May 4, 1973

To the Graduate Council:

I am submitting herewith a thesis written by Stephen Swift Gentry entitled "Trace Metal Distribution in Soil Overlying Sphalerite-Bearing Carbonate Rock." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

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TRACE METAL DISTRIBUTION IN SOIL OVERLYING SPHALERITE-BEARING CARBONATE ROCK

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Stephen Swift Gentry

June 1973

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ABSTRACT

The purpose of this research was to investigate relationships among particle size distribution, mineralogy, and trace metal content of a soil which overlies sphalerite-bearing carbonate rocks. Five samples were taken from the Copper Ridge area, Grainger County, Tennessee. Samples were separated into six size fractions. Mineralogy of the fractions was identified by x-ray diffraction. Chemical analyses were made for Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn by atomic absorption spectroscopy.

The dominate minerals in these acid soils are quartz, 7, 10, and 14A clays. The 14A clay is believed to be modified by aluminum-hydroxy interlayering. Clay mineralogy was found to vary with particle size distribution, and the five samples may be divided into two groups based upon mineralogy and particle size distribution.

Group I soils are clay rich, B horizon samples. Group II soils are silt and sand rich. They were taken from the lower A horizon. B horizon samples contain 7, 10, and 14A clays; however, A horizon samples contain only 7 and 14A clays. Some evidence was found to support the idea that 10A clays convert to 14A clays when exposed to more intense weathering conditions.

Cu and Co concentrations show some correlation with concentrations of clay minerals; however, the type of clay mineral present does not seem to be the controlling factor in determining the distribution of trace metals. In fact, the presence of clay minerals does not seem to be a prerequisite to the retention of most of the trace metals studied.

The possibility that trace metals may be associated with oxides of Fe and Mn was explored. A correlation was obtained between most trace metal concentrations and Fe concentrations. It was also determined that between 56 and 84% of the Fe is in an oxide form. The presence of hematite in certain soil fractions correlates with high trace metal content.

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I. INTRODUCTION

Purpose

The purpose of this research was to investigate relationships among particle size distribution, mineralogy, and trace metal content of a soil which overlies sphalerite-bearing carbonate rocks. The study is part of a program whose purpose is to investigate trace metal distribution in drainage systems of eastern Tennessee. As a part of this program, this research is designed to provide mineralogical and metal distribution data so that comparisons can be made between the minerals and metal distribution found in soil and those found within material transported by streams.

As the sampled soils were developed upon sphalerite-bearing rock, the data gathered in this study are also pertinent to the problem of trace metal retention by soils overlying mineralized bedrock and may be of benefit to the field of geochemical prospecting. Specifically, the study provides information regarding the correlation between particle size distribution and metal concentration, the effect of mineralogy upon metal retention, and the possibility that metal oxides serve as a site of trace metal accumulation.

Location and General Geology

Soil samples were taken from the crest of Copper Ridge in Grainger County, Tennessee. The sample site is located about 2 miles northeast of Puncheon Camp, Tennessee (Figure 1) and lies within the Copper Ridge zinc district. Copper Ridge has a northeast-southwest trend, and in the sample site area, an elevation of about 1500 feet. The samples were taken in rolling pasture land which lies about 200 feet above the adjacent valley bottom.

Underlying the sample site are the Kingsport and Mascot Formations both of which are Lower Ordovician units of the Knox Group. The Kingsport Formation is composed of interbedded limestone and siliceous dolomite. The Mascot is primarily a moderately cherty dolomite in the area under consideration (Hill, 1971, pp. 12-18). Strike of these formations follows the northeast-southwest trend of Copper Ridge. Dip is about 36° southeast.

Mississippi Valley-type sphalerite mineralization occurs in the upper part of the Kingsport Formation and in the lower part of the Mascot Formation. Ore is being mined from these formations at the Flat Gap Mine about 20 miles northeast of the sample site, and extensive drilling has located mineralization in the sample site area (Hill, 1971). Soil surveys made prior to the author's research have reported high zinc concentrations in the sample site soils (Hill, 1971).

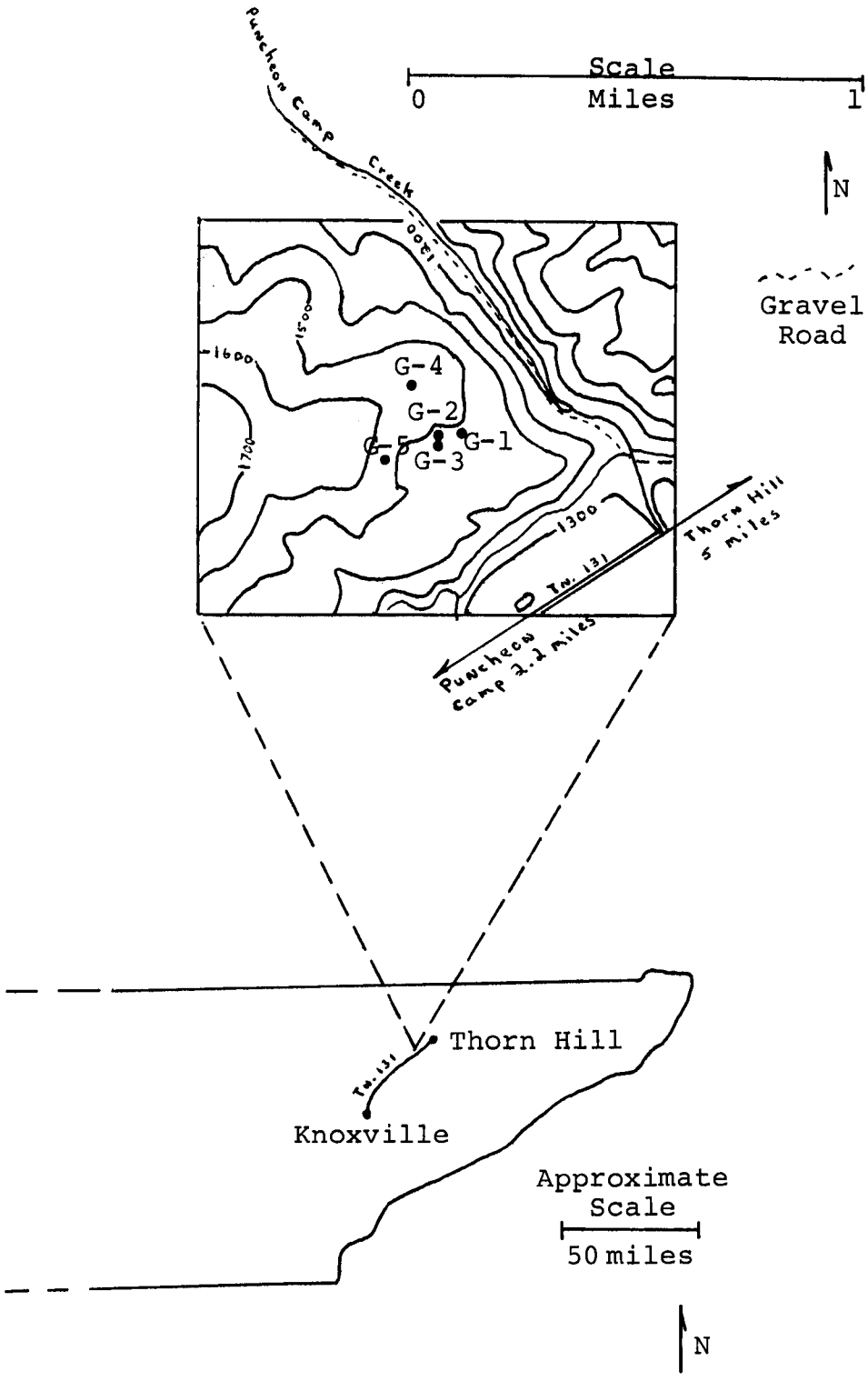


Figure 1. Location of sample site.

The soils studied have been classified as Red-Yellow Podzolics. Soils of the sample site area are well leached and have a pH of about 5. They contain a brown, silty A horizon and a yellow to red clay-rich B horizon. The A horizon ranges in thickness from a few inches to several feet. Drilling reveals that the B horizon ranges from a few inches to tens of feet in thickness. The total thickness of overburden is about 30 feet (Hill, 1971, pp. 29, 56).

The five samples used in this study were taken from a depth of 2 feet. A 2-foot sample depth was selected for several reasons. First, it was hoped that 2 feet would be sufficient to avoid disturbances caused by man. Secondly, because 2 feet is a convenient depth from which a large number of samples could be taken in a large scale geochemical study, it was deemed desirable to determine the consistency of those soil characteristics which influence trace metal concentrations at this depth. Third, Hill (1971) used a 2-foot sampling depth and obtained high Zn concentrations at this depth.

Two samples (G-1 and G-2) were taken below a very distinct color change and are B horizon samples. No distinct color change was observed above the other three samples (G-3, G-4, and G-5). The soil profile above these three showed a gradual color change from a dark brown to a yellowish brown. Here, it should be noted that samples G-1

and G-2 differ from samples G-3, G-4, and G-5 not only in color but also in particle size distribution and mineralogy. That this second group of samples may represent a completely different type of soil (unrelated to the first group) was considered and rejected. Samples G-3, G-4, and G-5 conform to the description given by Miller (1972) of A horizon soils formed from carbonate rocks in East Tennessee, and it is thought that these samples represent a somewhat unusually deep A horizon. This interpretation is not intended to reject the possibility that underlying rock type may have influenced differences found in the soil from one sample location to another. In fact, there is evidence which supports the contention that A horizon depth is controlled to some degree by the underlying rock. Miller (1971, p. 36) states that soils having a large amount of chert generally have thicker A horizons. Because this chert-A horizon thickness correlation is thought to be a cause and effect relationship, it follows that the amount of chert in the parent rock influences A horizon depth. Another bedrock related factor which probably causes local variations in the A horizon thickness within the sample area is underground drainage. The presence of a sinkhole in the sample site provides a good indication of locally intense leaching conditions which would cause local variations in the A horizon thickness. For these reasons, samples G-3, G-4, and

G-5 are thought to represent the A horizon of the same soil type as samples G-1 and G-2. Local variations in bedrock character and underground drainage probably account for the fact that two different soil horizons were sampled at the same depth over a relatively small area. In a subsequent section, it will be suggested that the differences in particle size distribution and mineralogy observed between the two soil groups are, like A horizon depth, largely a function of variations in the degree of weathering.

The location from which individual samples were taken within the sample site was determined by field colorimetric (dithizone) methods for Zn. An attempt to collect samples having high Zn concentrations and samples having low Zn concentrations was made. Analyses made in the laboratory indicate that the field testing method did not work well. With regard to the sampling technique in general, the author suggests that future studies sample vertical soil profiles because the results of this study indicate that those factors which influence trace metal retention vary vertically within the soil.

Research Performed

Five soil samples were collected. They were each separated into six size fractions, x-rayed, and analyzed chemically for Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn. Size

fractionation was accomplished by centrifugation, gravity settling, and sieving. The mineralogy of each fraction was identified by x-ray diffraction, and chemical analysis was by atomic absorption spectroscopy.

II. TERMINOLOGY AND GENERAL EXPERIMENTAL PROCEDURES

Terminology

Although groups of particles obtained by settling under the influence of gravity for varying periods of time or by centrifugation at various speeds are better defined by a parameter which incorporates both particle size and particle density, particle fractions of this study have simply been designated by size. A soil fraction labeled 0.2 - 2μ would in all probability contain some particles smaller than 0.2μ and some larger than 2μ due to variations in particle density. The reader should bear in mind that size connotations are only approximations of the true size range of the members of a particle fraction.

Clay minerals will be referred to by their basal spacing in angstroms. The clay minerals referred to as 1A, 10A, and 7A have basal spacings of about 14.15A, 9.93A, and 7.21A respectively.

Bulk soil analysis refers to chemical analyses of unfractionated samples of soil. This term is used to distinguish between analyses made on unfractionated soils and analyses made upon mechanically separated fractions of a soil.

Total metal analysis will be used to indicate metal analyses made of completely dissolved samples. This term is used to distinguish between analyses of completely dissolved samples and those of a chemically separated portion of a soil sample.

The five soils which were sampled will be referred to as G-1, G-2, G-3, G-4, and G-5. Because of similar characteristics, samples G-1 and G-2 are referred to as group I, and samples G-3, G-4, and G-5 are referred to as group II.

The term trace metal will be used to refer to Cd, Co, Cr, Cu, Ni, and Zn. Iron will not be considered a trace metal. Manganese will not be included under the term trace metal because it is much more abundant in these soils than are Cd, Co, Cr, Cu, Ni, and Zn.

Size Fractionation

Five soil samples were disaggregated, placed into suspension with deionized water, and separated into the following fractions: <0.2, 0.2 - 2, 2 - 5, 5 - 50, 50 - 100, and 100 - 5000μ. The three finer fractions were obtained by centrifugation and the three coarser fractions by wet sieving. All separations performed by centrifugation were done three times to effect as thorough a separation as possible in a reasonable time.

With regard to the size separation procedure and the results obtained from this procedure, several points must be

emphasized so that confusion may be avoided. First, soil particles, especially clay minerals, may be bound together by a cementing agent and thus form aggregate grains which are larger than the individual mineral grains. Many soil workers use chemical treatments to remove cementing agents and are thereby able to obtain particle size distributions which more closely reflect basic particle sizes. The use of chemical disaggregation was not feasible in this study because certain cementing agents (Fe and Mn oxides) were to be studied and because of the possibility that certain trace metals are associated with cementing agents. The disaggregation procedure used in this study was a relatively mild ultrasonification, and the resulting particles are probably more similar to the aggregates found in nature than particles produced by chemical disaggregation would be.

In addition to cementing agents, another factor which influences particle size is abrasion incurred during ultrasonification and centrifugation. It is conceivable that both natural aggregates and individual mineral grains are reduced in size during these procedures. The tendency of clay minerals to flocculate during centrifugation is a third factor which complicates size fractionation. The flocculation problem is further complicated by the tendency of certain clays to flocculate more readily than others. Because clay mineralogy varied among the five samples studied,

flocculation was dealt with on a sample by sample basis. A soil-water ratio which produced no visible flocculation was experimentally determined for each sample separately. Suspensions prepared in accordance with these ratios were centrifuged three times. The effect of triple centrifugation is to eliminate any "invisible" flocculation by removal of soluble salts during the first centrifugation. The elimination of flocculation by soluble salt removal is accomplished by centrifuging at a speed and time sufficient to settle the desired size particle and then decanting the supernate which contains finer-sized particles and much of the soluble salt. The settled material is then resuspended and centrifuged two more times. By the third repetition of this process, particles should be settling as free from the effects of flocculation as possible without resorting to deflocculating agents or more time consuming washings.

Confidence in the separation procedure is gained by observing diffractograms of silt- and sand-size fractions. If flocculation occurred to an appreciable extent, clay minerals should be detected within these size ranges. With one exception, clay minerals are not detected in fractions coarser than 5μ. It should be emphasized that this one exception does not necessarily indicate a failure to control flocculation. In fact, chemical analysis shows the presence of high Fe concentrations within this silt-size fraction. This may well indicate an abundanceof oxide cement. It follows that

silt-size clay accumulations may reflect a natural process which causes larger than usual aggregates of clay and oxides.

A detailed fractionation procedure and discussion thereof is in Appendix A.

Weight Percents and X-ray Analysis

Each size fraction was dried (Appendix B) from acetone and weighed. The percent of the total sample weight contributed by each size fraction was calculated. Each fraction from all five samples was split into two portions. One portion was reserved for chemical analysis and the other for x-ray analysis. X-ray analysis was by diffractometer methods using oriented samples for the <0.2, 0.2 - 2, and 2 - 5μ fractions. Hand packed mounts were prepared from the 50 - 100μ fractions. The 5 - 50 and 100 - 5000μ fractions were studied from both elutriated slides and hand packed mounts. Clay fractions were treated with ethylene glycol, heated to 375°C for 12 hours, and heated to 600°C for one hour.

Chemical Analyses

A portion of each size fraction was prepared for total metal analysis by dissolving in HF and $HClO_4$ after destruction of organic matter by hot HNO_3. Exchangeable ions were studied by equilibrating bulk soil samples with 1N neutral

ammonium acetate. Free Fe oxides were extracted from bulk soil samples by reduction with sodium dithionite ($Na_2S_2O_4$) followed by acidification (pH 3.5) to dissolve metal sulfides which may have formed.

Chemical analysis was done by atomic absorption spectroscopy. Detailed procedures are given in Appendix C.

III. EXPERIMENTAL RESULTS

Particle Size Distribution

Data indicate that the soils may be divided into two categories based on particle size distribution (Table 1, Figure 2). One category is represented by samples G-1 and G-2 and is characterized by a relatively large amount of clay- and silt-size particles. The other category is represented by samples G-3, G-4, and G-5. The soils of this second group have a greater content of coarse particles (100 - 5000μ), a greater content of 5 - 50μ particles, and a considerably smaller proportion of clay- and fine silt-size material. The significance of this division will become more obvious as mineralogical and chemical data are presented inasmuch as important differences in clay mineralogy and metal distribution are found between the two soil types.

The reader should bear in mind that the results obtained from a particle size analysis are very sensitive to the methods of disaggregation and separation used. For this reason, a detailed separation procedure is presented in Appendix A.

Table 1. Particle size composition of the five samples

Group	Sample	Fraction (microns) <0.2	0.2-2	2-5	5-50	50-100	100-5000
I	G-1	9%	42%	12%	30%	2%	5%
	G-2	nr	34%	14%	47%	5%	1%
	G-3	5%	12%	8%	57%	3%	16%
II	G-4	4%	17%	8%	50%	4%	17%
	G-5	3%	12%	9%	52%	4%	20%

nr = not recovered.

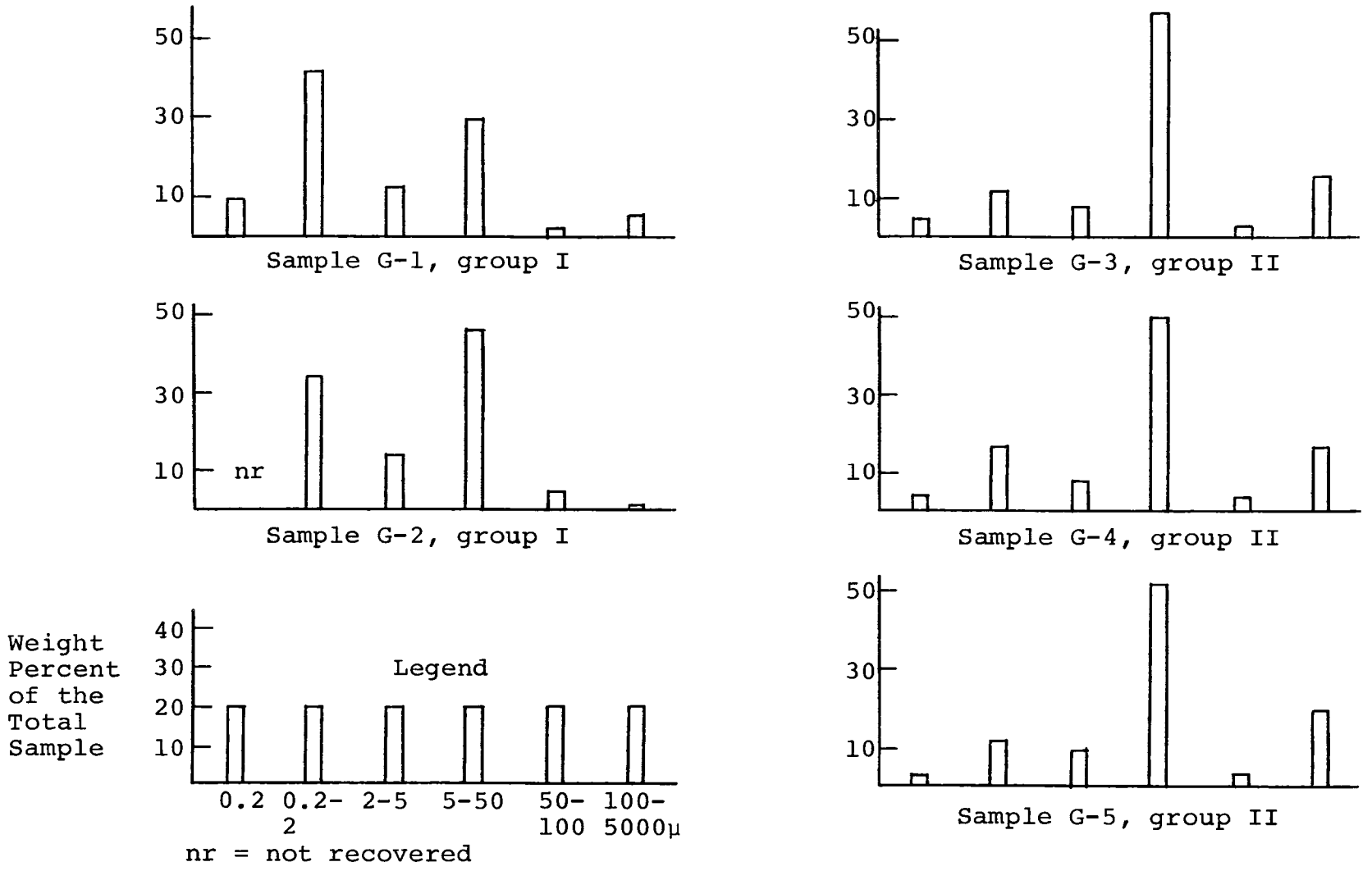


Figure 2. Particle size composition of the five samples.

The <0.2μ fraction of sample G-2 was not recovered. Sufficient quantities of the other <0.2μ fractions were recovered for weighing and x-ray analysis; however, chemical analyses were made only on the <0.2μ fraction of sample G-4.

Mineralogy

X-ray diffraction shows that the dominate minerals in the soils are quartz, 7A clay, 10A clay, and a 14A clay. Positive identification of the 14A clay has not been made; however, it can be characterized by its reaction to various treatments. Without any chemical treatment, the 14A clay has a basal spacing of about 14.15A (Figure 3a). Typically, no expansion is observed following ethylene glycol treatment (Figure 3b). Diffractograms made of the clay following heating at 375°C for 12 hours show a broad peak from about 10 to 14A (Figure 3c). The nonexpansible and partially collapsible nature of this 14A mineral is suggestive of a species intermediate between vermiculite and chlorite. A number of well-known clay workers (Dixon and Jackson, 1962; Rich and Obershain, 1955; and Tamura, 1958) have discussed the probability that acidic weathering conditions introduce some form of hydrated aluminum into the interlayer position of 14A soil clays. This interlayer material is thought to interfere with the normal expansion and collapse of 14A clays.

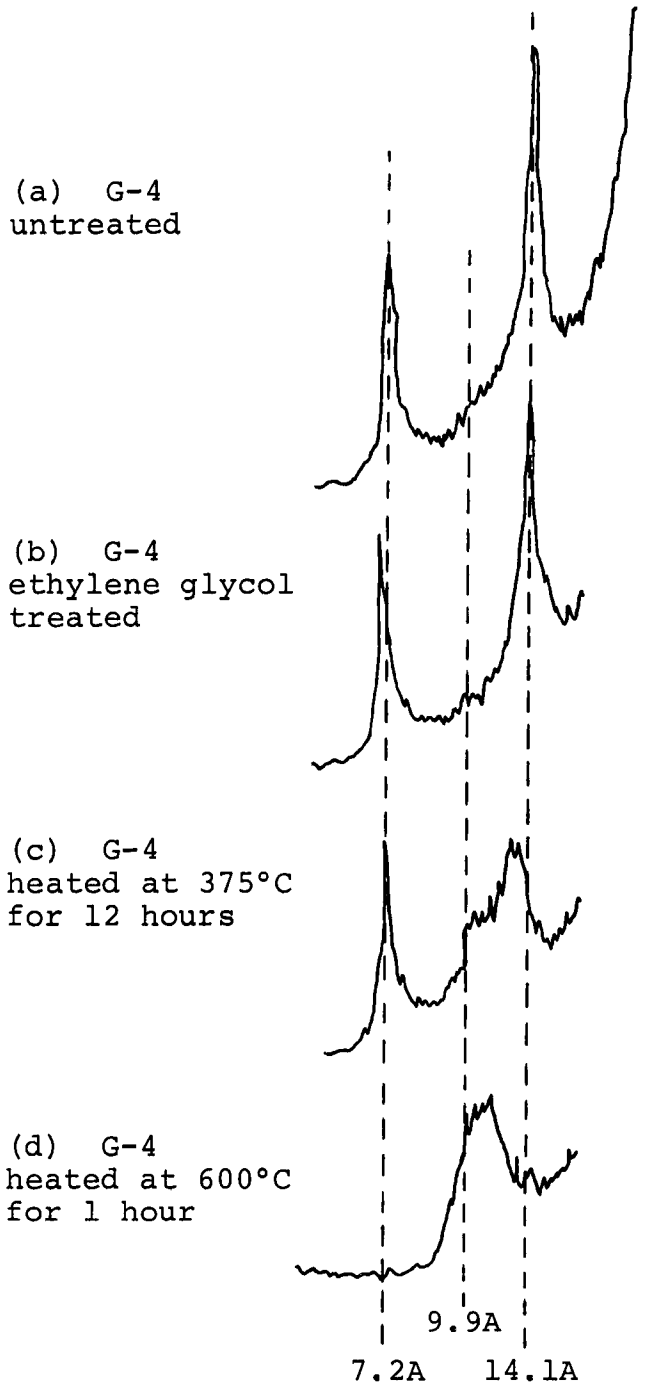


Figure 3. Diffractograms of the 14A mineral.

In an effort to remove interlayer metal from the clays, free oxides were extracted with sodium dithionite. Heating at 375°C for 12 hours and glycolation of the dithionite-treated clays produced samples having x-ray diffractograms very nearly identical to those of untreated samples. That is, there was no expansion upon glycolation and a broad peak between 10 and 14A was observed after heating.

Saturation of the 14A clay with potassium by the rather drastic method of boiling the dithionite treated sample in KOH + KCl for 3 hours followed by room temperature treatment with KOH + KCl for two days produced the same range of basal spacings as did heat treatment.

As the above treatments failed to produce an expansion or complete collapse to 10A of the basal spacing, the dithionite-treated samples were boiled in normal sodium citrate (pH 7.5) for three hours. The citrate solution was changed every hour. This method has been reported to remove aluminum from some soils and thus allow expansion (upon glycolation) of some 14A clays (Tamura, 1958). Clay fractions of sample G-4 treated by this process show a peak shift from 14 to 12.9A (Figure 4b). Glycolation of this material results in a peak shift back to 14A. This 14A peak has a low angle plateau extending from about 14 to 17.3A. It therefore seems that sodium citrate treatment reduces the basal spacing of this 14A mineral by removing interlayer

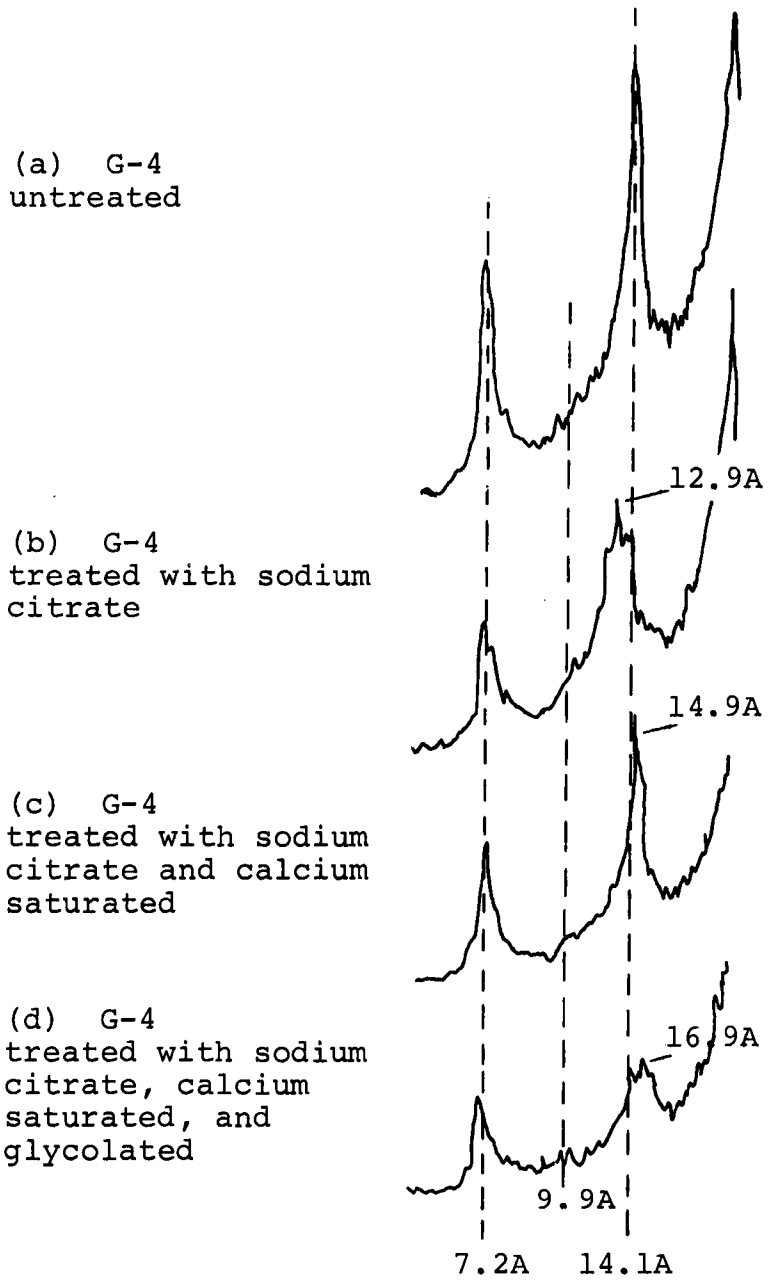


Figure 4. Peak shifts of the 14A clay induced by sodium citrate, calcium saturation, and glycolation.

material (probably hydrated aluminum). Furthermore, removal of this material allows enough expansion to produce a 14 to 17.3A plateau. It is not known if this plateau results from the expansion of a mineralogically distinct component of the original (before citrate treatment) 14A material or if the plateau is due to partial expansion of a basically homogeneous material from which interlayer material has been removed in varying amounts.

Saturation of the 14A material with calcium prior to any chemical treatment results in a broad asymmetrical peak which has a maximum height at 14.4A and tapers gradually to about 10A. Saturation with calcium after sodium dithionite treatment and sodium citrate boiling results in a peak shift from 12.9 to 14.9A (Figure 4c, page 20). This sharp and symmetrical 14.9A peak shifts to a broader less symmetrical peak centering at 16.9A when glycolated (Figure 4d, page 20).

Because the purpose of studying this 14A material was to provide support for ideas regarding clay genesis and trace metal retention rather than to provide a positive mineral identification, further investigation was not made. Although no name is offered, this material may be characterized by the following summary:

1. In its natural state, it has a sharp symmetrical 14.15A peak.

2. Well-crystallized samples of this material in its natural state do not expand upon glycolation.
3. Attempts to collapse the interlayer position by heating and potassium saturation result in a broad peak between 10 and 14A. This behavior indicates varying degrees of collapse upon treatment and suggests that the composition of the interlayer position is not uniform.
4. Treatment of sodium dithionite-treated samples with sodium citrate, a procedure reported to remove aluminum from clays (Tamura, 1958), results in a basal spacing collapse to 12.9A. This indicates that interlayer material has been removed and suggests that this material is aluminum. It is not known if the 12.9A peak represents complete removal of interlayer aluminum.
5. Saturation of the sodium citrate-treated sample with calcium results in a peak shift from 12.9 to 14.9A. This 14.9A peak is sharp and symmetrical. It seems that a combination of sodium dithionite, sodium citrate, and calcium treatments results in the replacement of original interlayer material with calcium.

6. Glycolation shows that this calcium saturated material is at least partially expansible.
7. Whether this 14A material is modified vermiculite or smectite or an interstratified combination of several clay minerals is unknown. Regardless of its name, it seems to be modified by interlayer material. The author suggests that the nature of this clay could be further investigated by removing interlayer material which interferes with collapse and expansion by treating samples with sodium citrate and then saturating them with various ions. Observation of the character of the peak shifts produced by glycolation and heating in uniformly saturated material prepared by the above method should yield information regarding the nature of this material because the uncertainty due to non-uniform interlayer composition will have been minimized.

During the course of mineral identification, several diffractograms were made of bulk soil samples and it became obvious that clay mineral identification from bulk soil samples was difficult at best. Fractionation of the samples into size groups facilitated clay mineral study by concentrating clay minerals and resulted in much stronger clay mineral peaks than were obtained from bulk samples (Figure 5).

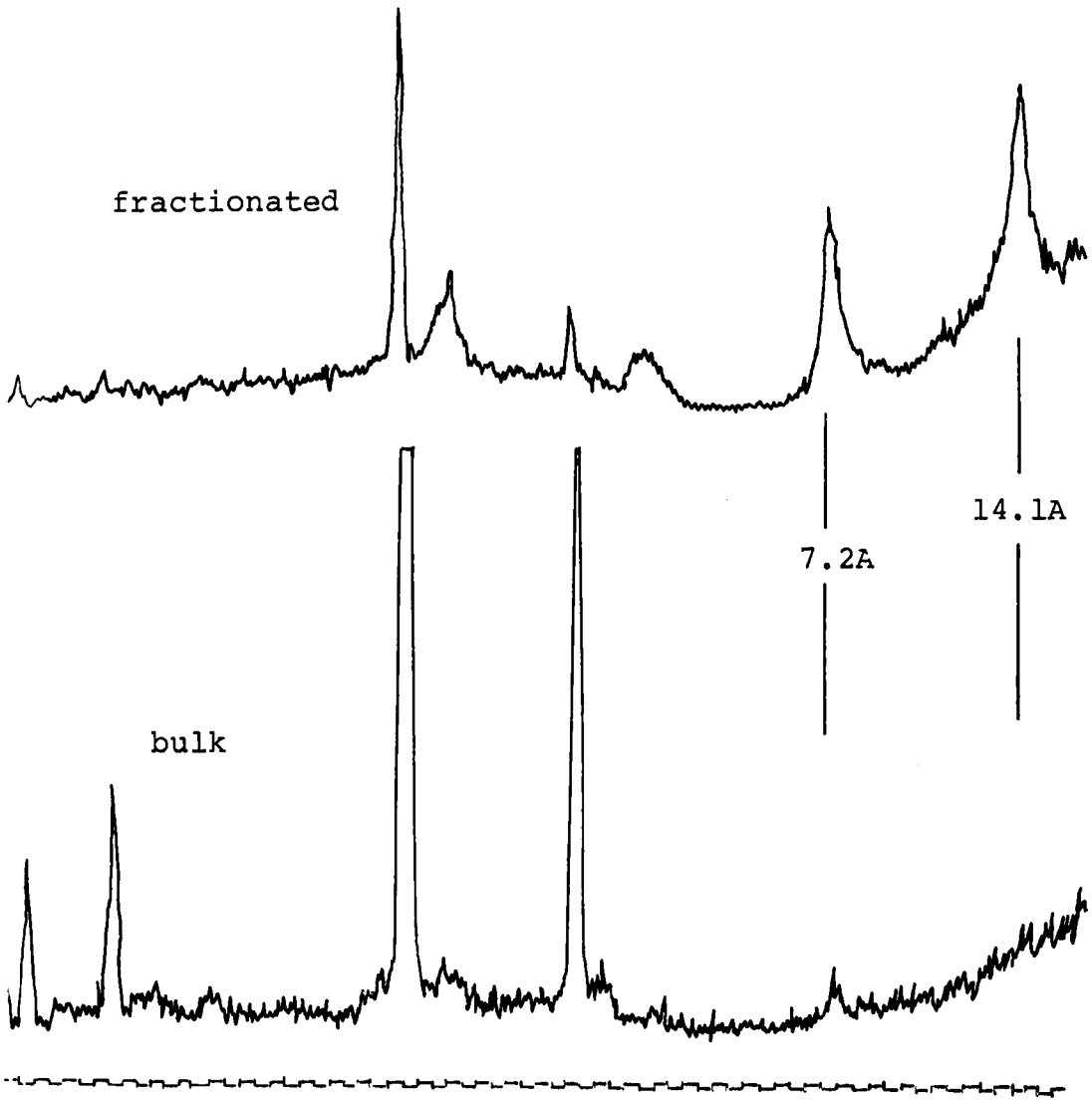


Figure 5. Clay peak comparison between bulk and size-fractionated samples.

The following are general observations which can be made from diffractograms of different size fractions:

1. The major mineral component of the >5μ portion of all samples is quartz (Figure 6a, b, and c; Figure 7a, b, and c).
2. The 100 - 5000μ fraction of samples G-3, G-4, and G-5 contains hematite; whereas, this fraction of samples G-1 and G-2 does not (Figure 7a; Figure 6a).
3. With the exception of the 5 - 50μ fraction of G-1, detectable concentrations of clay minerals are restricted to the <5μ portion of all samples.
4. The clay mineralogies of the five samples were sufficiently different to provide a basis for dividing the samples into two groups.
   a. The fine fractions of samples G-1 and G-2 produce diffractograms showing intense 7A peaks, moderate to weak 10A peaks, and weak 14A peaks (Figure 6e and f).
   b. Diffractograms of the fine fractions of samples G-3, G-4, and G-5 shows intense 14A and 7A peaks (Figure 7e and f). Samples G-4 and G-5 show no 10A peak, and G-3 shows only a very weak 10A peak.

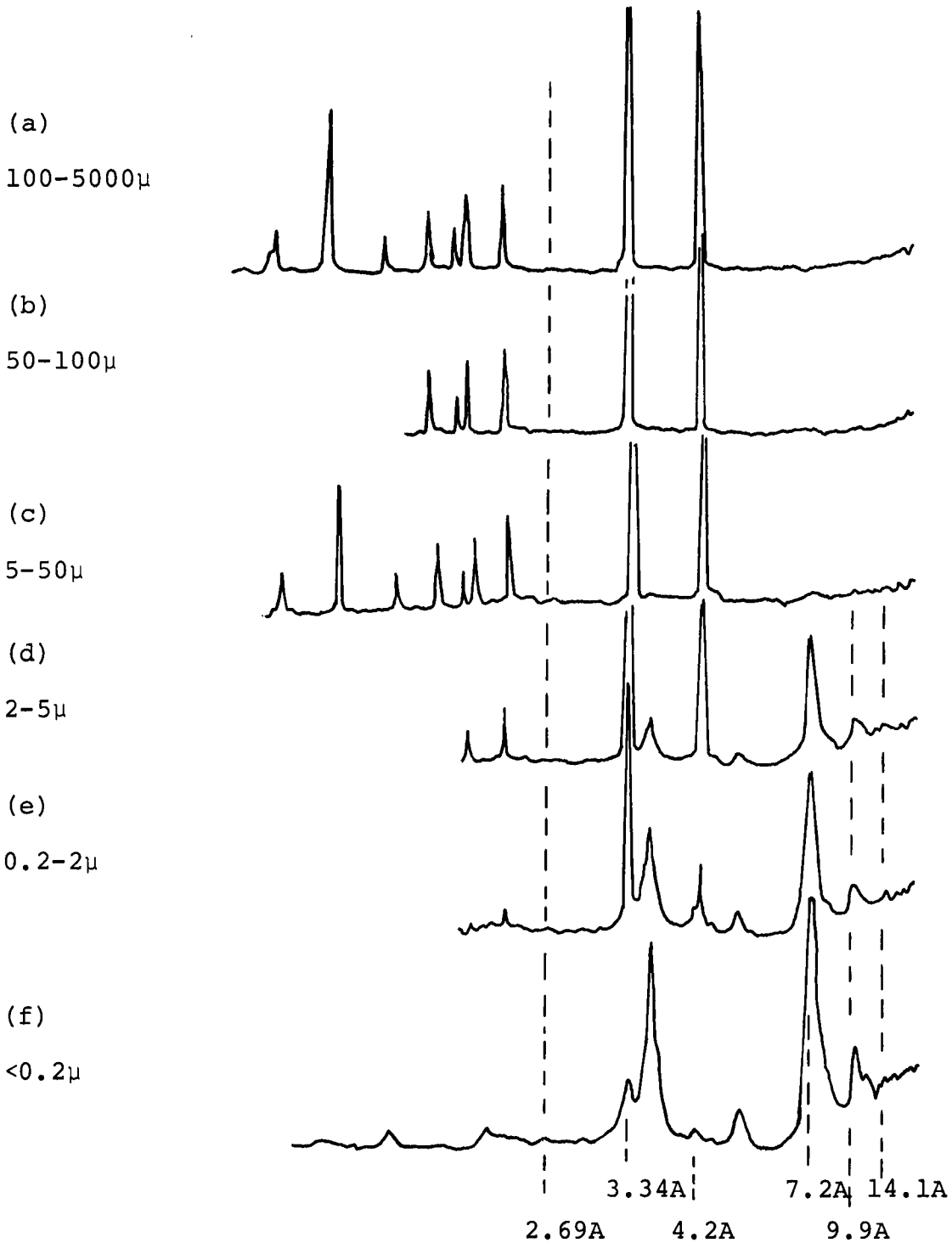


Figure 6. Diffractograms of the size fractions of sample G-1.

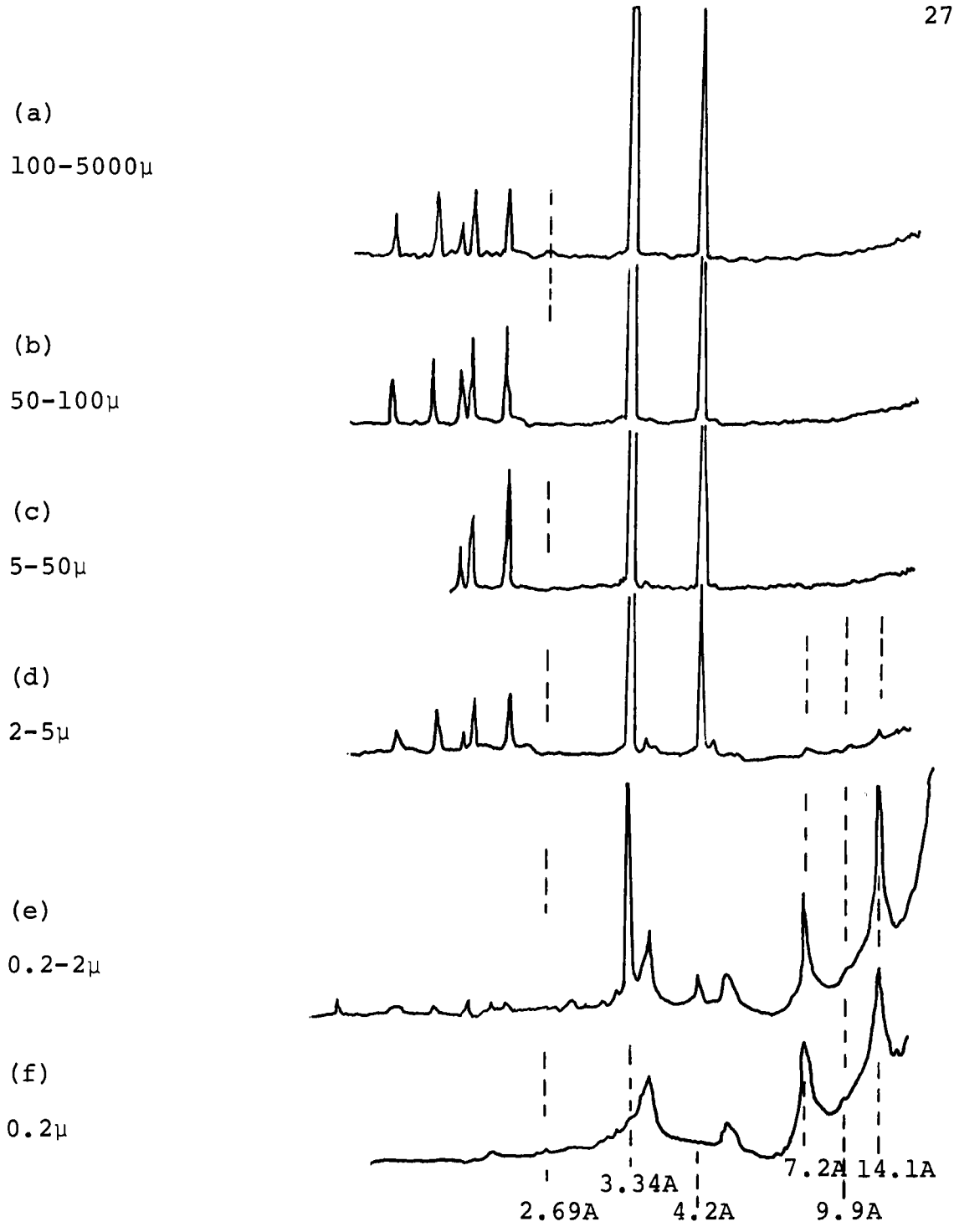
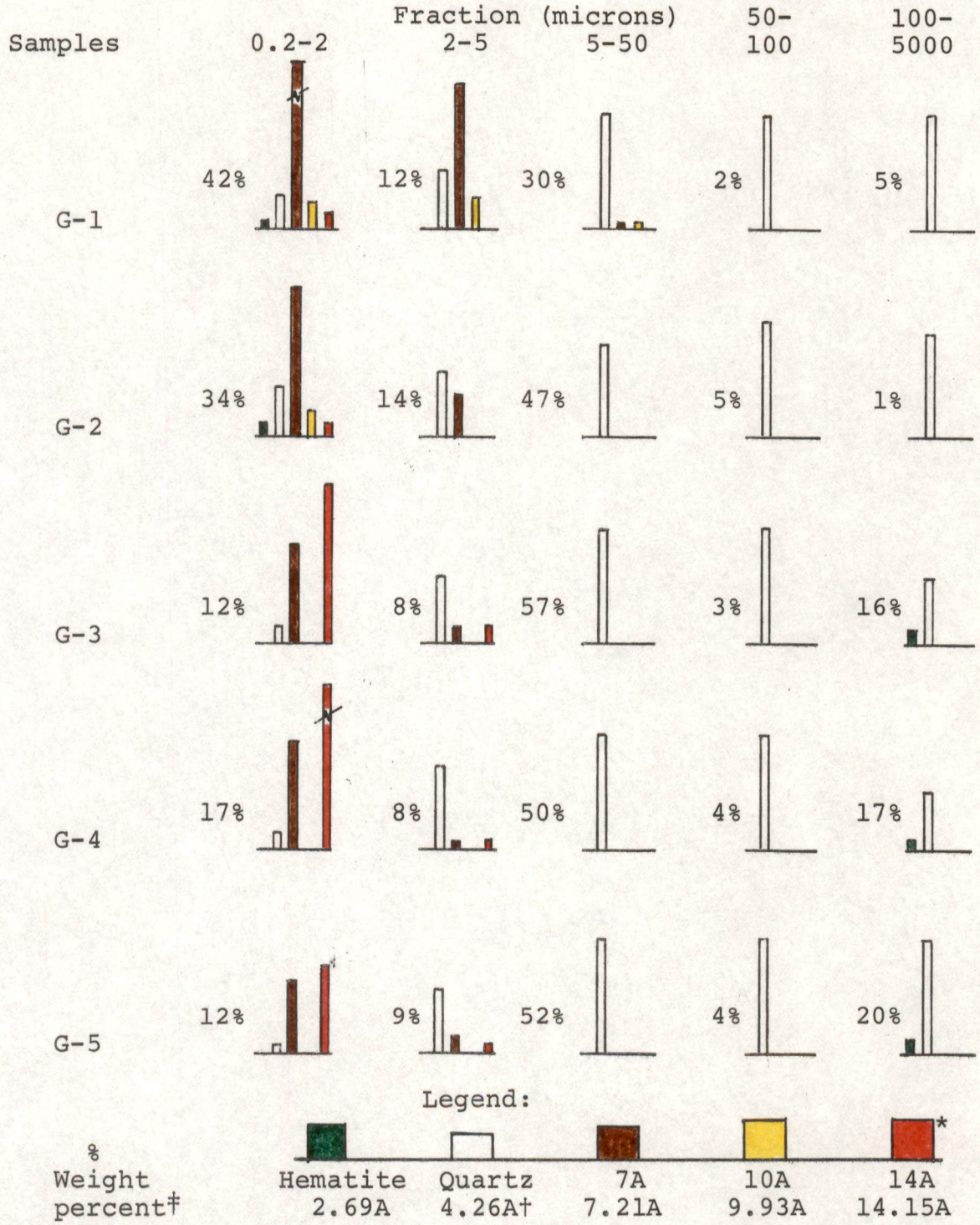


Figure 7. Diffractograms of the size fractions of sample G-4.

The information contained in observations 2 and 4 acquires special significance when it is compared to data in Table 1, page 15, and Figure 2, page 16. Comparison of these data show that group I and group II soils have distinctive mineralogies as well as distinctive particle size distributions. Group II soils have a low content of clay-size particles and show strong 14A peaks; whereas, group I soils have a high clay-size content and show peak 14A peaks. It is also notable that those samples characterized by strong 14A peaks have weak (G-3) or absent (G-4 and G-5) 10A peaks. In the following section, an explanation will be given for this 10A - 14A relationship and special significance regarding 14A clay genesis will be given to the 10A content of sample G-3.

Figure 8 shows the relationship between particle size distribution and mineralogy. The percentage of the total sample weight contributed by the particular fraction of the sample is shown at the left of each histogram. The bars of each histogram represent the area under certain peaks associated with various minerals as shown in the legend. All minerals are represented by their most intense peak except quartz. Quartz is represented by its 4.26A peak rather than its 3.34A peak because the 3.34A peak was allowed to run off the diffraction chart of many samples. The 4.26A peak areas are multiplied by 3 to approximate the 3.34A peak.



*Bar heights represent peak areas from diffractograms
†multiplied by three to approximate the 3.34A quartz peak
‡weight percent determined by mechanical analyses

Figure 8. Weight percent and mineralogy of sample fractions.

The histograms are designed to represent the variation of mineralogy within a sample, the variation in mineralogy between fractions of different samples, and the relationships between particle size distribution and mineralogy.

Chemical Analyses

Several important factors regarding the reliability of analytical data must be considered.

1. Analytical precision of the atomic absorption unit used was within 5%.
2. Sensitivity of the atomic absorption unit varies depending upon the element for which analysis is made. The approximate minimum concentrations (in ppm) detectable in a 0.2g sample (average sample weight) are as follows: Cd, 1.5; Co, 8; Cr, 15; Cu, 5; Fe, 70; Mn, 10; Zn, 4.
3. The variation in results of duplicate total metal analyses on bulk soil samples is typically about 30%. Such large variations are attributed to a lack of sample homogeneity and are significant because they restrict data interpretation to trends of trace metal distribution.

Total metal analyses for Cd, Co, Cr, Cu, Mn, Ni, Fe, and Zn were run on the bulk soil of all five samples (Table 2). Three important observations were made from the results of these bulk analyses.

Table 2. Metal concentrations in bulk soil samples

Sample	ppm Mn	ppm Cd	ppm Co	ppm Cr	ppm Cu	ppm Ni	ppm Zn	percent Fe
G-1	136	Trace	15	430	23	137	286	3.44
G-2	107	Trace	13	396	10	70	186	2.66
G-3	1,150	Trace	17	176	9	54	133	2.58
G-4	2,320	Trace	20	177	16	125	147	2.83
G-5	1,870	Trace	15	93	14	102	112	2.49

1. Zn concentrations were not nearly as high as had been expected.
2. Mn and Cr are the only two elements which show a significant variation in concentration between bulk soils of group I and group II.
3. The total concentration of Co + Cr + Cu + Ni + Zn correlates with the percent of the bulk soil weight composed of <5μ particles (Figure 9).

This third observation is particularly important to those persons who use soil as a guide to bedrock mineralization because it strongly suggests that the concentration of certain metals is related to particle size distribution which is a variable characteristic of a soil. That is, unusually high metal concentrations within certain samples taken on a geochemical soil survey may reflect particle size distribution rather than underlying mineralization.

Total metal analyses for Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn were run on the 0.2 - 2, 2 - 5, 5 - 50, 50 - 100, and 100 - 5000μ fractions of the five samples as well as the <0.2μ fraction of G-4 (Table 3, Figure 10). The following are observations made from 0.2 - 2, 2 - 5, 5 - 50, 50 - 100, and 100 - 5000μ fractions.

1. The highest concentrations of most metals in the group II soils are in the 100 - 5000 and 0.2 - 2μ fractions. An exception is Cu which is not concentrated in the 100 - 5000μ fractions.

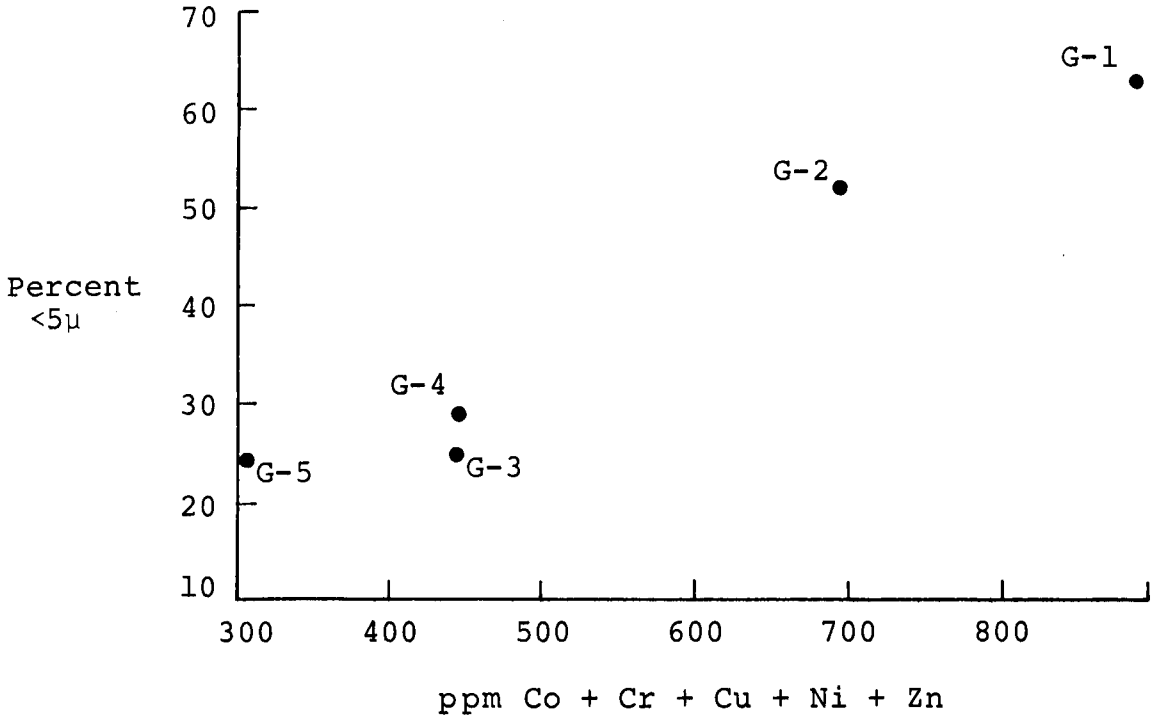


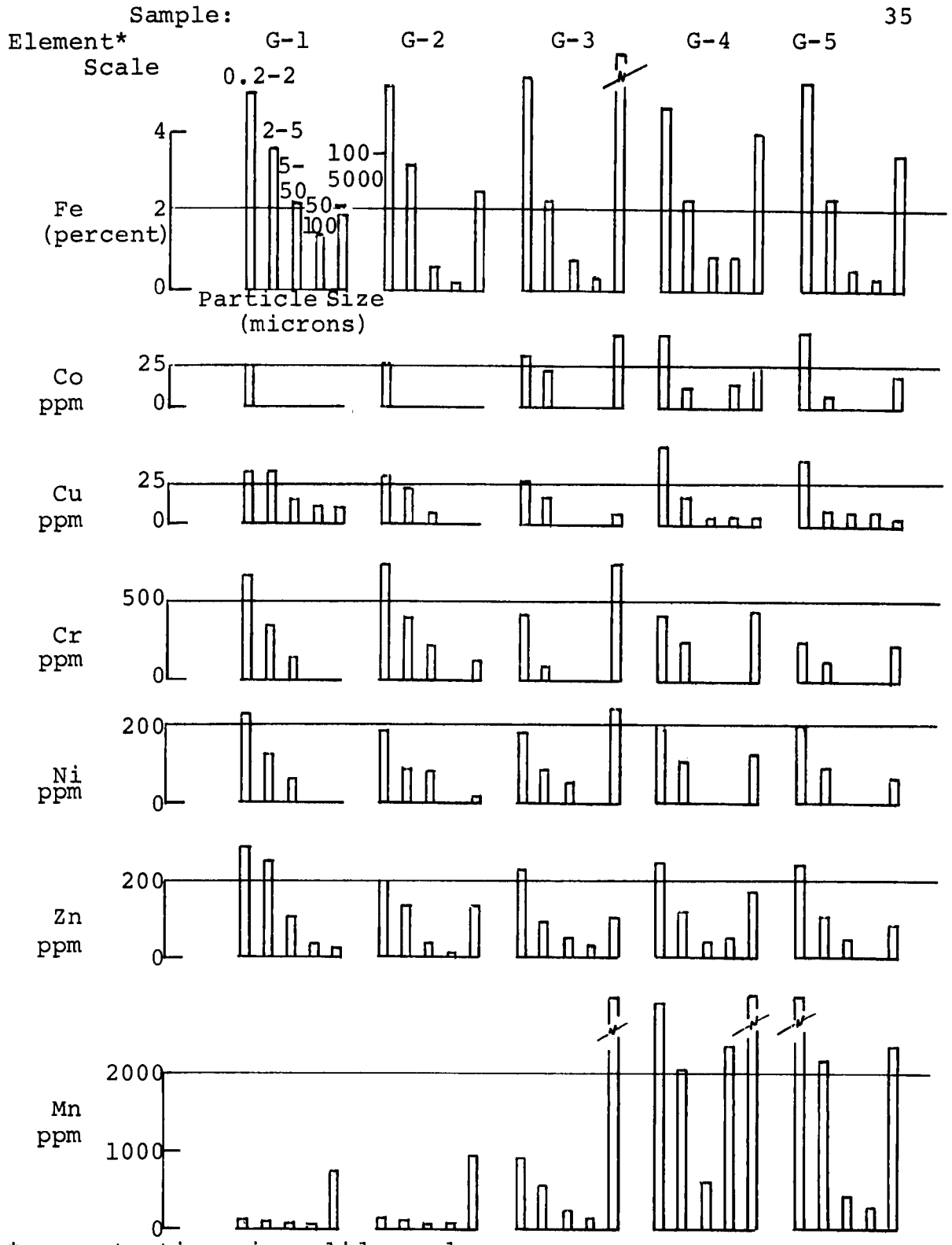
Figure 9. Correlation between the trace metal concentration in bulk samples and the percent of the bulk sample composed of <5μ particles.

Table 3. Total metal analyses of the size fractions

Sample	Fraction (microns)	ppm Mn	ppm Cd	ppm Co	ppm Cr	ppm Cu	ppm Ni	ppm Zn	percent* Fe
G-1	100-5000	768	nd	nd	nd	10	nd	23	1.91
	50-100	74	nd	nd	nd	11	nd	30	1.39
	5-50	75	nd	nd	149	15	60	104	2.24
	2-5	105	nd	nd	346	32	123	254	3.63
	0.2-2	134	1.5	25	689	33	226	292	5.02
G-2	100-5000	824	nd	nd	134	nd	17	134	2.45
	50-100	102	nd	nd	nd	nd	nd	7	0.24
	5-50	56	nd	nd	237	6	79	35	0.59
	2-5	116	nd	nd	400	24	96	137	3.30
	0.2-2	166	2.2	27	772	36	185	202	5.27
G-3	100-5000	4,455	nd	46	831	7	237	101	7.68
	50-100	179	nd	nd	nd	nd	nd	24	0.31
	5-50	256	nd	nd	nd	nd	45	43	0.74
	2-5	561	nd	24	96	16	80	96	2.28
	0.2-2	918	nd	33	436	28	181	234	5.43
G-4	100-5000	3,229	nd	25	460	4	128	174	4.08
	50-100	2,353	nd	15	nd	5	nd	49	0.89
	5-50	593	nd	nd	nd	4	nd	37	0.89
	2-5	2,057	nd	13	244	17	111	119	2.34
	0.2-2	2,916	nd	44	431	55	207	254	4.73
	<0.2	1,355	6.1	24	49	146	97	1,119	6.97
G-5	100-5000	2,355	nd	22	250	4	63	81	3.47
	50-100	305	nd	nd	nd	8	nd	nd	0.28
	5-50	474	nd	nd	nd	8	nd	46	0.61
	2-5	2,150	nd	7	132	10	89	107	2.43
	0.2-2	3,477	nd	52	258	43	197	238	5.24

*concentrations in solid sample.

nd = not detected.



*concentrations in solid sample
Legend: see upper left histogram

Figure 10. Distribution of metals with size fractions.

2. The highest concentration of most metals in group I soils is found in the 0.2 - 2μ fractions. An exception is Mn which is more concentrated in the coarse fraction than in the fine fraction.

Observations 1 and 2 are important for two reasons. First, they show that there is a basic difference in the distribution of metals between group I and group II soils. That is, high concentrations of metals are found in the coarse fraction of group II soils and not in the coarse fraction of group I soils. Secondly, they show that high concentrations of metals may or may not correlate with the presence of clay minerals. This is true because the 0.2 - 2μ fractions contain clay minerals (Figure 8, page 29) as well as high metal concentrations; whereas, the 100 - 5000μ fractions of group II soils contain high concentrations of metals but have no detectable clay content (Figure 8, page 29).

Other observations which may be made from Table 3, page 34, and Figure 10 follow:

3. Metal concentrations are low in the 5 - 50 and 50 - 100μ fractions (quartz fractions).
4. Because only one <0.2μ fraction was analyzed (sample G-4), no metal trends within this colloidal size fraction can be established; however, data suggest that Cu, Fe, and Zn are more highly concentrated in this fraction; whereas, Co, Cr, Mn, and Ni are less concentrated than in the 0.2 - 2μ fraction.

5. In the particle range of 0.2μ to 100μ, metal concentration increases with decreasing particle size.

Observation 5 is important because it suggests that the mechanism (or mechanisms) through which metals are retained by soil particles operates to a greater degree in smaller particles than in coarse particles. It is notable, however, that this generality does not hold true for the coarsest fraction of group II soils. In a following section, it will be suggested that increased surface area of smaller particles and adsorption at sites of electrical imbalance on clay mineral surfaces may be oversimplifications of such mechanisms.

Still more observations can be made from Table 3, page 34, and Figure 10, page 35. They include:

6. Metal concentrations in the fine fractions show that the distribution of some metals correlates with differences in soil type. The fine fractions of group II soils have higher concentrations of Co and Mn than do the fine fractions of group I; whereas, Cr has significantly higher concentrations in the fine fraction of group I soils.
7. Fe, Ni, and Zn do not show significant variations in concentration between the fine fractions of group I and group II.

Observation 7 is particularly important because it shows that the concentrations of Fe, Ni, and Zn do not correlate with the differences in clay mineralogy observed within the fine fractions of the soils studied. This suggests that the type of phyllosilicate clay present is not a major controlling factor in the distribution of certain metals.

To summarize briefly, those observations which are considered important to the problem of metal retention in soils will be reviewed. Metals are highly concentrated in those soil fractions which contain clay minerals; however, clay minerals are not essential to the retention of most metals studied. Phyllosilicate clay type does not seem to be the dominate factor controlling trace metal concentration.

The next section will discuss trace metals, soil components, and their relationship to each other; however, a final observation and the results of two experiments must first be presented.

8. High concentrations of Co, Cr, Ni, and Zn correlate with high concentrations of Fe (Table 3, page 34; Figure 10, page 35).

Because of the correlation between Fe and certain trace metals, it was deemed desirable to know if the Fe is in the form of an oxide. Oxides of Fe and Mn have been credited with the ability to retain relatively high concentrations of

trace metals (Hawkes and Webb, 1962, p. 121) and thus provide a possible explanation for the distribution of trace metals within these soils. Extraction of the oxides from bulk soil samples by reduction with sodium dithionite yielded the analytical data in Table 4. From this table it is obvious that most of the Fe and Mn is in a form extractable with the sodium dithionite procedure.

Analyses for trace metals in the extract solution and in the solid residue remaining after extraction were also made; however, duplicate extractions and analyses indicate poor reproducibility. The behavior of Cr and Ni during the dithionite treatment is not understood because the amount of Cr or Ni extracted plus that remaining in the residue is typically much less than the total concentrations indicated by total metal analysis. An explanation for this is presented on page 54.

Co and Cu are present in such low concentrations in the bulk soils that the ppm extracted or the ppm remaining in the residue may be below the limit of detection. Lack of sample homogeneity is another factor which causes inconsistent results especially for elements such as Co and Cu which are present in low concentrations. Typically, the ppm Co or Cu extracted plus that remaining in the residue deviates from the total metal value by ±3 to 15 ppm. In some cases this deviation represents as much as 50% of

Table 4. Fe, Mn, and Zn extracted by oxide reduction

Element	Sample	Total ppm*	ppm not extracted†	ppm extracted°	Percent extracted**
Fe	G-1	34,400	5,600	28,200	84%
	G-2	26,600	4,750	24,100	82%
	G-3	25,800	6,850	17,000	73%
	G-4	28,300	12,500	20,400	56%
	G-5	24,900	7,400	15,600	70%
Mn	G-1	136	16	91	88%
	G-2	107	16	85	85%
	G-3	1,150	83	780	93%
	G-4	2,320	180	3,480	92%
	G-5	1,870	200	1,150	89%
Zn	G-1	286	155	na	47%
	G-2	186	75	na	60%
	G-3	133	117	na	12%
	G-4	147	140	na	5%
	G-5	112	66	na	41%

*Concentration in bulk soil (from total metal analyses).

†Concentration remaining in solid residue of bulk soil after oxides have been reduced and the dissolved metal removed.

°Ppm of the bulk soil dissolved by the reducing solution.

**Based on the difference between ppm not extracted and total ppm (from total metal analyses).

na = not analyzed because standard sodium dithionite solutions produce Zn signals by atomic absorption spectroscopy.

the total metal value. If ppm extracted plus ppm remaining in the residue is used as the total metal value rather than the total metal value determined by total metal analysis, the effect caused by a lack of sample homogeneity is eliminated. This is because calculations of the percent extracted are based on one aliquot of a sample rather than two. Using this method, about 20% of the total Cu and about 10% of the total Co were extracted by dithionite from group I soils. No Cu was extracted from group II soils. About 50% of the Co was extracted from group II soils.

Equilibration of the bulk soil samples with 1N neutral ammonium acetate produced very little detectable exchange between ammonium in solution and the trace metals studied. Zn was the only metal detected in solution after equilibration. Exchangeable Zn comprises less than 0.25% of the total Zn in each of the five samples. Ideally, ions held to clay surfaces by simple adsorption would be largely replaced by ammonium in such an experiment. That the trace metals did not exchange with ammonium may indicate that they are not retained by simple adsorption; however, the results of this experiment are questionable because the ability of ammonium to replace trace amounts of the metals studied is not known.

IV. DISCUSSION OF RESULTS

General Soil Characteristics

The differences in particle size distribution, mineralogy and metal distribution observed between soils of group I and group II may be at least partially explained as a function of the degree of weathering to which these soils have been subjected. Clay-size particles seem to have been removed from group II soils leaving behind a silty soil containing concentrations of Fe and Mn oxides. Fe and Mn oxides have a low mobility (Hawkes and Webb, 1962, pp. 367, 369) and tend to become concentrated in the 100 - 5000μ fraction of group II soils. It was observed that these oxides act as a cement, binding quartz grains together. High concentrations of most trace metals studied within the coarse fraction of group II soils may possibly be attributed to retention within these oxide concentrations. Therefore, it seems that the weathering process results in a bimodal distribution (Figure 10, page 35) of most metals by creating a concentration of metals in the coarse fraction of well-weathered soils (group II).

Experiments performed by Mortland et al (1956) show that biotite (a 10A phyllosilicate) may be converted to a 14A clay mineral (vermiculite) by depotassification of the 10A mineral. Removal of interlayer potassium was accomplished by growing plants in biotite which contained no exchangeable potassium. From these experiments, it seems that interlayer potassium, which is not usually considered exchangeable, may be removed from 10A minerals when the ratio of "demand" for potassium to exchangeable potassium becomes high enough. The abundance of 14A clay and the absence of 10A clay in group II soils could be a result of potassium removal by leaching and depotassification of 10A clays with the resulting formation of 14A clays. Further support for this argument is found in a soil study done by Miller (1972).

In an extensive study of soils formed from carbonate rocks in Tennessee, Miller reaches the following conclusions regarding the clay mineral soil components:

1. Kaolinite is the major clay mineral in the soils. It is, however, only a minor constituent of the carbonate rock.
2. Kaolinite is forming in the soils.
3. The major clay component of the carbonate rock is 10A clay.

4. The 10A clay content of the soil decreases upward with increasing distance from the parent rock.
5. Soil vermiculite increases in abundance as 10A clay decreases in abundance (in vertical profile).
6. Soil vermiculite forms from the weathering of 10A clay.

As stated in a preceding section, the identity of the 14A mineral studied in this research is not known. It is referred to simply as the 14A mineral. Miller refers to a similar 14A mineral as soil vericulite. On the following pages the term soil vermiculite will be used in reference to Miller's work, and 14A will be used in reference to the mineral studied in this research.

Miller postulates weathering of 10A clay to soil vermiculite by the partial replacement of potassium in the 10A clays by calcium and magnesium. This replacement results in an interstratified intermediate product characterized by a broad diffracton plateau in the 10 to 14A region. This interstratified clay is typically found in the mid-B horizon between soil vermiculite in the surface soils and 10A clays near bedrock. An expansible component is often detected within the interstratified clay. Potassium saturation of this intermediate product results in a more thorough collapse to 10A than does potassium saturation of the end product,

soil vermiculite. This suggests that the intermediate product is gradational between the two end members. Soil vermiculite is formed from this interstratified material by replacing interlayer ions with aluminum-hydroxy interlayers. Miller's end product, soil vermiculite, has the same diffraction characteristics and the same reactions to heat and ethylene glycol treatment as does the 14A material found in samples G-4 and G-5.

Support for the process of 10 to 14A conversion is found by examining the fine fractions of sample G-3 which show characteristics of the intermediate product described by Miller. Sample G-3, although generally similar to G-4 and G-5 in mineralogy and particle size distribution, is somewhat atypical for several reasons. First, it is characterized by a weak 10A peak (Figure 11a). Secondly, the 14A peak tends to expand somewhat upon glycolation (Figure 11b). Glycolation produces a low angle plateau extending from the 14A peak to about 17A. Perhaps the most significant relationship which can be observed from G-3 is the broadness of the "10A" peak of the <0.2μ fraction (Figure 11c) which may indicate basal spacings in varying degrees of expansion.

Field observations show that group I samples are definitely B horizon soils. They contain 7, 10, and 14A clays. It might be suggested that the 14A component of group I soils is derived from the overlying horizon (group II) by an eluviation-illuviation process. Miller, however,

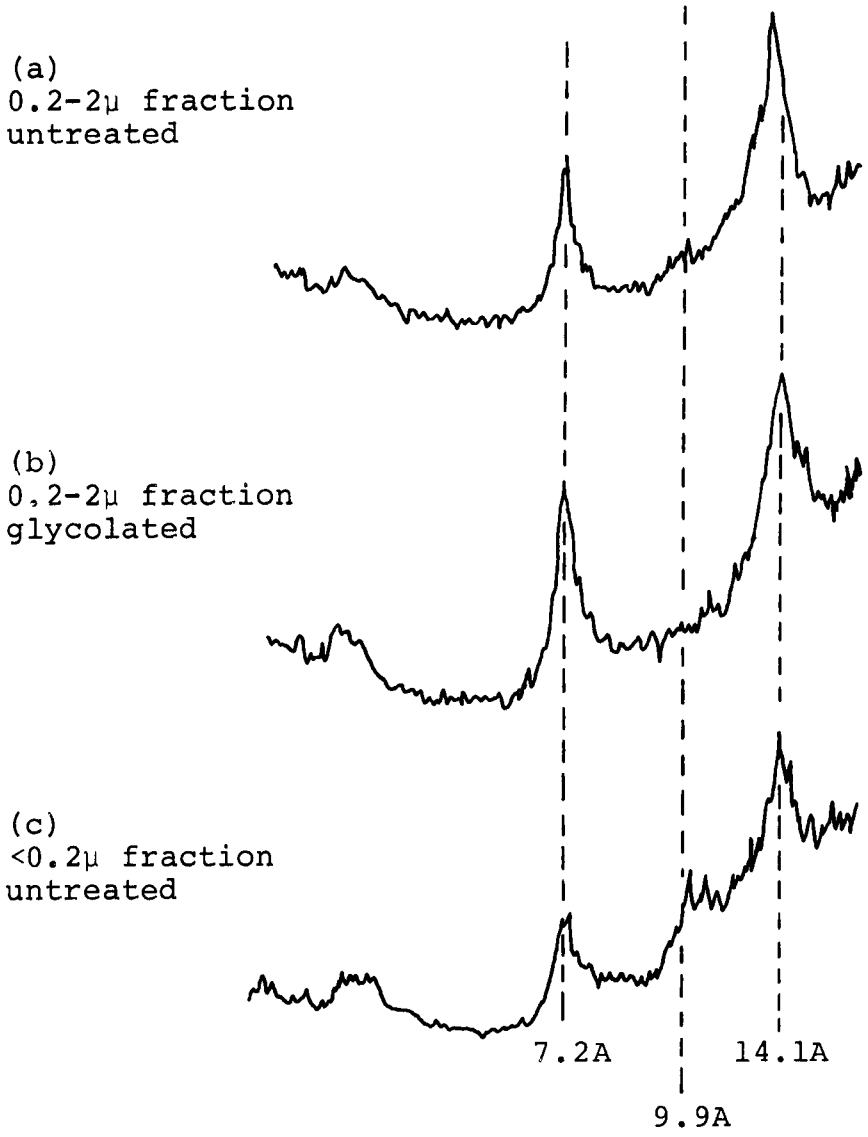


Figure 11. Diffraction peak characteristics of the clay fractions of sample G-3.

traced 10A peak symmetry vertically from bedrock to surface horizons and found that the symmetry of this peak decreases vertically upward and that the peak is absent or very weak in surface samples (Miller, 1972, p. 152). This decrease in symmetry, of course, correlates with the already mentioned increase in soil vermiculite. It seems, therefore, that the presence of both 10 and 14A clays in group I soils may reflect incomplete conversion of 10A clays to 14A clays. This incomplete conversion can be attributed to less intense weathering of group I soils (B horizon).

Trace Metal Retention

Because group II soils contain an abundance of 14A clays, it might be expected that the clay-size fractions of these soils would contain higher trace metal concentrations than the clay-size fractions of group I soils which contain primarily 10 and 7A clays. The high cation exchange capacity usually assigned to 14A clays could be expected to account for this greater concentration. Cu and Co do, in fact, show some correlation between concentration and the presence of phyllosilicate minerals. The following observations which may be obtained from Figure 8, page 29, and Figure 10, page 35, are suggestive of a clay mineral-trace metal relationship:

1. In clay- and fine silt-size fractions, Co concentrations are high only if 14A clays are present. Co is somewhat more highly concentrated in those clay- and silt-size fractions which produce strong 14A peaks by x-ray diffraction. It is notable, however, that Co is also highly concentrated in the coarse fractions of group II soils and that these fractions contain no detectable concentrations of clay minerals.
2. Cu is concentrated only in those fractions which produce strong clay mineral peaks. Cu is somewhat atypical inasmuch as it is the only trace metal studied which is not concentrated in the coarse fraction of group II soils. Hawks and Webb (1962, p. 364) rate Cu as very mobile in soils which have a pH of below 5.5. This high mobility may make necessary the presence of some characteristic of clay minerals such as charge imbalance or large surface area before Cu is immobilized in significant quantity. If this is true it would account for the absence of Cu in the coarse fraction of group II soils and for the correlation between Cu concentrations and the presence of strong clay mineral peaks.

Mn is the only metal which shows extremely higher concentrations in the clay fractions of group II than in the clay fractions of group I. Because Mn is more highly concentrated in all fractions of group II soils, Mn concentrations in the clay fractions probably do not so much reflect clay mineral type as they do the low mobility of Mn oxides. Zn and Ni concentrations do not vary significantly with clay mineral type. Because of the consistency of Zn and Ni concentrations in the clay fractions and because most trace metals are as highly concentrated in certain fractions which contain no detectable clay minerals as they are in fractions which contain an abundance of clays, it seems that phyllosilicate type is not a major factor in the retention of certain metals and that clay minerals are not the only soil constituents which influence trace metal retention.

Data presented in this study suggest two reasons why trace metals may not show strong correlations with clay minerals. First, clay charge imbalance may be neutralized by ions which are more abundant and more mobile than are the trace metals. This would have the effect of lowering the affinity of highly charged clays for trace metal ions and thus cause normally highly charged clays to behave similarly to clays having a low charge imbalance. Secondly, trace metal retention may be controlled by soil constituents other than phyllosilicate clays. These nonphyllosilicate constituents could have at least two effects which might

influence the correlation between metals and clay minerals. First, the affinity of these constituents for trace metals may be sufficient to withhold trace metals from the soil solution which might otherwise provide a medium of transport to interlayer clay sites. Secondly, the concentration of trace metal in these nonphyllosilicate constituents may be sufficient to mask variations in metal concentrations due to variations in phyllosilicate clay type. Discussion of these ideas will be presented in two parts.

The Role of Aluminum

It stands to reason that the interlayer position of the 14A soil clay will be occupied primarily by abundant ions which are mobile enough to move into interlayer sites. In acid soils, such an ion is the hydrated aluminum ion which is itself an acid (Black, 1968, p. 285). It has been suggested that in acid soils, hydrated aluminum ions form aluminum-hydroxy polymers in the interlayer position of clays (Jackson, 1963). Such aluminum interlayering would reduce the adsorptive capacity of clays by neutralizing interlayer clay charge imbalance and by blocking the access of ions to interlayer sites of charge imbalance.

That the interlayer position of the 14A clay found in group II soils is occupied by aluminum-hydroxy interlayers is suggested by two observations. First, the basal

spacing of the 14A clay is not uniformly collapsed by heat treatment (Figure 2, page 16). Such behavior has been attributed to "islands" of hydrated aluminum (Rich and Obenshain, 1955; MacEwan, 1950; Dixon and Jackson, 1962). Secondly, treatment of the clays with sodium citrate, a treatment known to remove aluminum from soils (Tamura, 1958), resulted in a basal spacing reduction from 14.15 to 12.9A (sharp symmetrical peak, Figure 4, page 20); whereas calcium saturation of untreated 14A material resulted in a broad peak which indicates only partial replacement of interlayer material. The collapse to 12.9A and the much more thorough saturation of the samples with calcium after treatment are taken as evidence of the removal of interlayer material which prevented collapse and calcium saturation in the untreated samples. That this interlayer material is primarily aluminum is suggested by the previously cited work by Tamura (1958).

Another behavioral aspect of the hydrated aluminum ion which probably influences the adsorptive capacity of clay minerals in these soils is its ability to act as an exchangeable ion on sites of electrical imbalance not located in interlayer positions (Black, 1968, pp. 280-284). The mere abundance of exchangeable aluminum in an acid soil should tend to decrease the probability of a trace metal being adsorbed to clay surfaces. The result of aluminum's

behavior would be to equalize the affinity of various clays for trace metals. That is, a relatively highly charged clay such as vermiculite would have no significantly higher affinity for trace metals than would a relatively uncharged clay such as kaolinite because the charges would be blocked or neutralized by interlayer aluminum and also probably by exchangeable aluminum.

The Role of Oxides

If it is true that the type of phyllosilicate found in these soils does not control trace metal retention and distribution, then other factors should be sought. As already stated, Fe and Mn oxides are thought to retain trace metals (page 38). The mechanism by which metals are bound to or within oxides is not known. Incorporation within oxide crystal lattices, occlusion of ions or microcrystals, and surface sorption have been suggested as possible mechanisms (Hawkes and Webb, 1962, p. 121).

Observations which support the idea that trace metals are associated with oxides within the soils studied are listed below:

1. High concentrations of most trace metals are found in the coarse fraction of group II soils (Figure 10, page 35). This fraction contains no detectable clay minerals. Thus, high trace

metal concentrations may exist independently of clay minerals.

2. The high concentrations of trace metals found in the coarse fraction of group II soils correlate with both high Fe concentrations and the presence of hematite within this fraction (Figure 10, page 35, Figure 7, page 27).
3. A general increase in trace metal concentrations with iron concentration is noted in almost all fractions of all samples (Figure 10).

The above observations leave little doubt that some relationship exists between trace metals and Fe; however, the results of this study do not define the relationship. It is significant that most trace metal concentrations correlate with Fe concentrations and that most of the Fe is in an oxide form but that far from 100% of any trace metal is extracted when oxides are removed. Speculative explanations follows:

1. Trace metals are located in a number of different materials within these soils. This idea is supported by work done by White (1957) from which he concludes that Zn is contained in both oxides and clay minerals. Although it has been pointed out that most trace metals do not show a good correlation with clay mineral

type, it should also be noted that if trace metals are located in several different types of materials, a correlation between trace metal concentration and any one given material might not be discernible. The fact that trace metal concentrations correlate with Fe but that they are not completely extractable with Fe oxides has led to further work on the problem of trace metal retention in both soils and stream sediments, and attempts are being made to isolate the various possible sites of trace metal retention such as clay minerals, oxides, and organic matter.

2. Trace metals are located in oxides, but they are not all in a form which is soluble in sodium dithionite solutions. If trace metals are removed by the sodium dithionite solution as colloids (for example as colloidal-size micro-crystals) rather than by solution, they may not be detected by atomic absorption analysis. This is a possible explanation for the "loss" of Ni and Cr during the dithionite procedure (page 39).

V. SUMMARY

The significant results and conclusions of this research are listed below:

1. Particle size analyses show that two types of soil were sampled. One is clay-rich; the other is silt- and sand-rich.
2. The clay-rich samples are B horizon soils, and the silt- and sand-rich samples are probably lower A horizon samples.
3. Clay-rich samples (B horizon) contain 7, 10, and 14A clays; however, silt- and sand-rich samples (A horizon) typically contain only 7 and 14A clays. A correlation therefore exists between particle size distribution and clay mineralogy.
4. The correlation between particle size distribution and clay mineralogy probably results from a difference in the degree of weathering to which the two soil types have been subjected. More thorough leaching of the A horizon samples may account for their low clay content and for the concentration

of sand and silt, some of which is cemented together by accumulations of relatively immobile Fe and Mn oxides. More intense weathering in the A horizon may also be responsible for the lack of 10A clays within the A horizon.

5. Other studies suggest that 10A clays are converted to 14A clays as they are exposed to more intense weathering conditions, and data reported in this study tend to support this suggestion.
6. The conversion of 10A clays to 14A clays has been reported to involve the replacement of potassium by hydrated aluminum ions. Data indicate that the 14A mineral studied in this research is the end product of this process. Samples which may be intermediate between 10 and 14A were also identified.
7. Although the presence of Cu concentrations correlates with concentrations of clay minerals and Co concentrations show some relationship to 14A clay content, phyllosilicate clay type does not seem to be the controlling factor in the distribution of trace metals within the soils studied.

8. Aluminum interlayering probably reduces the 14A mineral's affinity for other metals, and the association of trace metals with non-phyllosilicate soil constituents may reduce the likelihood of trace metals being adsorbed to phyllosilicates.
9. Clay minerals are not essential for the immobilization of the trace metals studied. Cu is probably an exception to this statement.
10. Most trace metal concentrations correlate with the distribution of Fe, and between 56 and 84% of the Fe is in an oxide form. In well-weathered soils (A horizon), trace metals tend to accumulate in the coarse soil fraction. This coarse fraction contains no detectable concentrations of clay minerals; however, it does produce hematite peaks by x-ray diffraction. Thus, circumstantial evidence suggests that most of the trace metals are at least to some degree associated with oxides, probably both Fe and Mn.
11. Direct evidence of an oxide-trace metal association is not good. Attempts to remove trace metals by dissolving oxides have thus far met with a high degree of inconsistency.

Each of the trace metals studied is partially extractable with the oxides; however, the quantities are variable and the reasons for this are not yet known.

12. If it is true that oxides cause the retention of trace metals, it follows that an increase in surface area probably does not completely explain higher trace metal concentrations in the finer fractions. Increasing trace metal concentrations with decreasing particle size in the range of 0.2 - 100μ might best be explained by an increase in trace metal concentrations with increasing oxide content. In other words, the oxide content may increase with decreasing particle size due to increased surface area, and the increased concentration of trace metals may be a result of this increase in oxide.

13. Particle size distribution, oxide content (possibly), and weathering which seems to modify both particle size and oxide distributions exert controls on trace metal concentrations which may reduce the effectiveness of bulk soil analyses as indicators of underlying mineralization.

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APPENDICES

APPENDIX A

SIZE FRACTIONATION

Discussion and Procedure

Several major technical problems having significant effects upon the distribution of soil particles within the size fractions were encountered. It was immediately obvious that flocculation of the soil particles was causing an inordinate amount of clays to settle in the coarser size fractions during size fractionation. As it was deemed desirable to have an obvious correlation between the size fractions and their mineral content, only a minimal amount of flocculation could be tolerated.

Deflocculating agents were ruled out because their effect on the trace element chemistry of the soil-water system was unknown. Removal of the soluble salts prior to centrifugation by washing was undesirable, because of the number of washings required to produce a deflocculating effect.

Flocculation was overcome by reducing the concentration of soil in the suspension prepared for the first centrifugation to a level which produced no visible flocculation. Supsensions meeting this requirement were centrifuged to

settle >5μ particles, decanted (<5μ particles), resuspended (>5μ particles) a total of three times. If the third supernate was reasonably clear and only a very little material was added to the supernate upon resuspension and centrifugation a fourth time with a deflocculating agent, the soil to water ratio was considered suitable.

The five bulk soil samples were found to vary considerably in the weight of soil which could be supsended in 100 ml of water without visible flocculation. Values ranged from about 0.15 g soil per 100 ml water to about 1.5 g soil per 100 ml water. Samples with a high clay content required lower soil-water ratios.

Despite the above precautions, the 2 - 5 and 5 - 50μ fractions were observed to contain slowly settling material which would remain in suspension longer than the time required to settle the smallest particles theoretically present in these size fractions. These "impurities" could have been the result of imperceptible flocculation or centrifuging error resulting from the low speed and running time necessary to separate the sample at 5 and 2μ. Because of these results, the 2 - 5 and 5 - 50μ fractions were "purified" by gravity settling with the supernates combined with the next lowest size fraction.

The following is the procedure used by the author for size fractionation after the removal of chert fragments greater than 5000μ:

1. Determine the maximum weight of bulk soil which can be dispersed in a given volume of deionized water without flocculation.
2. Prepare a suspension based upon specifications determined in 1 above.
3. Disaggregate soil aggregates by ultrasonification (see comment 17a).
4. Centrifuge at an rpm and time suitable to settle all soil particles >5μ (see comment 17b).
5. Decant and save supernate.
6. Resuspend settled material.
7. Repeat steps 4, 5, and 6 twice (total of three times) using resuspended settled material and saving supernates.
8. After the third repetition, collect and save the settled material (>5μ) for sieving.
9. Combine and centrifuge all supernates at an rpm and time suitable to settle >2μ particles.
10. Make this separation a total of three times. Settled material is the 2 - 5μ soil fraction.
11. Combine and centrifuge the supernates obtained in 8 to effect a separation at 0.2μ.
12. Make this separation a total of three times.
13. Settled material is the 0.2 - 2μ particle fraction.

14. Centrifuge the combined supernates from step 12, and settle the remaining suspended material (see comment 17c).
15. Settled material is the <0.2μ particle fraction.
16. Wet sieve the >5μ fraction through 100μ and 50μ stainless steel sieves to obtain the 100 - 5000, 50 - 100, and 5 - 50μ fractions.
17. Comments on procedure:
    a. The time of ultrasonification will vary depending upon the type of ultrasonifier used, the type of soil, and the results desired. The author ultrasonified all samples for 15 minutes in a Crystal Gallery, Inc., ultrasonic cleaner.
    b. Centrifuge running time and rpm on a horizontal head machine may be calculated with the following equations:

$$T = \frac{(9.1)(10^{14})(1_N R_2/R_1)}{(S)(rpm)^2}$$

where:

T = Time in seconds

R_2 = Maximum radius of the centrifuge in centimeters as measured from the center to the bottom of the suspension.

R_1 = Minimum radius (cm) (measured from the center to the suspension's top).

S = Sedimentation coefficient (Svedberg units).

Sedimentation coefficients may be calculated with the following equation:

$$S = \frac{d^2(Pp - Pm) \times 10^{13}}{18N},$$

where:

S = Sedimentation coefficient (Svedberg units)

d = Particle diameter (cm)

Pp = Particle density (g/cc)

Pm = suspending liquid density (g/cc)

N = viscosity of suspending liquid (poises).

If water is used as the suspending liquid, the sedimentation coefficient equation simplifies to:

$$S = \frac{d^2(Pp - 1)10^{-13}}{0.18}.$$

Examples of the sedimentation coefficients in water for several sizes of particles having a specific gravity of 2.65 follow:

S	Size (μ)
40,000	0.21
4,000,000	2.1
23,000,000	5.0

c. The lower size limit of this last fraction is about 0.01μ below which Brownian motion dominates particle behavior.

APPENDIX B

COMMENTS ON SAMPLE DRYING

Samples were dried from acetone under a heat lamp at about 50°C prior to weighing; however, moisture adsorbed to the weighing bottles necessitated oven drying at 90°C. The coarser fractions were oven dried overnight and the 2 - 5, 0.2 - 2, and <0.2μ fractions were oven dried for three hours.

Comparison of diffractograms from oven dried clays with diffractograms from undried clays indicate that neither the acetone treatment nor the drying temperatures used had a detectable effect upon the clays.

APPENDIX C

TOTAL METAL ANALYSIS

PROCEDURE

1. Place about 0.2 g of sample in a Teflon beaker. Add about 1 ml HNO_3.
2. Heat on sand bath at about 90°C until mixture is pasty.
3. Remove from sand bath and cool for about 5 minutes.
4. Add 5 ml HF and 2 ml $HClO_4$.
5. Heat at about 110°C (sand bath) until fuming strongly (requires several hours).
6. Heat at about 220°C (sand bath) until reactants form a small, viscous, yellow globule.
7. Transfer globule to a pyrex beaker using deionized water and concentrated HCl to wash Teflon beaker.
8. Heat over low flame (do not boil) until volume is less than 10 ml and no precipitant is present.
9. Transfer to 10 ml volumetric flask and bring to volume with deionized water and concentrated HCl.

10. Comment: Use as little concentrated HCl as possible. Several drops added during steps 7 and 9 should prevent precipitation. Experimentation may be required to determine the exact amount because of variations in the material being dissolved. Standards which contain the same amount of each acid used for the samples should be run through the whole procedure.

VITA

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