi contents of the stream sediments and corresponding leachates and M-1 fractions. It is evident that there is little, if any, significant variation in the ranges of Pb content of the three stream-sediment-sample series (table 1a). The oxalic-acid leachates (table 1c) present a strikingly different picture. The variation in the range of Pb content in the M-1 fraction of the three series (table 1b) is similar to that of the leachates, with the exception of the range of the "900" series, which falls very substantially below that of the equivalent leachates.

Bismuth and cadmium were detected only in the leachates. The five reported Bi values occurred in five of the six leachates of the "600" series with Pb contents equal to or greater than 1,000 ppm (fig 2b).

A comparison of Ag, Pb, Mo, and La contents of bulk rocks and of the corresponding leachates is shown in figure 3. The rock samples were collected along a mineralized fracture zone within the M-1 anomaly. Enhancement of the trace metals in the leachates relative to the whole rock is similar in degree to that seen in the "600" series leachates relative to the stream sediments.

A comparison of Cu contents of stream sediments, oxalic-acid leachates, and M-1 fractions along a 2-mi (3.2 km)-long traverse through the Copper Flat mineral deposit is shown in figure 4a. The correlation coefficient between the Cu contents of the M-1 fraction and of corresponding leachates is 0.93, whereas that between the stream sediments and corresponding leachates is -0.28. Copper contents of the soils and corresponding leachates, collected along the traverse shown in figure 4a, are shown in figure 4b. The correlation coefficient between these two sample media is 0.89.

A- and B-horizon soil samples were collected at 25 locations along a 6-mile (.6 km)-long traverse through the Cu-Ni-Co mineral deposit in northeastern Minnesota. Respective Cu values of the B-horizon soils and corresponding leachates along this traverse are shown in figure 5. The Cu values of the sieved B-horizon samples range from 10 through 3,000 ppm, whereas those of the leachates range from 50 to 7,000 ppm. Fig. 6 shows a comparable plot of the Cu contents of A-horizon soils and corresponding leachates along a 4-mile (6.4 km)-long traverse through an area of no known mineralization in northeastern Minnesota.

The respective Cu-Ni relationships in 97 B-horizon soil samples and leachates from the mineralized area are shown in figures 7a and 7b. In the bulk sample, the Cu-Ni correlation coefficient is 0.79, whereas in the leachates it is 0.78. In both instances the samples deemed anomalous fall within the 1:1-10:1 Cu/Ni ratio zone. The Cu-Ni correlation coefficient of 72 outcrop samples collected in this area is 0.88. Mineralized outcrop samples, like the anomalous soils and leachates, also fall into the 1:1-10:1 Cu/Ni ratio zone.

Discussion

The four major components of an oxalic-acid leachate are alumina, Fe oxide, silica, and Mn oxide. The relative abundance of each component within a leachate is dependent upon the amount of clay within the bulk sample. Thus, the composition of an oxalic-acid leachate is determined by

(a) bulk sample type and

(b) the degree of clay-forming processes acting upon it.

Gallagher and Walsh (1943) noted that in boiling a podsol B_1-horizon soil in 1.0 N oxalic acid for 20 minutes they were able to extract 1.07 percent of the SiO_2, 7.16 percent of the Al_2O_3, and 1.11 percent of the Fe_2O_3. A similar treatment of the B_2 horizon from the same soil profile, on the other hand, extracted 0.88 percent of the SiO_2, 3.93 percent of the Al_2O_3, and 7.90 percent of the Fe_2O_3. Goni (1966) found that a 4-hour leach of intrusive rocks using a 0.1-M mixture of oxalic and citric acids produced leachates that averaged 52 percent Fe_2O_3, 21.2 percent SiO_2, and 20.8 percent Al_2O_3. A fifth component, water, was introduced during the leaching process T. T. Chao (oral commun., 1974) determined that the average hot-plate-dried leachate contained about 1/3 water, 70 percent of which was water of hydration and the remainder, hygroscopic. This component can, however, be easily eliminated by heating the leachate to 450°C prior to analysis.

The leached Fe and Mn oxides are the most important trace-metal carriers (Mitchell, 1964), whereas the alumina and silica act primarily as diluents within the leachate; thus, the trace-metal content of the leachate is determined by

(a) the major-element composition of the leachate and

(b) the trace-metal content of the oxalic-acid-leachable Fe and Mn oxides.

In general, assuming a uniform scavenging ability for the oxalic-acid-leachable Fe and Mn oxides from area to area and from sample type to sample type, their trace-metal content will be governed by the following factors:

(a) source of trace-metal:
    (1) mineralized rock,
    (2) unmineralized rock of varying but generally low-level trace-metal content;
(b) rate of supply of trace metals to the oxides:
    (1) nature of sample,
    (2) climatic setting,
    (3) topographic setting; and
(c) time:
    (1) length of time over which process "b" operates,
    (2) effect of aging on the scavenging ability of Fe and Mn oxides.

The exploration geochemist is primarily concerned with the initial source of the trace metal. Our data indicate that the trace-metal variation brought about by the lithologic and climatic variations are in a different range from those produced by mineralization. For example, stream-sediment leachates collected in a rhyolitic area in southwestern New Mexico have an average Pb background value of 28 ppm. Leachates of soil samples collected in a swampy northeastern Minnesota area, predominantly underlain by gabbroic rocks, have a background Pb content of 18 ppm. Leachates of stream sediments collected within a mineralized portion of the same rhyolitic unit in southwestern New Mexico have a mean Pb content of 1,280 ppm (fig. 1).

The limited data collected to date indicate that the alumina and silica dilution pose more of a problem. Shown below are average leachate/bulk-sample Cu ratios in three mineralized areas:

Bulk-sample type	Leachate/bulk-sample Cu ratios
New Mexico stream sediment	21:1
New Mexico soil	7.4:1
Northeast Minnesota soil	6.2:1

It can be seen that sample types increasingly rich in clays produce progressively lower ratios of bulk to leachate Cu. Presumably, the concentration factor could be increased in the soils by eliminating the clay fraction prior to leaching.

Carbonate-rich samples present a more serious problem. Metals such as Pb precipitate out with calcium oxalate and are thus removed from the leachate. This fact renders the method unusable in areas with widespread limestone outcrops.

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Table 1. Pb-content ranges of <0.25-mm stream sediments, the corresponding oxalic-acid leachates, and the M-1 fractions of the "400", "600", and "900" series of southern San Mateo samples.

Pb (ppm)	<0.25-mm stream sediments			M-1 fraction			Oxalic-acid leachates		
	400	900	600	400	900	600	400	900	600
10				3			1		
15									
20							4		
30	4	3	4	5			3		
50	6	4	3	1	1		2		
70		2	3	1	4				
100		1			5			1	
150								1	
200						1		2	
300						2		2	2
500						3		3	1
700						1		1	1
1000									1
1500						1			2
2000						1			3
3000									
5000						1			

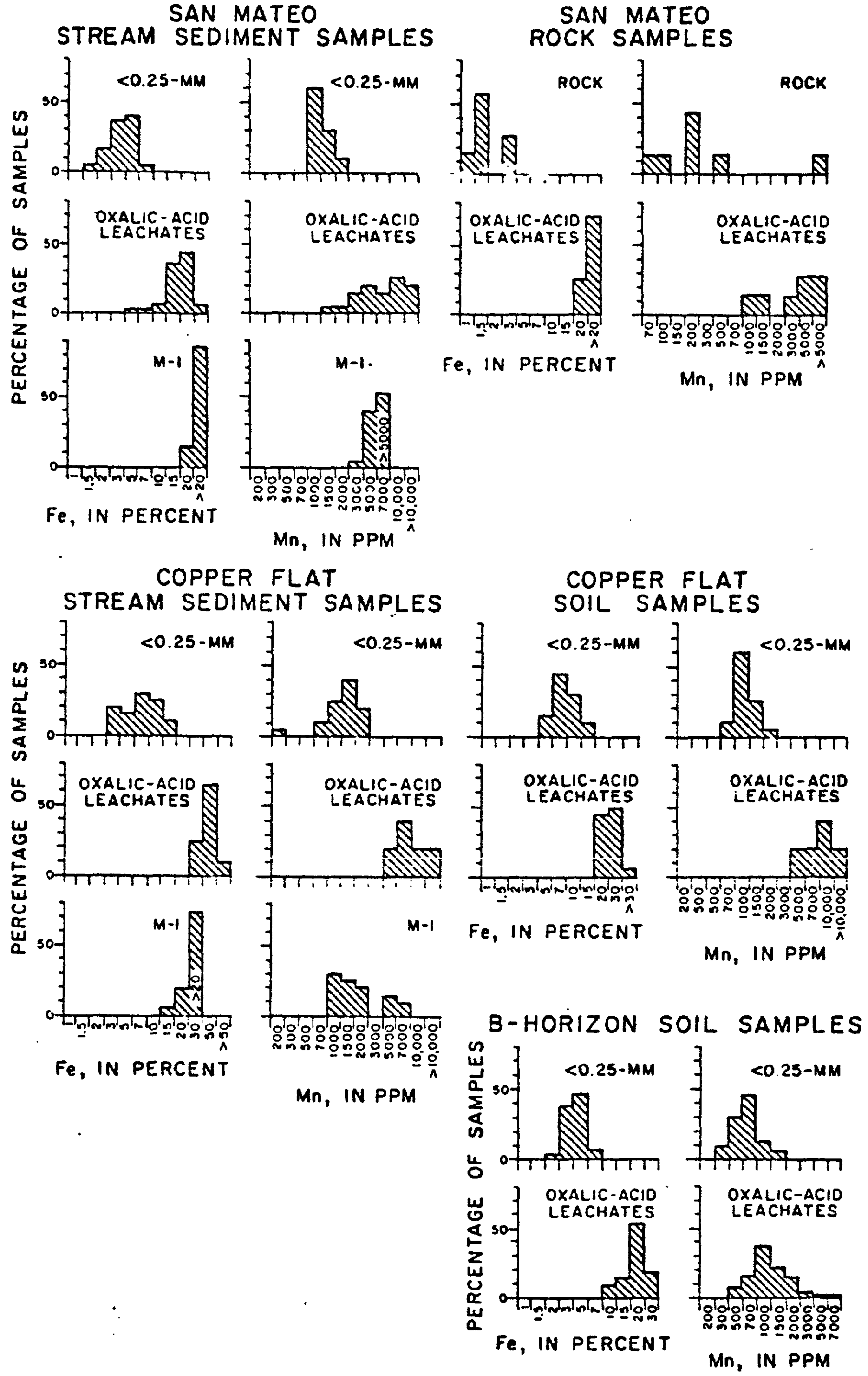

Figure 1. Comparison of the Fe and Mn contents of rocks, <0.25-mm stream sediments, <0.25-mm-mesh soils, M-1 fraction, and oxalic-acid leachates derived from the bulk-sample types, as determined by semi-quantitative spectrographic methods.

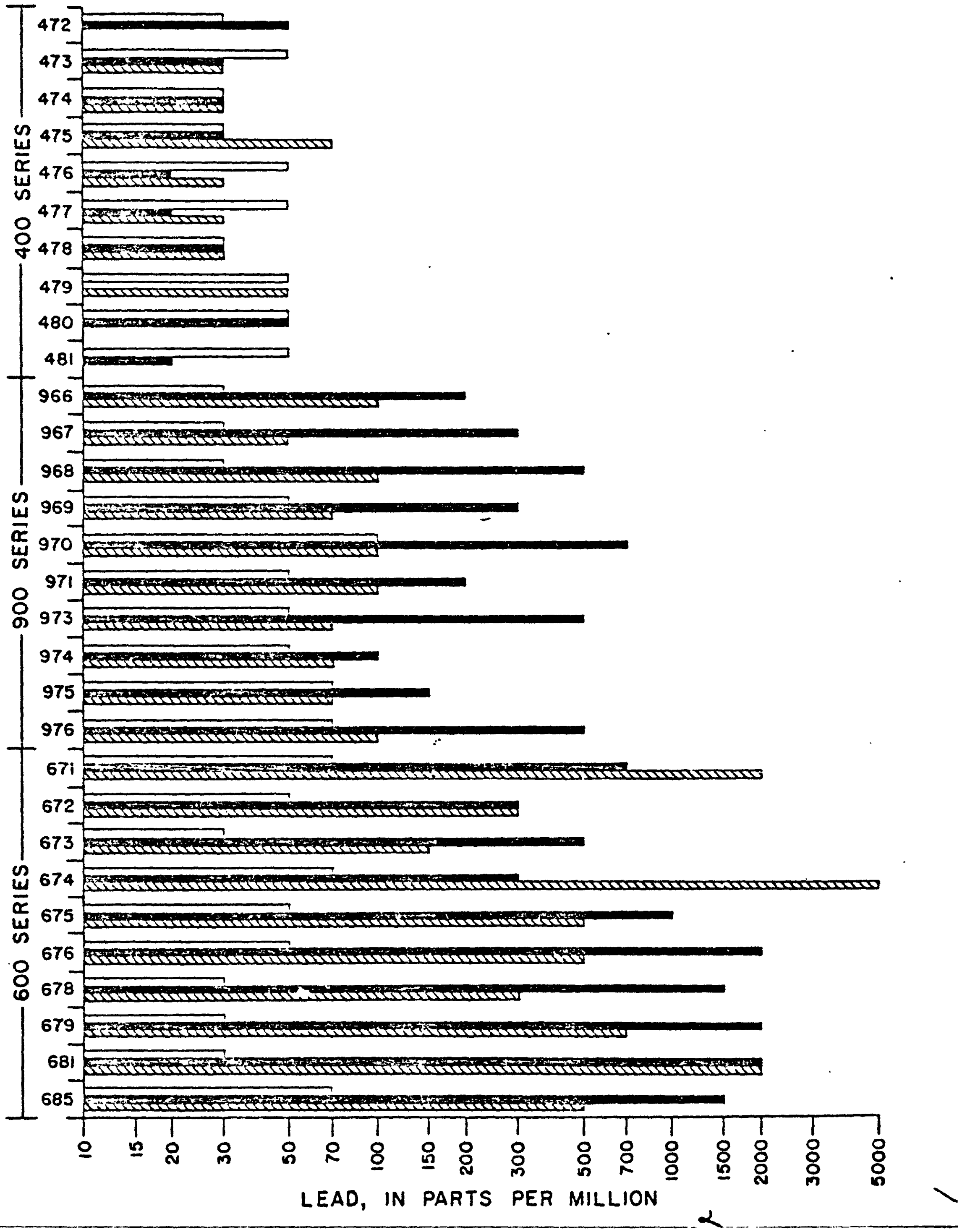

Figure 2A. Pb contents of southern San Mateo <0.25-mm stream sediments, the corresponding oxalic-acid leachates, and M-1 fractions, as determined by semiquantitative spectrographic methods.

☐ <0.25-mm stream sediment

■ Oxalic-acid leachate

▨ M-1 fraction

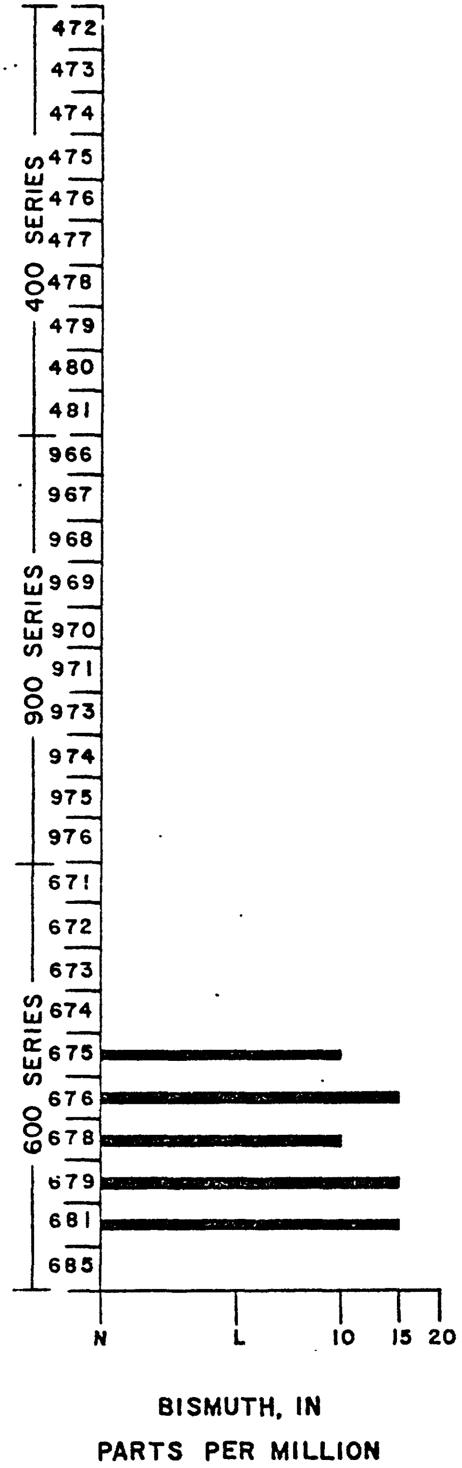

Figure 2B. Bismuth content of southern San Mateo <0.25-mm stream sediments, the corresponding oxalic-acid leachates, and M-1 fractions, as determined by semiquantitative spectrographic methods. L indicates that Bi was detected but is below the lowest (10 ppm) spectrographic standard. N indicates that Bi was not detected.

▬ Oxalic-acid leachate

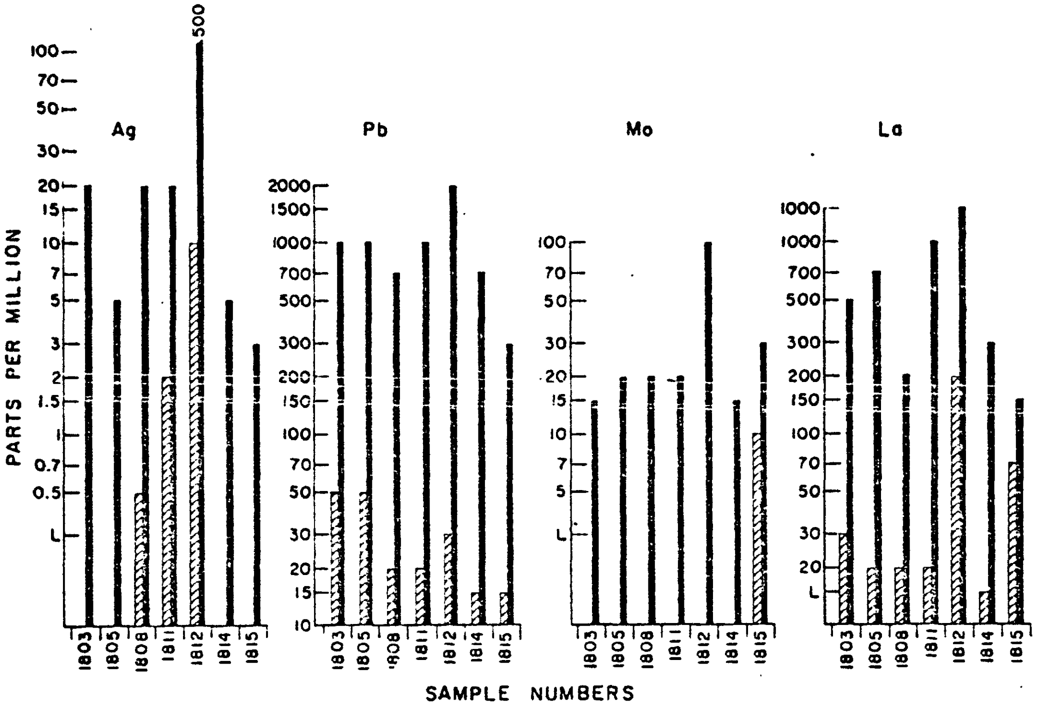

Figure 3. Ag, Pb, Mo, and La contents of mineralized southern San Mateo outcrop samples and corresponding oxalic-acid leachates, determined by semiquantitative spectrographic methods. L indicates that element was detected but content is below the lowest shown spectrographic standard. N indicates that the element was not detected.

▨ Outcrop sample

■ Oxalic-acid leachate

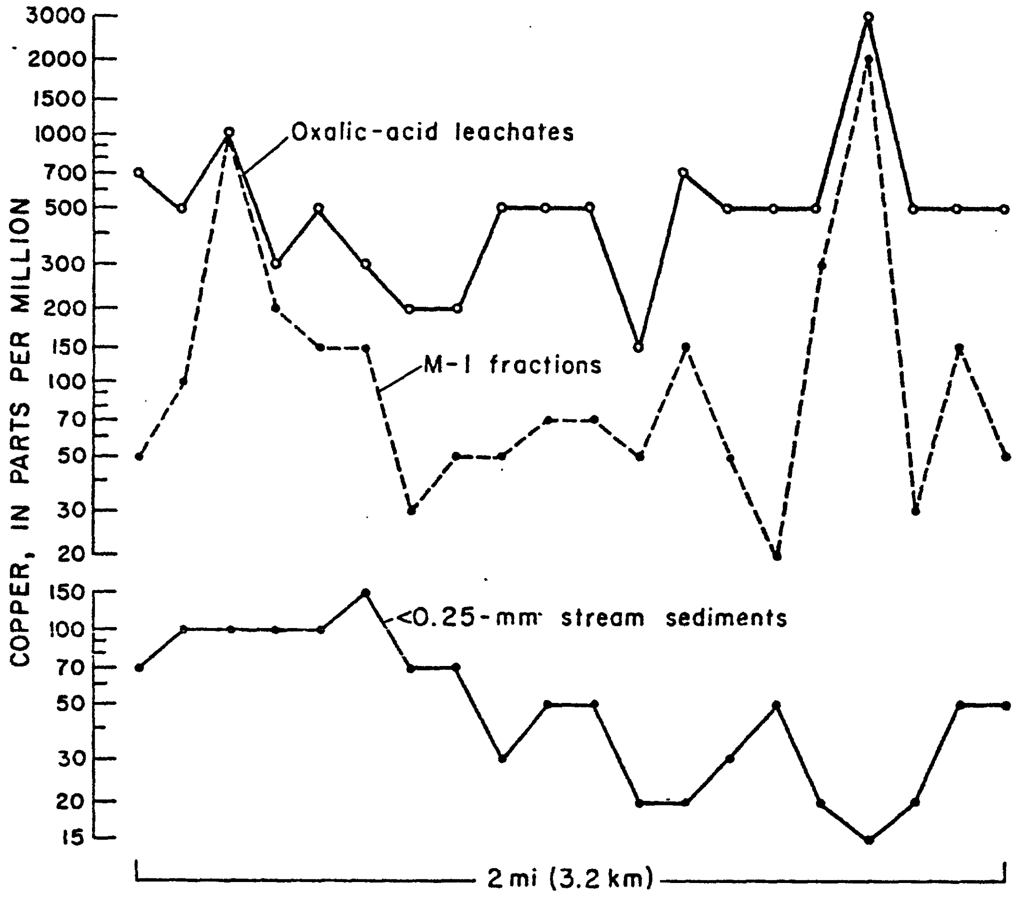

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Figure 4A. Copper contents of Copper Flat <0.25-mm stream sediments, the corresponding oxalic-acid leachates, and M-1 fractions, determined by semiquantitative spectrographic methods.

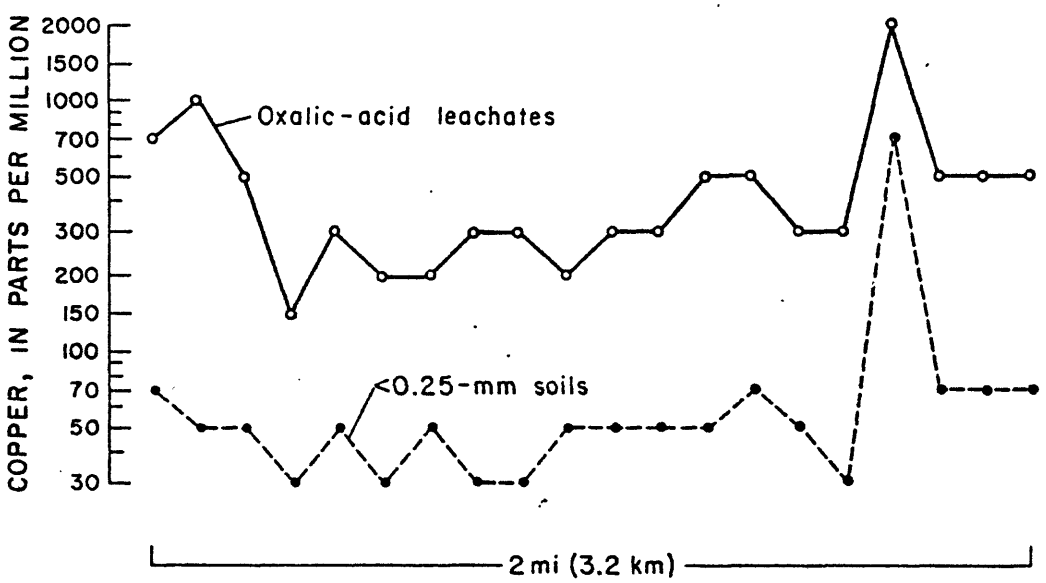

Figure 4B. Copper contents of Copper Flat <0.25-mm soils and the corresponding oxalic-acid leachates, determined by semiquantitative spectrographic methods.

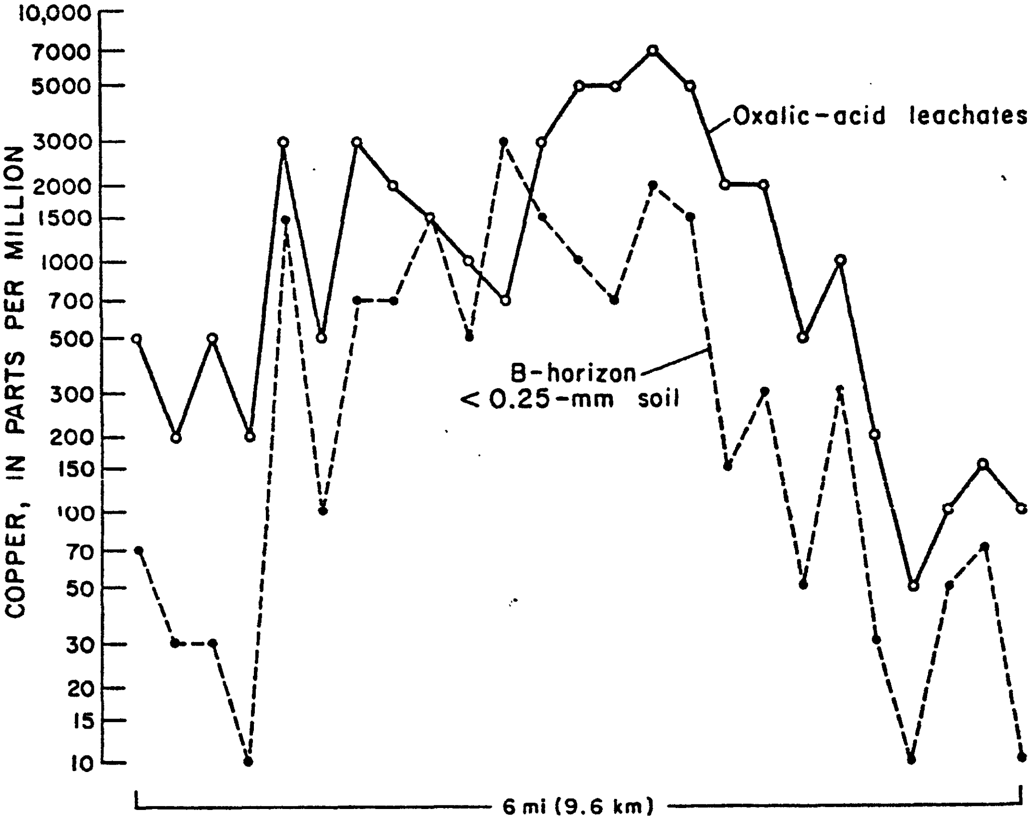

Figure 5. Copper contents of <0.25-mm B-horizon soils and the corresponding oxalic-acid leachates from a mineralized area in northeastern Minnesota. Semiquantitative spectrographic determinations.

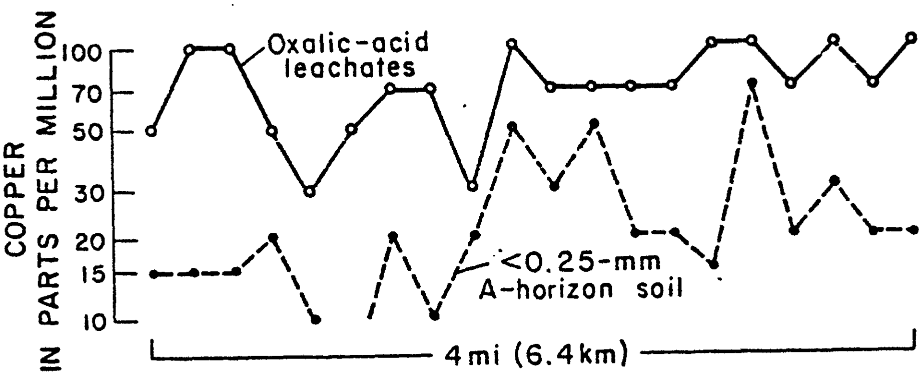

Figure 6. Copper contents of <0.25-mm A-horizon soils and the corresponding oxalic-acid leachates from an unmineralized area in northeastern Minnesota. Semiquantitative spectrographic determinations.

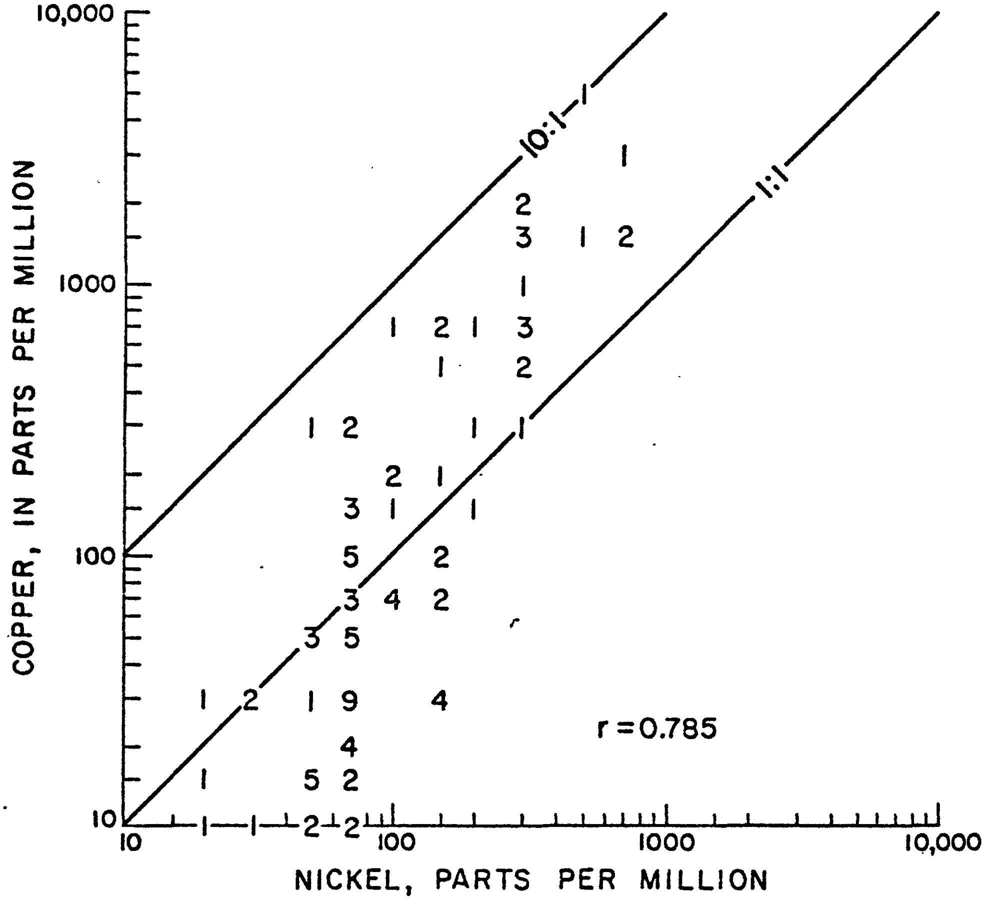

Figure 7A. Cu-Ni relationship in <0.25-mm B-horizon soils from a mineralized area in northeastern Minnesota. Semiquantitative spectrographic determinations. Number in circle indicates the number of samples in a given Cu-Ni class. r indicates the correlation coefficient of the Cu and Ni contents.

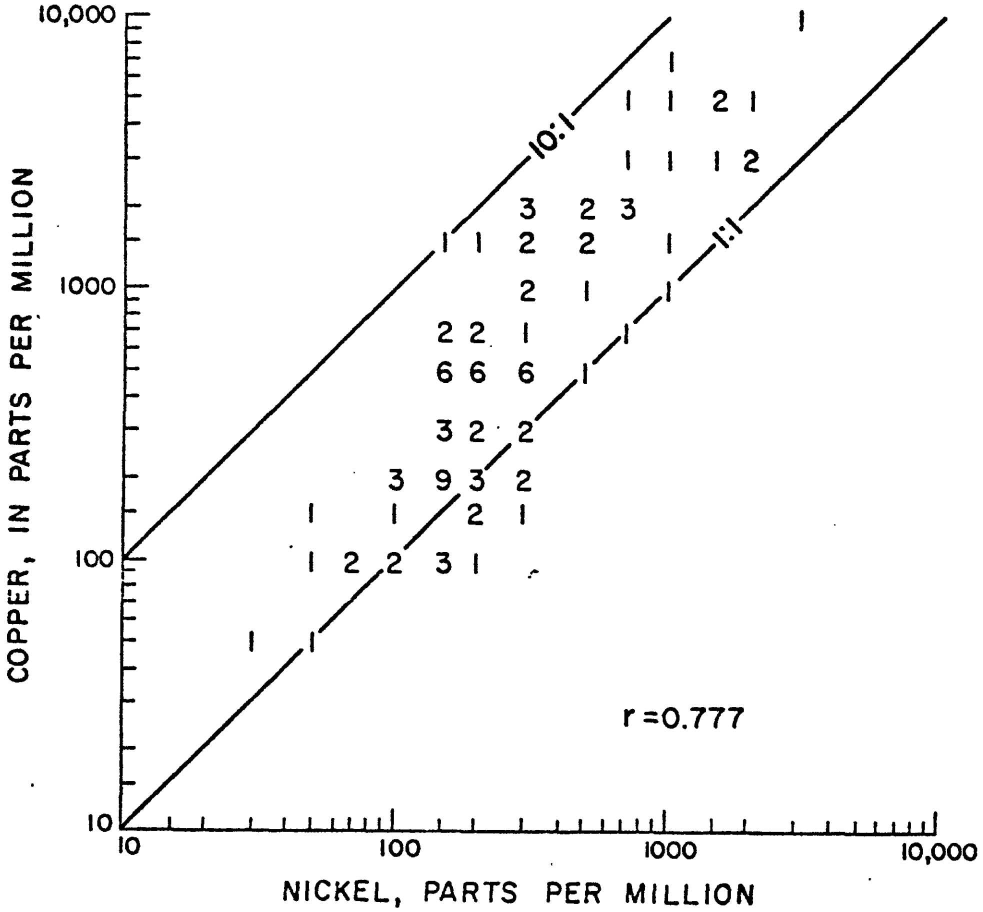

Figure 7B. Cu-Ni relationship in oxalic-acid leachates derived from the <0.25-mm, B-horizon soil samples shown in Figure 7A. Semiquantitative spectrographic determinations. Number in circle indicates the number of samples in a given Cu-Ni class. r indicates the correlation coefficient of the Cu and Ni contents.