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DISTRIBUTION AND MODE OF OCCURRENCE
OF ZINC AND LEAD IN GLACIAL SOILS
FROM THE THURMAN AREA, SOUTHEAST ADIRONDACK MOUNTAINS,
NEW YORK.

David R. Cole and Arthur W. Rose*

Earth Science Laboratory, Univ. of Utah Research Inst.
Salt Lake City, Utah

*Dept. of Geosciences, The Pennsylvania State University
University Park, PA

ABSTRACT

The distribution and mode of occurrence of zinc and lead have been examined in glacial soils developed over a complex Precambrian marble - paragneiss terrain in the Adirondack Mountains of New York. Based on distribution within the soil profiles, zinc is enriched in the B₁ horizon of soils sampled over marble and lead is generally enriched in the A horizon, particularly in soils developed over paragneiss. Calculations of contrast using t-values for zinc, lead and cold-extractable heavy metals between anomalous and background soils sampled over marble and paragneiss indicate that the B₁ soil horizon is the most suitable for sampling on a regular basis.

The distribution of zinc and lead among exchangeable, organic, iron-manganese oxides, clay, silt and sand fractions of two anomalous and one background soil indicates that both zinc and lead are tied up principally in iron and manganese oxides. In terms of total contribution to the sample, however, significant proportions of zinc and lead are associated with the clastic fraction, particularly silt-sized grains. Anomalous metal contents in this area of the Adirondacks can be linked with soils rich in weather-resistant calc-silicate phases such as diopside, phlogopite and serpentine, and carbonates derived from marble not farther away than 1.5km.

The processes of weathering and the development of trace element dispersion patterns in glaciated areas are materially different from those of simple residual weathering. In glaciated terrains, residual soils have been stripped away, and in places the soils have been replaced by transported glacial debris of variable composition and permeability. Secondary halos must necessarily be young, and therefore, they are not usually well developed. The movement and removal, or mixing, of soil and rocks by glacial events coupled with the subsequent local dispersion of metals via deep rooted plants and groundwater make interpretations of geochemical data most difficult.

Although residual soils and well-developed drainage systems, traditionally regarded as best suited to geochemical methods are lacking in glaciated terrains, the apparent difficulties have not inhibited some researchers in applying these methods in glacial areas (Govett, 1973). Geochemical methods have been moderately successful in many glaciated areas of the Canadian Shield because of the careful selection and adaptation of well-established sampling and analytical procedures and an understanding of the glacial history. Soil surveys have been used effectively in many areas, such as in Boyle's (1966) work in Cobalt area, Ontario where soil geochemistry outlined areas of Ni-Co-As and Ag-Ni-Co-As mineralization. Emmengen (1957) demonstrated that good surface expression of mineralization in bedrock existed through 9 to 12 meters of overburden at Chibougamau, Quebec. Even in an area of permafrost in the Northwest Territory, Allen and Hornbrook (1970) have reported response to copper mineralization in B horizon arctic soils.

In order for geochemical soil surveys to be successful in complex glaciated terrains, the geochemical behavior of the metals of interest must

be determined prior to detailed grid soil sampling. Specifically, the distribution and mode of occurrence of the target metals within the soil should be established during an orientation survey of the field area of interest. The optimum sampling horizon can be determined by statistical examination of the trace element distributions in soil profiles. Partial-chemical extraction techniques are used to delineate the distribution of metal among the various components of the soil (exchangeable cation fraction, organic fraction, iron and manganese oxide fraction, sand fraction, silt fraction, and clay fraction). Data on the mode of metal occurrence are critical for the selection and design of future analytical techniques to be used in a given survey. In addition, these data can lead to important conclusions concerning the source, transportation and fixation of metal into the soil and the true nature of anomalies.

The Thurman area in the southeast Adirondack Mountains of New York is an ideally suited locale to apply the techniques outlined above that have been used sparingly in geochemical exploration in other glacial terrains. The presence of anomalously high zinc and lead values detected in a reconnaissance soil survey of the area, coupled with the striking similarity of the marble and paragneiss units found at Thurman with those mapped in the Balmat-Edwards Zinc District, northwest Adirondacks, make this area a prime exploration target. This paper will address the following:

- 1) Determination of the distribution of zinc, lead and cold-extractable metal (cxMe) in different soil horizons developed on glacial deposits and quantification of the optimum sampling horizon, and
- 2) Determination of the mode of occurrence of zinc, lead, iron, and manganese in both anomalous and background soils in order to evaluate their behavior in the soil-forming process.

The highland area of northeast New York State known as the Adirondack Mountains is a southeasterly extension of the Grenville Province of the Canadian Shield, and is similar in most respects to the lower Ottawa Valley (Wilson, 1965). The Grenville Province is part of the Grenvillian Orogenic Belt south of the Grenville Front exposed in the eastern Canadian Shield, with prevailing radiometric K/Ar dates of 950 ± 150 m.y. (Wynne-Edwards, 1972). The Precambrian rocks composing the Adirondack mountains have been conveniently subdivided on the basis of topography and lithology into two parts; the Central Highlands which comprise 80 percent of the area, and the Northwest Lowlands, where the Balmat-Edwards Zinc District is located (Isachsen, 1966).

The Thurman study area is located in the southeast portion of the Highlands, within the Johnsburg 7.5 minute Quadrangle and is underlain almost exclusively by rocks of Grenville age (Fig. 1). Geologic mapping of Precambrian terrain located near the Town of Thurman indicates that an interbedded sequence of clastic and carbonate units has been metamorphosed and complexly folded and faulted (Fig. 2). The original sedimentary sequence included impure limestones and dolomites, quartzites, shales and greywackes which were subjected to granulite facies metamorphism and structurally deformed during the Grenvillian Orogeny approximately 0.96 billion years ago. The two dominant lithologies present in the area are calc-silicate marbles which can contain calcite, diopside, serpentine, dolomite, quartz and pyrite, and paragneisses which can contain quartz, plagioclase, hornblende, biotite, microcline, magnetite, sphene and garnet. Original bedding is exhibited by contacts between paragneiss and marble units and by quartz layers within marble. Compositional layering and foliation present in calc-silicate marbles and quartzo-feldspathic

paragneisses may also represent bedding in original sedimentary units.

Structurally, the rocks in the Thurman area have been subjected to at least three phases of deformation. The first period of folding was the most intense and produced isoclinal to tight folds which plunge approximately 20° to the northeast. A second phase of north-plunging, gentle to open folds dominates the structural pattern observed in the area, refolding phase one folds. During the first and second periods of deformation flow folding in both marbles and paragneisses predominated. However, the last period of folding produced open folds and reversals in north-plunging fold traces. Lineations produced during these phases of folding are generally parallel to the axial traces of the folds.

Faulting in the area consists of a post-folding system of north and northeast-trending normal faults. Displacement along these faults is not well known, but is probably on the order of 150 to 600 m. Joints in the Thurman area are well developed, laterally continuous in m and tens of m and do not terminate at lithologic boundaries. The majority of the joints have a near-vertical attitude and each joint set is oriented roughly parallel to one of the major fold axes, NE-SW, N-S, and NW-SE. Sheeting joints are also present with attitudes near that of bedding or foliation.

The Thurman area was completely glaciated during the Wisconsin Stage of Pleistocene continental glaciation (Miller, 1914; Boyle et al., 1975). Based on glacial striae, boulder trains, drumlins and eskers, Miller (1914), Chadwick (1928) and Buddington and Leonard (1962) all concluded that the direction of ice movement in this area of the Adirondacks was to the south.

The glacial deposits observed in the Thurman area can be classified as glacial drift, which may be divided into two main groups based on

sedimentological character (Nichol and Bjorklund, 1973). The first group, which is the more extensive of the two in the area, is till, a nonstratified, unsorted to poorly sorted material transported and deposited by the glacier (Nichol and Bjorklund, 1973). The second group is stratified drift, composed of stratified and sorted material, deposited by glacial melt water adjacent to or beyond the ice front (Nichol and Bjorklund, 1973). Stratified drift was observed at two profile pit localities (#1 and #8) which characteristically contained layers of dark minerals or pebble-size fragments in the C soil horizon. Elsewhere in the area, till consists of a heterogeneous mixture of various particles ranging in size from fine sand to boulders.

In the Thurman area, two large prongs of glacial drift extend into the map area from the north, occupying weathered or scoured troughs in the carbonate units that underlie these deposits. Based on measured sequences of drift, the minimum thickness of glacial drift in these two troughs is between 18 and 25 m. The thickness of drift in areas of well-exposed outcrops is probably on the order of 1.5 to 3 m. Bedrock was commonly encountered during the course of the profile sampling over well-exposed areas, and no pits were dug that exceeded 1.2 m.

In glaciated areas problems arise in the interpretation of geochemical data because of glacial transport and mixing (Hawkes and Webb, 1962). Much evidence suggests that the bulk of material moved by ice rarely travels more than one or two miles (Hawkes and Webb, 1962; Chazlet, 1973; Levinson, 1974). Bayrock and Pawluk (1967) showed a good correlation between drift and bedrock geochemistry in Alberta, and Larsson and Nichol (1971) suggest similar correlations in western Ireland. The presence of serpentine, phlogopite, diopside and carbonate in the sand fraction of two soils used in the component analysis (Samples 153 and 184 in Fig. 2), suggest that

much of the glacial material in the area is of very local origin. The calc-silicate and carbonate assemblages were almost certainly derived from the calc-silicate marbles located in the Thurman area.

ELEMENT DISTRIBUTIONS IN SOIL HORIZONS

In order to determine the nature of the glacial deposits, the soil developed over them, and the distribution of elements within soil horizons, a soil profile survey was conducted in the Thurman area. The ultimate goal of this survey was to statistically determine the best soil horizon to sample during subsequent detailed soil sampling in the area. Based on geologic mapping and reconnaissance soil sampling, fifteen soil profile pits were sampled in known areas of anomalous as well as normal background soils, over both marbles and paragneisses (Fig. 2) and analyzed for Zn, Pb and cxMe. A composite soil profile of the fifteen pits is presented in Table 1. Although the pits studied occur on variable thicknesses of glacial drift, over different rock types, differences in the soil profiles are not sufficiently great to differentiate them into distinct groups.

Soils derived from parent glacial drift in the Thurman area exhibit distinct soil horizons that were initially classified by Cline (1963) as podzol-type. The A horizon in normal podzol soils develops primarily as the result of partial losses of soluble bases, clays and colloidal sesquioxides by leaching and mechanical removal (Rose et al., 1979). Unlike this typical bleached A horizon, the soil in the Thurman area exhibits a dark brown A horizon that grades downward into a lighter red-brown or red B horizon. This distinctive B horizon is characteristically enriched in iron oxides, but lacks the abundant clay fraction typical of mature podzol B horizons. The B horizon is divided into an upper red silty sand, the B₁ horizon, and a lower yellow-brown to yellow-red fine sand, the B₂ horizon. The gray-brown parent - C horizon is

comprised of fine to coarse sand, pebbles, cobbles and boulders, unsorted material indicative of a glacial origin.

Based on the above description and Table 1, the podzol classification by Cline (1963) and the brunisolic (absent B horizon) classification given by Boyle et al., (1975) for soil in this portion of the Adirondacks, are misleading and do not apply to the Thurman area. Leaf litter over dark brown-friable surface soil grading downward through lighter colored soil, as is characteristic of the Thurman area, represents an intermediate type between these two classes that has been termed brown forest soil (Hunt, 1972). This weakly acidic soil type occurs in temperate climates with annual precipitation of about 76 cm and usually develops over a calcareous parent-material (Hunt, 1972).

Zinc

The distribution of zinc in fifteen soil profile pits is shown in Figure 3. Composite profiles for pits sampled in anomalous and background soils are shown in Figure 4. A second group of composite soil profiles is given in Figure 5 for sample localities over marble and paragneiss bedrock, respectively. An arbitrary threshold of 70 ppm total metal (Pb + Zn) was used to define an anomaly during the reconnaissance survey. Based on this threshold and the local geology, the soil profile pits in the Thurman area can be grouped as shown in Table 2.

The characteristic feature of the distributions is the enrichment of zinc in the B₁ horizon with a decrease in metal concentration with depth. The distribution of zinc in the composite profiles also exhibits the trend of zinc enrichment in the B₁ horizon, especially for anomalous pits and pits sampled over marble.

The difference in trace element content between soil horizons in

anomalous soils and background soils is termed contrast. In order to evaluate the contrast between anomalous and background soil horizons more quantitatively, t-tests were performed using the following equation:

$$t = \frac{\bar{X}_A - \bar{X}_B}{S_r \sqrt{n}}$$

where \bar{X}_A and \bar{X}_B are the means for anomalous and background soils of a particular horizon, and

$$S_p = \sqrt{\frac{n-1(\sigma_A)^2 + n-1(\sigma_B)^2}{n_A + n_B - 2}}$$

where n is the number of values and σ_A and σ_B are the standard deviations of the two populations. The t values calculated for zinc, lead and cxMe in soil horizons from various anomalous and background soils samples over marble and paragneiss are given in Table 3.

A comparison of t-values calculated for zinc in each soil horizon indicates that the highest contrasts occur in the B₁ horizon. The t-value for zinc in the B₁ horizon soils sampled over marble is significant at the 5 percent probability level. The B₁ soils sampled over paragneiss are significant at the 10 percent probability level. The fact that the contrast values for soils sampled over marble are significantly greater than contrast values for soils samples over paragneiss suggests that the source and amount of zinc is not totally dependent on the C horizon-glacial material, but may be a function of the zinc variation in the local bedrock. Whole rock zinc values for marbles in the area range from 10 to 150 ppm, whereas zinc contents in pargneiss range from 10 to only about 60 ppm (Cole, 1976). Therefore, soils derived from local marble units would be expected to exhibit greater contrast because of the greater zinc variability in marbles.

Leaching of zinc from the A₀ + A₁ and A₂ soil horizons is most conspicuous in profiles sampled from anomalous soils. In background soils, especially over paragneiss, concentrations of zinc from the A₀ + A₁ and A₂ horizons are similar to and in places are greater than the zinc content of the B₁ horizon. This trend suggests that the nature of the binding of zinc in the A horizon differs from area to area as a function of changes in parent-glacial material, concentrations of zinc in local bedrock and the form in which zinc is transported in groundwater. Significant differences in zinc content between B₁ and B₂ horizons in many sample localities suggest that either chemical leaching of B₁ horizons is very slow or that leaching in the B₂ and C horizons is extremely fast. The absence of abundant iron oxides and clay in the B₁ horizons suggests that zinc may occur in the sand and silt-rich fractions, which are resistant to the types of leaching that commonly remove metal from soils. In addition, the absence of appreciable amount of iron oxides and clays in lower soil horizons may inhibit the accumulation of any zinc removed from the B₁ horizon.

The data are generally consistent with results from other glaciated areas. Kauranne (1967) reported enrichment of zinc in the B horizon in an area in central Finland. In New Brunswick, Presant (1971) and Govett (1973) found zinc enriched in the B and C soil horizons. Although there are local variations, zinc seems to give a fairly consistent pattern of enrichment in the B₁ soil horizon in the soils developed from glacial debris in the Thurman area.

Lead

The distribution of lead in the soil horizons is very different from that of zinc. Figure 3 shows that lead generally is enriched in the A₀ + A₁ horizons, with some significant amounts present in the B₁ horizons from

anomalous soils. This trend also is evident from both plots of the composite profiles (Figures 4 and 5).

Although the A horizon is enriched in lead, contrast values (t-values) calculated for all soil horizons given in Table 3 indicate that the higher contrast for lead occurs in B₁ soils developed over marble. The t-value for the B₁ horizon is 3.16 and is significant at the 5 percent probability level. The t-values calculated for soil horizons sampled over paragneiss are similar with the A₀ + A₁ horizon having the highest value of 0.79. The contrast values for soils sampled over marble are significantly higher than the contrast values for soils sampled over paragneiss. This trend also is exhibited by zinc and suggests that marble may be contributing anomalous amounts of lead as well as zinc to the soils.

Marbles exhibit whole rock Pb values of between 10 and 60 ppm, with a mean of 29 ppm. Pb values in paragneiss range from 9 to 37 ppm, with a mean of 22 ppm. The variability of Pb in marbles could produce the observed contrast between anomalous and background soils sampled over this rock type if (1) Pb was added to the soil in the form of metal-bearing rock particles, or (2) if Pb was leached from marbles by soil or groundwaters. The fact that the highest Pb as well as Zn contents are associated with profile pits sampled over marble supports the hypothesis that metal is derived from local rock sources.

Trends in the decrease of lead content with depth in the soil profile differ for marble and paragneiss terranes. The concentration of lead drops sharply from the A to the B₁ horizon in soils over paragneiss, where the reverse generally is true of soils sampled over marble. The distribution and composite plots for profiles sampled over marble indicate that minor amounts of lead are leached from the A horizon and that most of the lead present in the profile remains in the B₁ horizon. The similarity of this

trend with one observed for zinc in soils sampled over marble, coupled with the low iron-oxide and clay content in the soil, suggests that lead also may occur in sand or silt-fractions, in which leaching reactions are minimal.

Lead enrichment in the A horizon in soils sampled over paragneiss suggests two possibilities. The lead may have been absorbed from the soil by plants and accumulated in an insoluble form in humus, derived from dead plant material in the A horizon soils. However, the absence of abundant iron oxides and clays, which are also good scavengers of lead, coupled with the low lead values obtained from the analysis of organic component suggest that lead in the A horizon soils may also be tied up in the clastic fractions. It was observed that the A horizon soils are composed primarily of fine sand and silt which could contain discrete minerals bearing lead as well as zinc and other metals. The differences in metal distribution between soils sampled over marble and paragneiss also suggest the presence of two different types of soil environments, one being calcareous (over marble) and a second type being a non-calcareous, more acidic soil (over paragneiss).

Cold-Extractable Total Heavy Metal

Soil profile samples were also tested for cold-extractable total heavy metal (cxMe) using the method described by Hawkes (1963). Hawkes (1963) concluded that this test was not suitable for residual anomalies, glacially dispersed geochemical fans or stream sediments containing material of purely detrital origin. However, several successful studies using cxMe methods in glacial terrains have been reported (Bischoff, 1954; Byers, 1956; Ermengen, 1957; Dreimanis, 1960; and Kaurrane, 1967).

Values of cxMe were very low in the soil profile samples from the

Thurman area, and in soils from adjacent areas with high zinc and lead contents. Bischoff (1954) reported that dithizone tests work best on finer sediment fractions. Therefore the soils were sieved using 60 mesh nylon screen and retested. CxMe values for the sieved fractions were markedly higher, and data are plotted with the unsieved and atomic absorption results in Figure 3.

The distribution of cxMe in unsieved samples is highly irregular whereas the distribution of cxMe in the finer (-60 mesh) component of the soil horizons is relatively regular, and closely parallels the trend observed in the distribution of zinc and lead. The distribution of cxMe in sieved soils sampled over marble indicates that the B₁ horizon is enriched in metal. The cxMe values observed in profile pits sampled over paragneiss are highest in the A₀ + A₁ soil horizons. The trend of cxMe enrichment in the A₀ + A₁ horizon also is present in soil profiles sampled in both anomalous and background soils.

The highest contrast calculated for the cxMe values in Table 3 is for the B₁ horizon over marble. Similar results were obtained for soils sampled over paragneiss, but the B₁ horizon contrast values are not as extreme. These trends coupled with the distributions and contrast values of zinc and lead for the soil profiles indicate that the best horizon to sample is the B₁ horizon.

MODE OF OCCURRENCE OF ZINC AND LEAD IN SELECTED SOIL SAMPLES

Migration of metals in a glaciated environment involves not only physical (clastic) mobility but chemical mobility as well. It has been shown that zinc in an oxidizing or slightly acid environment is very mobile, while lead is only slightly mobile (Andrews-Jones, 1968). The most

effective way of determining the mechanism involved in the mobilization of zinc and lead is by the use of different chemical extractions to evaluate the distribution of these elements among the different components which characterize a soil. This component distribution, coupled with knowledge of the distribution of the metals in the soil profile, makes it possible to distinguish between soil anomalies directly over mineralization, displaced from mineralization, and anomalies unrelated to the mineralized source (Bradshaw, et al., 1974).

Two anomalous and one background sample were used for the component analysis. Each sample was broken down into seven different major components and analyzed to determine which component(s) has(have) the highest zinc and/or lead concentration and which contribute the most to the total metal content of the samples (Fuchs and Rose, 1974). The major components that were analyzed have been described by Fuchs and Rose (1974), Rose (1975) and McNeal (1975). The components are given in order of their removal.

1. Exchangeable and Adsorbed Metal

(referred to as "exchangeable"): Metal ions in exchange sites in clay minerals, such as montmorillonite and vermiculite, adsorbed on colloidal organic particles, and metal cations occurring as counter ions on clays, Fe- and Mn-oxides, and organic material.

2. Organic Material and Sulfides

(referred to as "organics"): Highly oxidizing NaOCl dissolves organic material, releasing metal cations bonded in organic compounds, and zinc and lead sulfides either enclosed in organic material, or as discrete mineral grains.

3. Mn-oxides

Mn-oxides are dissolved releasing enclosed zinc and lead minerals

or adsorbed metal cations trapped during later Mn-oxide precipitation.

4. Fe-oxides

Analogous to Mn-oxides

5. Clay

(less than 2 microns): Zinc and lead occurring in non-exchange lattice sites of clays, defects and intergrowths within clays, and as metal cations in silicate, carbonate or oxide clay-size grains not attacked in previous steps.

6. Silt

(2 microns to 325-mesh): Zinc and lead in lattices of silt-size silicate, carbonate or oxide grains, or zinc and lead sulfides as mineral inclusions intergrown with silt-sized grains.

7. Sand

(325-mesh to 60-mesh): Analogous to silt fraction.

In addition to the above components that were analyzed, heavy and light fractions of the silt and sand components were separated using bromoform and examined microscopically. The separation of the seven components was done by modification of methods given by Jackson (1956), Fuchs and Rose (1974), de Endredy (1962), McKeague and Day (1966) and Chao (1972), as described in Cole (1976). The components were analyzed for zinc and lead, and all except "exchangeable" and "organic" were analyzed for iron and manganese.

After the Fe-oxides separation step, the sample was still brownish in color, probably because some Fe-oxide was still present. Apparently the ammonium oxalate procedure is not as effective as the dithionite procedure, which left the clays gray to white (Fuchs, 1972). However, the amount of Fe-oxide remaining cannot be large, because the clays, with the highest surface area, contain relatively low Fe contents, indicating only a small

remaining coating.

The three samples selected for this study were from the west-central portion of the map area (Fig. 2) because the soil horizons in this area are more pronounced than elsewhere. This assured the consistent sampling of the B₁ soil horizon at each site. In addition the trace element values in soils of this area are higher in magnitude (Cole, 1976). The samples selected were:

Sample 153	425 ppm Zn	57 ppm Pb
Sample 156	51 ppm Zn	13 ppm Pb
Sample 184	599 ppm Zn	44 ppm Pb

Location of these samples is given on the geologic map, Figure 2. Each sample was taken from the center of the B₁ horizon over an interval of approximately 15 to 20 cm.

Results of the component analysis for zinc, lead, iron and manganese are summarized in Tables 4 and 5 and Figures 6 and 7. Quantities are summarized according to the concentration of metal in the component itself and the percent contribution to the total metal in the soil. The results of microscopic examination of the silt and sand fractions are given in Table 6.

It is important to note that the values determined by the author using LiBO₂ fusion (listed as "Total" in Table 4) are significantly higher than values given above, obtained by a nitric-perchloric extraction method. The value of 182 ppm obtained on the "background" sample (156) was much higher and it technically cannot be considered background. However, it is still lower than the other two samples, and for the purposes of discussion, it will be considered a background sample.

Zinc

Fuchs (1972) ranked his soil sample components in order of decreasing metal content in order to discuss the distribution of the metals among the various components. Similarly, the zinc data from the Thurman area can be ranked based on data in Table 4 and Figure 6.

The overall ranking by concentration for the three samples is remarkably consistent (Table 5). In decreasing order the overall ranking is MnOx, FeOx, clay, silt and sand. The order in this ranking of "organics" and "exchangeable" cannot be determined because no attempt was made to measure the organic content or the exchange capacity in each sample.

Based on these data, several conclusions on the distribution of zinc can be drawn. Because all three samples show the same relative order among phases, the zinc in the samples is probably distributed in an approximately equilibrium fashion among the phases, although the deviations from a constant ratio indicate some departures from equilibrium. In addition, for each component, the mass of zinc per unit weight of total sample increases from the low ("background") to high ("anomalous") samples, indicating that the anomalous zinc is shared among all the components, and occurs in the clastic components (sand, silt) as well as the components formed in the soil. However, the amount of zinc increases by a factor of 5 - 30 in the Fe-oxide, Mn-oxide and "exchangeable" components, but only by a factor of 2 - 5 in the sand, silt and clay. Part of the zinc in the sand, silt and clay may exist in Fe-oxide not removed in the Fe-oxide step, as previously noted, but only part of it can occur in this manner, based on the Zn/Fe ratio in the Fe-oxide fraction and the amount of Fe in the clay, silt and sand.

The data on Fe and Mn indicate that both of these elements have been added to the soils with greater zinc and lead contents. Therefore, the larger amounts of zinc result partly from added amounts of these oxides. For the Fe-oxides, the content of zinc in this component also increases. In contrast, the zinc content of the Mn-oxide component is lower in the high zinc samples, but because the content of Mn-oxide increases, so does the amount of zinc in this form.

In an examination of metals in glacial soils, Present (1971) indicated that zinc had a weak association with Fe-oxides and a strong association with humus material. The low zinc content in the organic fraction indicates zinc is not present in organics or sulfides, which would be dissolved in the organic-removal step. It is possible that zinc adsorbed on organic material, later coated (armored) by Mn- and Fe-oxides, would not be released into solution until each oxide phase was selectively attacked during the component analysis. Jenne (1968) concluded that Mn and Fe hydrous oxides generally furnish the principal controls on the fixation of metals in soils and stream sediments.

The decreasing concentration of zinc from clay to silt to sand is usually the pattern in soils derived from glacial materials (Kauranne, 1967). The presence of zinc in the clay component may be explained in several ways:

- 1) Zinc may occur in the crystal structure of clays in the octahedral sites, as in the clay mineral sauconite, a zinc-montmorillonite (Deer, Howie and Zussman, 1969). The ionic radius of Zn^{2+} in octahedral coordination with oxygen is 0.83\AA which is not too large to prohibit substitution into octahedral sites of clays (Whittaker and Muntus, 1970).

- 2) The possibility also exists for the atomic substitution of zinc (Zn^{2+}) for other cations in mineral lattice sites during metamorphic

recrystallization. In particular, there could be substitution of zinc (Zn^{2+}) for either iron (Fe^{2+}) or magnesium (Mg^{2+}) in such minerals as diopside, garnet, hornblende, biotite, serpentine, or dolomite, which were eventually weathered to clay-size particles. The ionic radius of Zn^{2+} is approximately 0.83\AA whereas Fe^{2+} and Mg^{2+} have ionic radii of 0.86\AA and 0.80\AA , respectively (Handbook of Chemistry and Physics, 4th edition, 1973-74). This substitutional phenomena (similar ionic radii and charge) might explain the high zinc values reported in hornblendes (up to 216 ppm), garnets (up to 263 ppm) and pyroxenes (up to 300 ppm) from the Balmat-Edwards Zinc District by Engel and Engel (1960) and Engel et al., (1961, 1964).

3) In thin section studies of the rocks from the Thurman area, tiny opaque grains of pyrite and magnetite were observed to be disseminated within grains and at grain boundaries. Inclusions of sphalerite enclosed within these tiny opaque grains would not be attacked by the earlier steps in the component analysis if the host grains were enclosed in more massive carbonate or silicate assemblages. It is possible, but highly improbable, that clay-sized silicate or carbonate particles could act as hosts for sphalerite-bearing pyrite or magnetite grains. More likely this phenomena occurred in sand or silt-size grains, which are abundant in the three samples analyzed.

The order in ranking of percent contribution to the total in the three samples is variable (Table 5). Fuchs and Rose (1974) concluded that variation was a function of the proportion of the different size fractions: sand, silt and clay. This variation is demonstrated by the sand fraction which, even though low in concentration of Zn, ranks third in sample 184 constituting 32 percent of the sample and third in sample 156 where it constitutes 43 percent of the total weight.

Of the several important trends evident from the percentage ranking the most significant is the top ranking of the silt fraction in all samples. In addition, at least two clastic fractions are present in the top three rankings and all three clastic fractions are present in the top four rankings. These trends strongly indicate that contribution to the total zinc content is controlled by zinc content in clastic grains, resistant to complete breakdown during weathering. The presence of garnet, hornblende, biotite and magnetite in both anomalous and background samples and the absence of diopside, serpentine, phlogopite and carbonate in the background sample (Table 6) suggest that enrichment of zinc in the anomalous samples may be due to the presence of zinc-bearing calcsilicate minerals and/or carbonates.

The Mn-oxide fraction is lowest in the background sample and "exchangeable" is last or ranked second to last in all three samples. There appears to be a good correlation between low zinc content and low manganese content in the background sample. The Fe and Mn components in the anomalous samples exhibit a wide variety of different rankings which is a function of the amount present in each sample.

The contribution of zinc in "organics" is large for the background sample and small for the two anomalous samples. Enrichment of zinc in the organic fraction is probably a function of the amount of organic material present, as was the case with the zinc and oxide components.

Lead

The mode of occurrence of lead is similar to that of zinc in terms of concentration of metal in each component. The rankings by concentration in each component and percent contribution to the total are given in Table 5.

Lead exhibits nearly an identical pattern in ranking by concentration

with the order exhibited for zinc. The important role of organic material, in particular humus, on the fixation of lead has been described by numerous authors (Rose et al., 1979; Kennedy, 1965; and Swanson et al., 1966). The high lead content in many of the A horizon soils from the soil profile pits, along with modest contribution of lead by "organics" to the total concentration suggest that Pb is influenced more than Zn by the presence of organic material. Unfortunately, no estimate was made of the organic content or cation exchange capacity in these samples.

The average ranking by concentration for lead in the three samples is, in decreasing order: Mn Ox, Fe Ox, clay, silt and sand. Because the order of ranking of components for lead and zinc is similar, the factors controlling their distribution in these components are probably similar. Like zinc, the lead in the samples is probably distributed in an approximately equilibrium fashion among the phases. The mass of Pb per unit weight of the total sample for each component increases from the low (background) to high (anomalous) samples, indicating that like zinc, the lead is shared among all the components, and is contained within the clastic components as well as components formed in the soil. However, the largest percentage increases in lead occur in the Fe- and Mn-oxide phases by a factor of 3 - 18 times the amount in background, but only by a factor of 1 - 3 in the sand, silt, clay, "organic" and "exchangeable" components. However, because the ammonium oxalate step was not successful in removing all the iron from the samples, it is likely that some lead attributed to clay, silt and sand is actually in the Fe-oxide.

According to the ranking by concentration, Mn-oxide has the greatest affinity for lead, and Fe-oxide the next highest, as in the case of zinc. Because of this affinity, plus the considerable increase in the Mn- and Fe-oxides in the anomalous samples, these components show the greatest

contrast from background to anomalous.

The presence of lead in clastic material may be a function of: (1) substitution of Pb^{2+} into octahedral sites in clay lattices, (2) substitutional or interstitial solid solution of Pb^{2+} in mineral phases, (3) inclusions of galena in host silicate or carbonate grains and (4) incomplete removal of Mn- or Fe-oxides in previous steps of component analysis. Substitution of Pb^{2+} , whose ionic radius is 1.26Å in octahedral coordination with oxygen, into the octahedral sites of clays would be very difficult. Lead substitution in potassium feldspars, micas, and calcium minerals may be more important as suggested by Rankama and Sahama (1950). The differences in lead content in the sand, silt and clay fractions between anomalous and background samples are not sufficiently great to rule out the possibility of Pb^{2+} substituting for K^+ or Ca^{2+} . Various amounts of feldspar are present in all three samples which could contribute lead to the individual fractions (Table 6). The lead content from potassium feldspars in the paragneiss in the Balmat-Edwards Zinc District is less than 50 ppm and less than 25 ppm in feldspars from marbles (Engel and Engel, 1960).

The presence of minute galena inclusions in a pyrite, silicate or carbonate host mineral also is a possibility, although neither sphalerite nor galena were observed in polished thin sections.

The ranking of each component in terms of percent contribution to total lead is similar to the ranking developed for zinc. As for zinc, silt ranks first in all three samples. Also, sand, silt and clay hold the top three ranking positions for all samples. The influence of clastic materials on the percent contribution to the total lead content in these samples is more extreme than those for zinc. These data suggest that lead is tied up in clastic grains, either between clay layers, within mineral

phases as inclusions of galena or Pb^{2+} substitutioning for other cations. It is important to note that the sum of the lead values in the sand, silt and clay fractions in all three samples, constitute anomalous values. This is also true for the values determined for zinc in the clastic fractions.

In contrast to the high ranking of "organics" for zinc in the background sample, the organic fraction of the anomalous samples is intermediate for lead. Typically, lead contents correlate with "organics" content, either as adsorbed metal on humates or with organics taken up by plants forming metal-organic bonds. The "organics" in sample 184 and 153 rank intermediate (4th) and low (6th), respectively, which is similar to the trend observed for "organics" and zinc.

Based on the ranking in terms of percent, lead seems to associate with Fe-oxides somewhat more than with the Mn-oxides. Rose et al., (1979) observed that the low mobility of lead was due to its association with limonite, by either adsorption or coprecipitation. In a study of soils in New Brunswick, Presant (1971) observed moderate association of lead (Pb^{2+}) with some iron oxides, as well as with organic material. The ranking of Fe and Mn is very low in the background sample, second to last and last, respectively. This trend, accompanied by the low ranking of Fe- and Mn-oxides in the anomalous sample is indicative of the low mobility of lead in the soil environment. The lead remains in clastic material either within lattices of resistant minerals or as inclusions in minerals, with very little lead being released upon leaching by groundwater.

The low ranking of "exchangeable" lead, as well as zinc is probably indicative of the low clay content in the soils (less than 14 percent by weight) and the ability of Fe- and Mn-oxides and organic material to scavenge metals from solution. Typically, podzol-type soils have as much as 50 percent clay in the B_1 horizon with a minimum of approximately 25

percent by weight. The soils in the Thurman area are of glacial origin and can contain as much as 47 percent sand and 50 percent silt. This suggests that one possible explanation for low metal content in the background sample, 156, might be due to its relatively small clay content (approximately 10 percent by weight).

CONCLUSIONS

Several important conclusions can be drawn from the data presented which have a significant bearing on exploration geochemistry strategy in this type of glaciated terrain. The distribution of zinc in soil profiles sampled over marbles (potential ore hosts) and in anomalous areas indicate that the B₁ soil horizon is enriched in zinc. Upper A horizon soils sampled over paragneiss and in background soils exhibit slightly higher zinc values than the B₁ horizon. In general, lead is enriched in the upper A horizon of all the profiles studied with the exception of two pits sampled over marble. The cxMe distribution in the soil profiles most closely parallels that trends observed for zinc, the dominant trace metal present in the Thurman area. Calculations of contrast using t-values for zinc, lead, and cxMe between anomalous and background soils sampled over marble and paragneiss indicate that the B₁ soil horizon is the most suitable for sampling on a regular basis.

These distributions suggest that zinc is somewhat more mobile than lead in this particular glacial soil environment. However, the absence of zinc and lead in the C-horizon soils, coupled with the close association of soil metal enrichment over marbles indicate that both metals are restricted in their mobility and may be derived from very local rock sources.

Component analysis of anomalous and background B₁ soils indicates that a significant proportion of zinc and lead are tied up in the clastic

fraction, particularly silt-sized grains. Anomalous metal contents can be linked with soils rich in weather-resistant calc-silicate phases such as diopside, phlogopite, and serpentine, and carbonates. Zinc and lead have probably substituted into octahedral sites of clays or are in solid solution with other cations in silicates, carbonates, and oxide phases. This trace element-mineralogic association has resulted in restricted zinc and lead mobility in the Thurman soils which appear to be derived from the local rock environment. The close association of soil metal enrichment with rock type indicates that rock as well as soil sampling should prove useful in an exploration program.

If this soil-rock association is real, however, why then do we see low metal values in the C-horizon parent glacial material? It can be safely assumed that mineral assemblages observed in the B₁ clastic fraction could also occur in the C-horizon material, yet no metal enrichments are noted. In general, B-horizon soils are comprised of clay to sand-sized grains coated with abundant iron and manganese oxides. Conversely, C-horizon material is devoid of oxides and consists of sand to boulder-size fragments. These boulders are chiefly comprised of quartzo-feldspathic paragneisses. Based on the component analysis, we know that zinc and lead have been absorbed or co-precipitated with manganese and iron oxides in the B₁ horizon. We also know that the B₁ horizons sampled over marble are rich in dioxide, serpentine, phlogopite and carbonate. It appears as though metals scavenged by oxides and the presence of trace-metal bearing calc-silicates and carbonates in the B-horizon soils contribute to the metal enrichment pattern observed in profile pits. Marble-derived mineral phases would be more prone than paragneiss phases to fine disaggregation through the mechanical processes affiliated with glaciation. In addition, these finer grains could be found stratigraphically above coarser grains and rock fragments even in a poorly-sorted sediment environment such as

observed in the Thurman area. Any metal present in the C-horizon could also be leached and transported vertically as well as laterally by soil waters moving in response to vertically-controlled capillary processes. This metal could then be adsorbed onto oxide surfaces or exchange with other cations within the clays found in the B horizon.

Because metal dispersion in the Thurman area is dependent on mechanical as well as hydromorphic processes, detailed soil surveys must take into account the scales of transport associated with each process. Detailed mineralogic mapping of Thurman lithologies (Cole, 1976) suggests that calc-silicate and carbonate phases observed in profile pits 184 and 153 were derived from no farther away than 1.5 km. Element distributions in soil profiles and mode of metal occurrence in Thurman soils suggest a much smaller scale chemical transport of metals on the order of meters to perhaps tens of meters. Therefore, if the individual ore targets in the Thurman area were on the order of 0.7 m to 16 m in thickness by 16 to 170 m along strike, as they are in the Balmat-Edwards Zinc District (Lea and Dill, 1967), then the initial soil sample spacing should certainly be less than 1 km by 1 km and more on the order of 100 or 150 m sq. The latter spacing should be adequate in detecting mechanically-dispersed metal anomalies, which could be traced and verified with a closer spaced detailed soil survey.

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Table 1. Typical Soil Profile - Thurman Area
(composite of 15 profiles)

Horizon	Description
A ₀ + A ₁	Organic-rich silt to fine sand, 6.4 cm, medium to dark brownish black, many plant roots, a few pebbles of paragneiss
A ₂	Silt to fine sand, 4.6 cm, medium to dark brown, loosely bonded, a few pebbles of paragneiss, plant roots and humus are common
B ₁	Clay to fine sand, 32.5 cm, medium red to red-brown (iron oxide accumulation), pebbles, cobbles and boulders of paragneiss present in only 5 of 15 profiles, minor organics
B ₂	Silt to coarse-sand, 13.7 cm, light red to light yellow-reddish brown, many pebbles, few cobbles and boulders, minor organics
Transition	Fine to coarse sand, 3.3 cm, light yellow-brown to gray-brown, many pebbles and cobbles of paragneiss, no organics
C	Fine to coarse sand, thickness unknown, bedrock never reached, light to medium gray-brown, many pebbles, cobbles and boulders of paragneiss, trace of marble

Table 2. Grouping by rock type of anomalous and background soil profile pits.

Anomalous		Background	
Marble	Paragneiss	Marble	Paragneiss
			1
		2	
	3		
			4
		5	
			6
		7	
		8	
	9		
			10
			11
12			
13			
14			
15			

Table 3. Comparison of total metals in anomalous and background soil sampled over marble and paragneiss

		t (Marble)		t (Paragneiss)	
		Anom. vs Bkg.		Anom. vs Bkg.	
		(Pits 12,13,14,15)	(Pits 2,5,7,8)	(Pits 3,9)	(Pits 1,4,6,10,11)
Zn	A ₀ + A ₁	2.12*	(6 d.f.)	0.71	(7 d.f.)
	A ₂	---		1.31	(3 d.f.)
	B ₁	4.75**	(6 d.f.)	2.42*	(5 d.f.)
	B ₂	1.18	(5 d.f.)	1.38	(5 d.f.)
	T	0.46	(4 d.f.)	---	
	C	0.29	(4 d.f.)	0.54	(5 d.f.)
	Pb	A ₀ + A ₁	1.04	(6 d.f.)	0.79
	A ₂	---		0.31	(3 d.f.)
	B ₁	3.16**	(6 d.f.)	0.64	(5 d.f.)
	B ₂	1.65	(5 d.f.)	0.66	(5 d.f.)
	T	0.53	(4 d.f.)	---	
	C	0.31	(4 d.f.)	0.51	(5 d.f.)
cxMe	A ₀ + A ₁	1.52	(6 d.f.)	0.12	(7 d.f.)
	A ₂	---		1.02	(3 d.f.)
	B ₁	1.69	(6 d.f.)	1.07	(5 d.f.)
	B ₂	0.87	(5 d.f.)	0.51	(5 d.f.)
	T	0.99	(4 d.f.)	---	
	C	0.49	(4 d.f.)	0.45	(5 d.f.)

$$t_{0.95} (7 \text{ d.f.}) = 2.36$$

$$t_{0.95} (6 \text{ d.f.}) = 2.45$$

$$t_{0.95} (5 \text{ d.f.}) = 2.57$$

$$t_{0.95} (4 \text{ d.f.}) = 2.78$$

$$t_{0.95} (4 \text{ d.f.}) = 3.18$$

$$t_{0.90} (7 \text{ d.f.}) = 1.90$$

$$t_{0.90} (6 \text{ d.f.}) = 1.94$$

$$t_{0.90} (5 \text{ d.f.}) = 2.02$$

$$t_{0.90} (4 \text{ d.f.}) = 2.13$$

$$t_{0.90} (3 \text{ d.f.}) = 2.35$$

* - significant at 10 percent probability level

** - significant at 5 percent probability level

Significance at a given probability level determined from tables given by Pearson and Hartley (1966).

Table 4. Component analysis of soil for zinc, lead, iron and manganese

	% of Total Weight	Zn AMV ^a	Zn Concn. ^b (ppm)	Zn ^c %	Pb AMV ^a	Pb Concn. ^b (ppm)	Pb ^c %	Fe Concn. ^b (ppm)	Fe ^c %	Mn Concn. ^b (ppm)	Mn ^c %
184 Exchangeable	--	31	--	4	5	--	2	--	--	--	--
184 Organic	--	95	--	12	25	--	9	--	--	--	--
184 Mn-Oxide	--	110	16,923	14	8	1,213	3	1,900	3	6,500	62
184 Fe-Oxide	--	71	2,186	9	12	360	4	32,480	57	--	--
184 Clay	13.6	123	904	16	45	331	16	4,150	7	1,544	15
184 Silt	50.3	249	495	32	133	264	48	13,300	23	2,163	21
184 Sand	31.9	103	323	13	50	157	18	5,580	10	335	3
184 Total		782 ^d	758 ^e		278 ^d	239 ^e		48,200 ^e		10,930 ^e	
wt. sum of components	95.8										
153 Exchangeable	--	15	--	3	4	--	2	--	--	--	--
153 Organic	--	22	--	4	11	--	5	--	--	--	--
153 Mn-Oxide	--	63	9,403	12	18	2,612	8	1,100	2	6,700	68
153 Fe-Oxide	--	110	3,929	21	25	879	11	28,000	60	--	--
153 Clay	--	59	428	11	54	391	25	4,425	10	1,274	13
153 Silt	13.8	148	449	28	72	218	33	9,898	21	1,372	14
153 Sand	46.7	106	227	20	37	79	17	3,305	7	442	5
153 Total		523 ^d	510 ^e		220 ^d	194 ^e		37,650 ^e		10,300 ^e	
wt. sum of components	93.4										
156 Exchangeable	--	5	--	2	3	--	2	--	--	--	--
156 Organic	--	48	--	26	9	--	7	--	--	--	--
156 Mn-Oxide	--	4	44,444	2	1.5	11,110	1	400	1	90	3
156 Fe-Oxide	--	6	217	3	2.5	90	2	27,720	45	--	--
156 Clay	10.0	25	253	14	34	343	26	1,700	3	579	20
156 Silt	43.7	52	119	29	57	130	44	11,100	18	1,404	49
156 Sand	42.8	42	98	23	24	56	18	21,100	34	783	27
156 Total		182 ^d	189 ^e		131 ^d	119 ^e		50,500 ^e		2,450 ^e	
wt. sum of components	96.4										

^aAMV=actual measured values ^bconcentration of metal in each component ^cpercent contribution to total metal

^dtotal ppm in sample based on actual measured values ^etotal from LiBO₂ fusion

Table 5. Summary of the ranking by concentration and percent of metal in two anomalous (184, 153) and one background (156) soil samples.

#184		#153		#156	
Zn	Pb	Zn	Pb	Zn	Pb

I. Ranking by concentration of metal in component.

MnOx	MnOx	MnOx	MnOx	MnOx	MnOx
FeOx	FeOx	FeOx	FeOx	Clay	Clay
Clay	Clay	Silt	Silt	FeOx	FeOx
Silt	Silt	Clay	Clay	Silt	Silt
Sand	Sand	Sand	Sand	Sand	Sand

II. Ranking by percent contribution to total metal content.

Silt	Silt	Silt	Silt	Silt	Silt
Clay	Sand	FeOx	Clay	Organics	Clay
MnOx	Clay	Sand	Sand	Sand	Sand
Sand	Organics	MnOx	FeOx	Clay	Organics
Organics	FeOx	Clay	MnOx	FeOx	Exch.
FeOx	MnOx	Organics	Organics	Exch.	FeOx
Exch.	Exch.	Exch.	Exch.	MnOx	MnOx

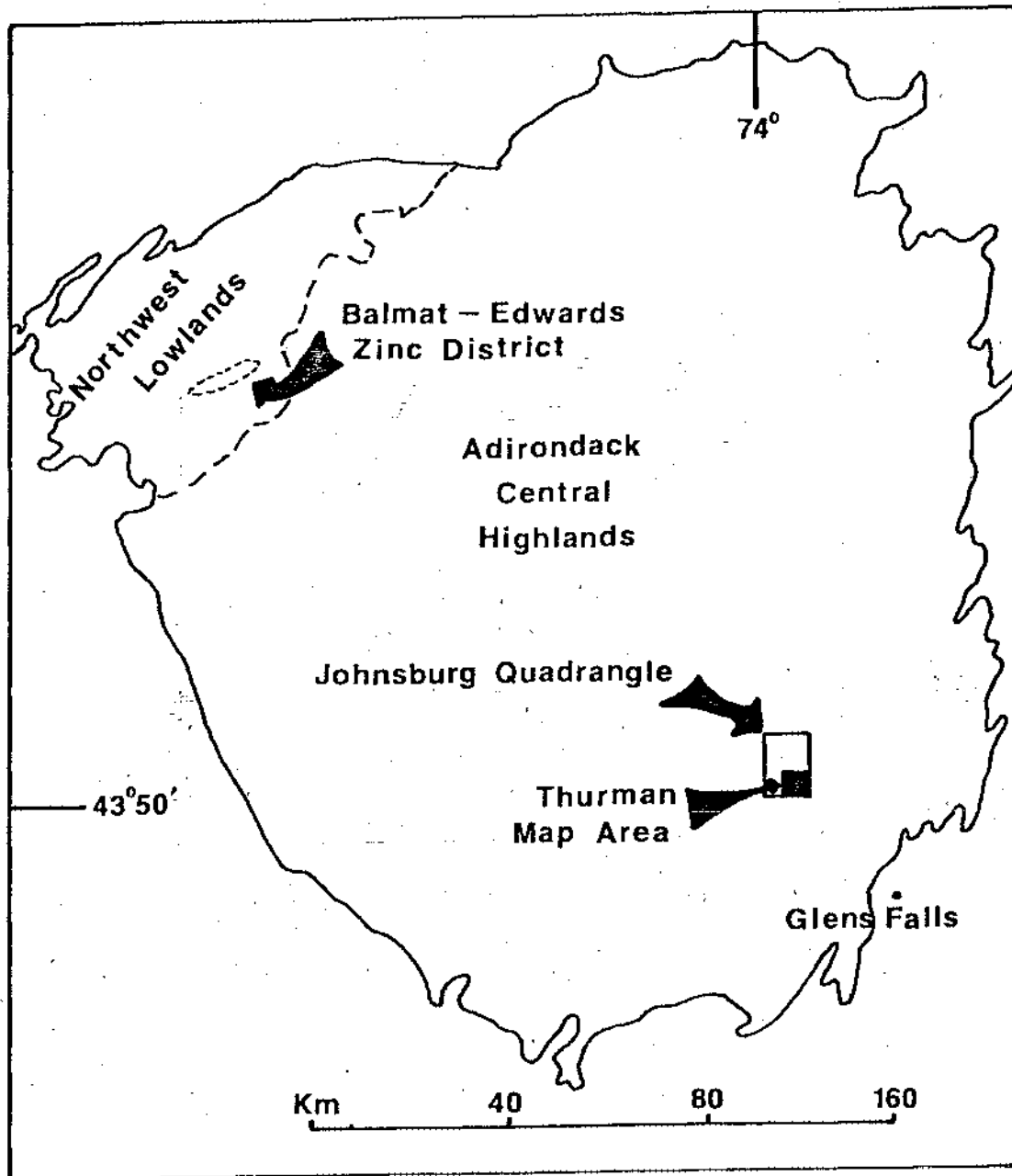
Table 6. Mineralogy of Sand and Silt Fractions from Two Anomalous and One Background Soil

Sample	Heavies	Relative Abundance	Lights	Relative Abundance
156	Garnet	Dom	Quartz	Dom
	Biotite	Acc	Pink feldspar	Acc
	Hornblende	Dom	Plagioclase	Rare
	Diopside	Rare	Chlorite	Rare
	Sphene	Rare		
	Magnetite	Dom		
	Labradorite	Rare		
184	Garnet	Dom	Quartz	Dom
	Biotite	Acc	Phlogopite	Acc
	Hornblende	Rare	Pink feldspar	Rare
	Diopside	Acc	Carbonate	Acc
	Magnetite	Acc		
	Serpentine	Acc		
153	Garnet	Acc	Quartz	Dom
	Biotite	Acc	Phlogopite	Rare
	Hornblende	Dom	Pink feldspar	Acc
	Diopside	Acc	White diopside?	Rare
	Sphene	Rare	Carbonate	Acc
	Magnetite	Acc		
	Serpentine	Acc-Rare		

Note: Dom = Dominant
Acc = Accessory

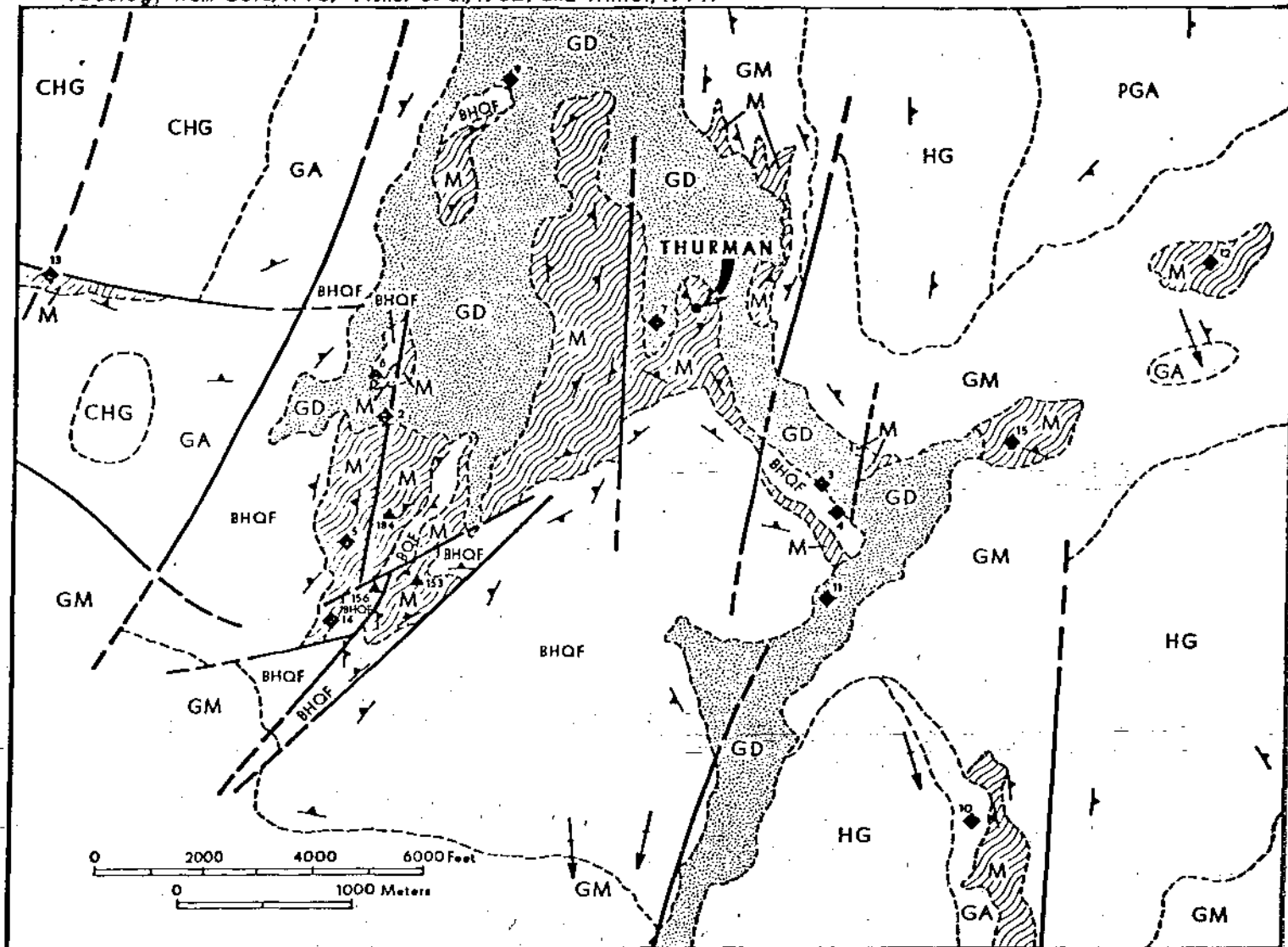
Figure Captions

- Fig. 1. Location map of the study area.
- Fig. 2. Generalized geologic map of the Thurman area giving locations of soil profile pits and samples used in the component analysis.
- Fig. 3. Distribution of Zn, Pb and cxMe in soil horizons from pits sampled in the Thurman area. Single dash-dot line is for sieved samples (-60 mesh). Double dash-dot is for unsieved samples.
- Fig. 4. Composite profiles for Zn, Pb and cxMe distribution in anomalous (solid) and background (dashed) soils.
- Fig. 5. Composite profiles for Zn, Pb and cxMe in soils sampled over marble (solid) and paragneiss (dashed).
- Fig. 6. Percent contribution of soil components to total zinc.
- Fig. 7. Percent contribution of soil components to total lead.



GEOLOGY OF THE THURMAN AREA ADIRONDACK MOUNTAINS, NEW YORK

(Geology from Cole, 1976; Fisher et al, 1962; and Miller, 1914)



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|-------------|------|-------------------------------------------------------------------------|-------|---------------------------------------|
| Precambrian | GD | Glacial Drift (dominantly unsorted to poorly sorted) | ▲ | Strike and Dip Direction of Foliation |
| | M | Marble (locally rich in dolomite, calc-silicates, quartz, pyrite) | --- | Lithologic Contact |
| | GM | Mixed Paragneiss (interlayered garnet-BHQF with amphibolite and marble) | - - - | Fault, dashed where inferred |
| | GA | Pink Hornblende Granitic Paragneiss (poorly banded) | ↘ | Glacial Striae |
| | PGA | Porphyroblastic Hornblende Granitic Paragneiss (poorly banded) | ◆ | Soil Profile Pit |
| | HG | Quartz-Poor Hornblende Feldspar Paragneiss (poorly banded) | ▲ | Component Analysis Soil Sample |
| | CHG | Quartz-Poor Hypersthene Feldspar Paragneiss (poorly banded) | | |
| | BOF | Biotite Quartzo-Feldspathic Paragneiss (highly banded) | | |
| | BHOF | Biotite-Hornblende Quartzo-Feldspathic Paragneiss (highly banded) | | |

