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**Secondary Sulfate
Minerals From Alum
Cave Bluff:
Microscopy and
Microanalysis**

R. J. Lauf

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Metals and Ceramics Division

**SECONDARY SULFATE MINERALS FROM
ALUM CAVE BLUFF: MICROSCOPY AND MICROANALYSIS**

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ABSTRACT

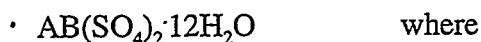
Microcrystals of secondary sulfate minerals from Alum Cave Bluff, Great Smoky Mountains National Park, were examined by scanning electron microscopy and identified by X-ray fluorescence (XRF) in the SEM. Among the samples, the author discovered three new rare-earth sulfates: coskrenite-(Ce), levinsonite-(Y), and zugshunstite-(Ce). Other minerals illustrated in this report include sulfur, tschermigite, gypsum, epsomite, melanterite, halotrichite, apjohnite, jarosite, slavikite, magnesiocopiapite, and diadochite. Additional specimens whose identification is more tentative include pickeringite, aluminite, basaluminite, and botryogen. Alum Cave is a "Dana locality" for apjohnite and potash alum, and is the first documented North American occurrence of slavikite.

1. INTRODUCTION

Alum Cave Bluff in the Great Smoky Mountains National Park is a long-known sulfate locality; Dana's System mentions two sulfate minerals (potash alum and apjohnite) from "Alum Cave" [1]. The locality was studied during the 1800's; however, the present study represents the first systematic examination of the sulfate minerals at the site by modern electron microscopic techniques.

Alum Cave Bluff is on a southern spur of Mount Le Conte, at an elevation of about 1,600 meters. No cave exists; Alum Cave Bluff is a rock shelter about 30 meters high and 10 meters deep, Figure 1. The site is 3.6 kilometers via a hiking trail from a parking lot on the main highway through the Park (U.S. 441). Salts at Alum Cave Bluff have been known since at least 1837 [2], and gave the site its name. According to Jenkins [2], "the minerals of Alum Cave, contiguous to each other, include alum, Epsom salts [epsomite], saltpeter, magnesia, and copperas [melanterite]." Many tons of alum and Epsom salt had accumulated at the site. The easily mined salts were depleted by the mid-1840's and activities there gradually diminished, except for a brief revival of mining for saltpeter during the Civil War.

Alum in the modern sense is a general term for hydrous alkali sulfates [3] with the formula



A is potassium or a higher alkali metal (rarely sodium), thallium(I), or ammonium;

B is a trivalent ion of relatively small ionic radius (0.5 - 0.7 Å) such as Al, Fe, or Cr.

Alum per se is uncommon at the locality. However, the hair-salt series, apjohnite-halotrichite, is abundantly present. These minerals were originally called alums and were used for the same purposes (astringents, dyeing, etc.). In view of the abundance of hair salt at Alum Cave Bluff, and the small amount of true alum present, it is probable that nineteenth-century authors were not referring to alum in the present strict sense. The Dana mention of potash alum at Alum Cave Bluff [1] does not cite any reference; if it is based on historical accounts of "alum" in the broad sense, then it may be called into question. Although some true alum is present, all samples analyzed in the present study had no potassium and are probably tschermigite [ammonia alum, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$].

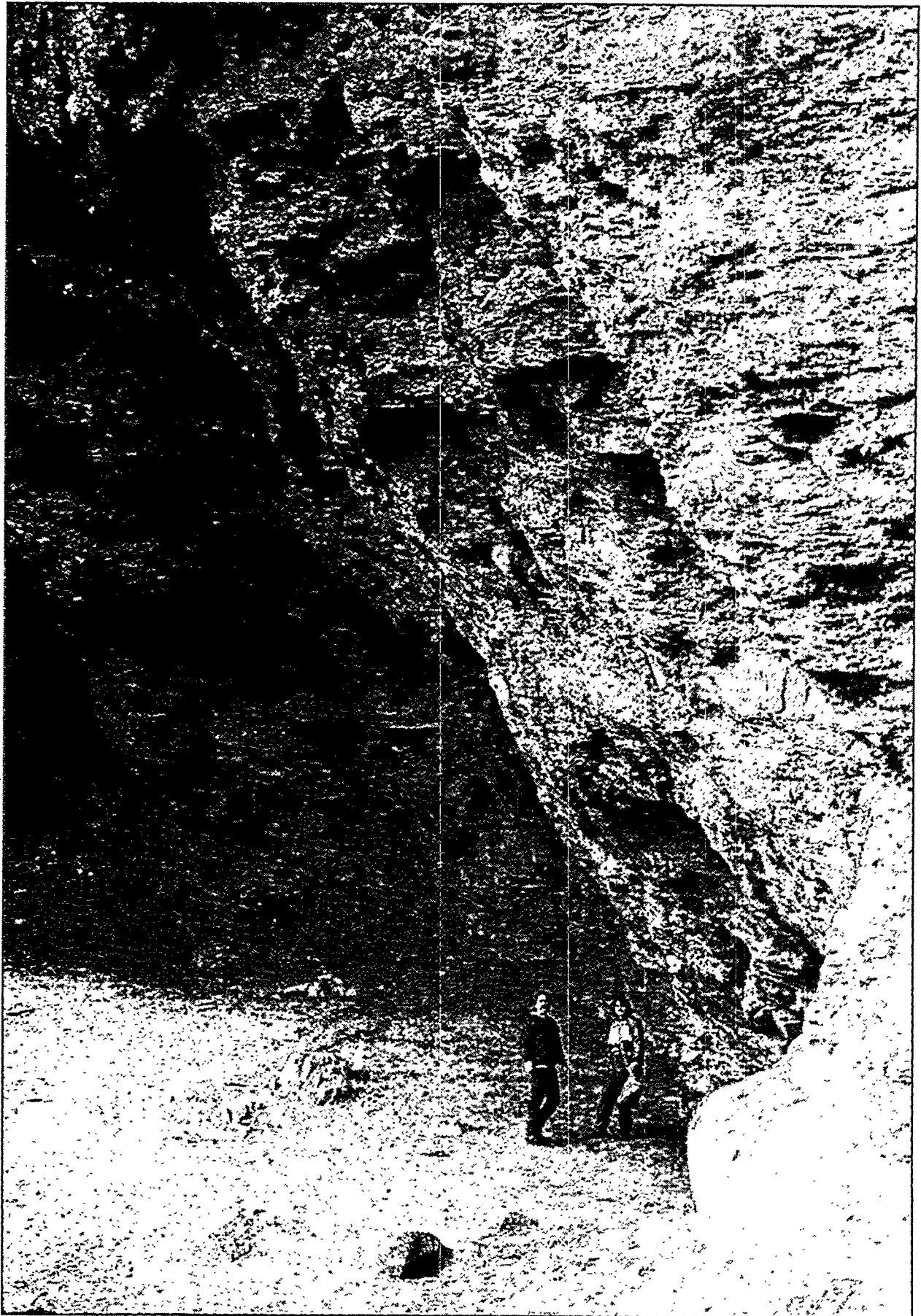


Figure 1. Alum Cave Bluff is actually a natural shelter protected by the overhanging rock. There is no real cave at the site.

2. GEOLOGY

Bedrock at Alum Cave Bluff is the Anakeesta Formation, a dark-gray phyllite of late Precambrian age. It is rich in carbon and pyrite, as is true of much of the Precambrian rock of the area [4]. The chief minerals composing the rock are muscovite, biotite, chlorite, quartz, and pyrite. Chloritoid is commonly observed as 1- to 2- μ m crystals in the finer-grained beds. X-ray fluorescence analysis showed the chloritoid to be near the iron end-member; both manganese and magnesium were very low. Tiny manganese-rich garnet dodecahedra (approximately .75 spessartine, .20 almandine, .05 pyrope [5]) are also present. A bulk chemical analysis of one sample of Anakeesta is given in Table 1; note the comparatively high manganese content, which accounts for the existence of spessartine garnets in the greenschist-facies rock and the presence of apjohnite among the secondary minerals.

Table 1. Bulk chemistry of the Anakeesta Formation

| | | | | | |
|--------------------------------|-------|-------|-------------------------------|-------|--------|
| SiO ₂ | | 55.80 | H ₂ O- | | 0.14 |
| Al ₂ O ₃ | | 23.24 | H ₂ O+ | | 2.73 |
| Fe ₂ O ₃ | | 1.28 | TiO ₂ | | 0.68 |
| FeO | | 2.58 | CO ₂ | | 0.09 |
| MnO | | 1.07 | P ₂ O ₅ | | 0.13 |
| MgO | | 1.39 | SO ₃ | | -- |
| CaO | | 0.52 | S | | 1.30 |
| Na ₂ O | | 2.41 | C | | 2.78 |
| K ₂ O | | 4.37 | BaO | | -- |
| | | | | | 100.51 |

Source: Hadley and Goldsmith [5]

3. SECONDARY MINERAL FORMATION

The pyrite-rich Anakeesta is presently exposed to weathering, and the oxidation of the pyrite produces a weak solution of sulfuric acid and ferrous sulfate. The acid solution then attacks the other minerals of the rock. In addition, the ferrous iron is partly or completely oxidized to ferric iron. The ferric iron in solution also acts as an efficient oxidizing agent; the net result is that acidic water bearing dissolved Fe, Mg, Al, K, Na, Ca, Mn, and sulfate trickles down the face of the bluff. When the acid solution passes beneath the overhang of Alum Cave Bluff, it becomes concentrated by evaporation in the arid microclimate of the rock shelter, and eventually begins depositing sulfate salts. Some of the evaporation and deposition takes place on the face of the rock, but most occurs after the seepage reaches the dirt floor, Figure 2. Some areas of the site are exposed to more direct rainfall and runoff than others, Figure 3, and at these locations the salts were easily seen, even during a moderate rain. The minerals are thus constantly renewed. The suite of minerals deposited at any one place depends on the relative concentrations of the metal ions and on the pH; these constantly change as various salts are precipitated or redissolved, so that the suite of salts varies from place to place within the site and probably changes somewhat with the seasons [6].

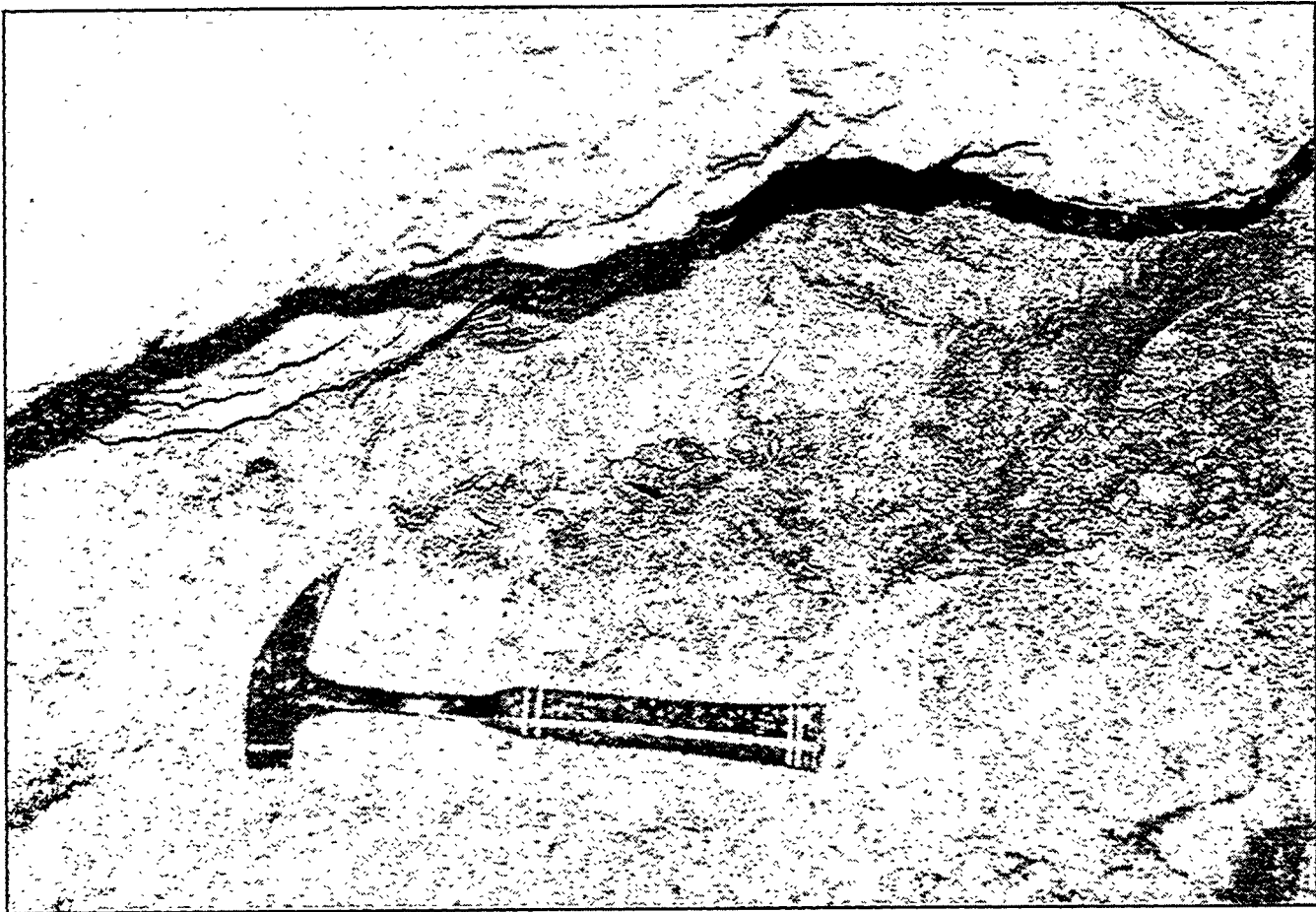


Figure 2. Secondary sulfate minerals accumulating as a shallow subsurface deposit in the soil at Alum Cave.

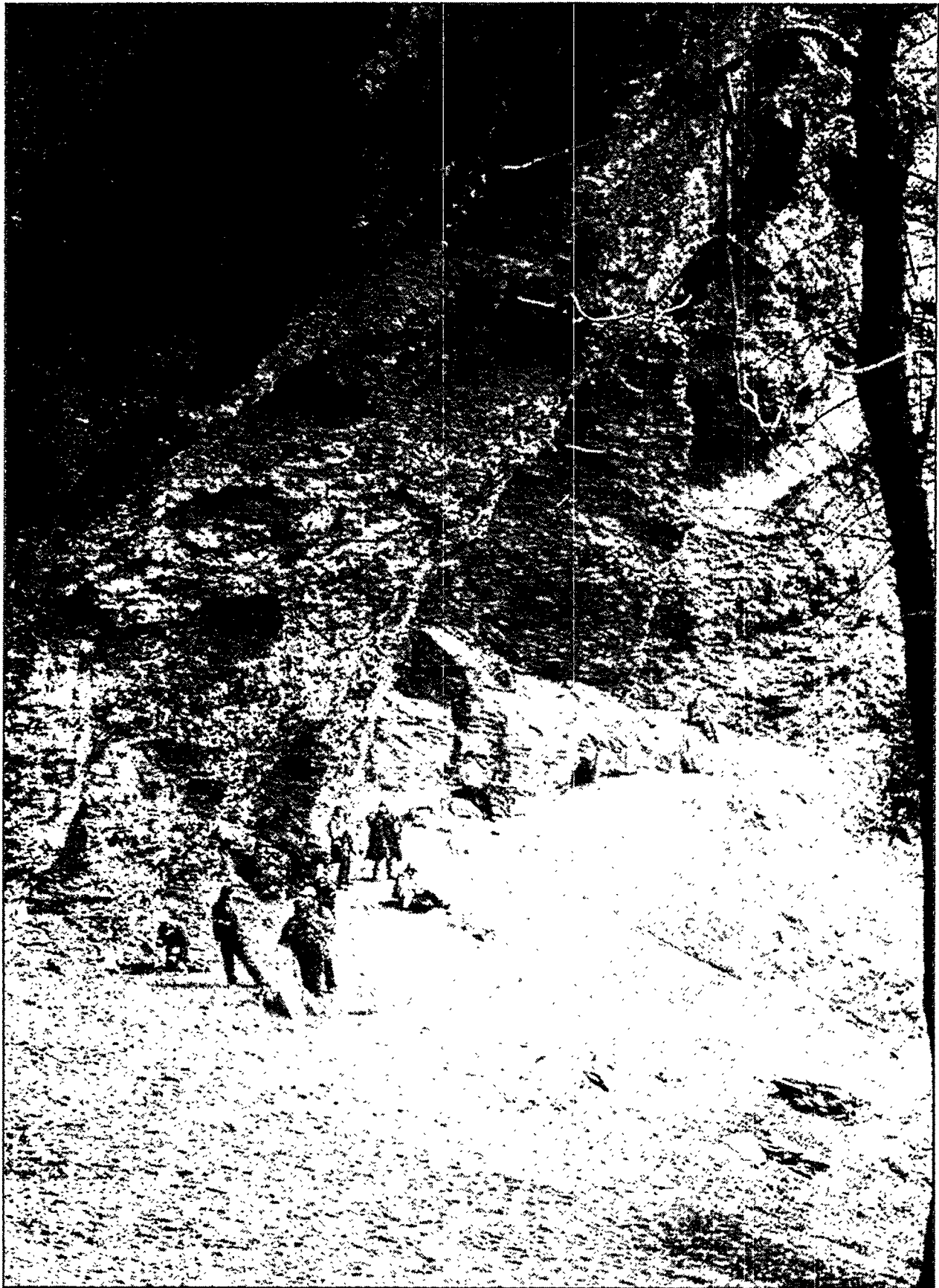


Figure 3. Photo taken during a rain shower. Note the darker area in the lower right, further out from the overhang, which is subject to direct impingement of rainfall and runoff from above.

4. EXPERIMENTAL

Samples of minerals were separated from surrounding soil or were scraped from exposed rock surfaces. Small aggregates generally less than 1 mm, and in some cases tiny isolated crystals, were mounted on carbon stubs and sputter-coated with gold to prevent charging in the SEM. Microscopic examination was done in an ISI model SS-40 scanning electron microscope at 30 kV. Microanalysis employed a Tracor-Northern TN-2000 energy-dispersive X-ray analysis system, in which Na is the lightest element that can be detected.

It is important to note that XRF *alone* cannot be considered a conclusive identification method because it does not detect light elements and the indicated concentrations of metals are semiquantitative at best, particularly when dealing with raw mineral specimens that have not been polished. The presence of impurities and/or X-ray emission from adjacent mineral phases is another complication that must be kept in mind when analyzing natural materials. Consequently, XRF analysis must be supported by consideration of other characteristics such as color, crystal habit, symmetry, etc., and of course, by the experience of the microscopist.

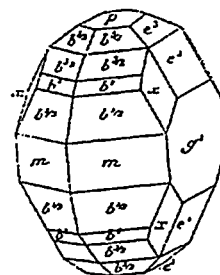
5. RESULTS

Illustrations of individual minerals and selected mineral associations were selected from well over 100 photomicrographs and approximately 70 XRF analyses. When a particular identification is tentative, it is indicated by (?) after the mineral name. Crystal drawings are taken from Goldschmidt [7]. Representative XRF data are reproduced in the Appendix.

Sulfur

S

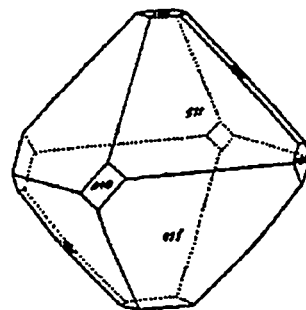
Elemental sulfur occurs as minute ($\sim 100 \mu\text{m}$) sharp to rounded clear highly modified crystals. Figure 4 shows several small crystals on apjohnite.



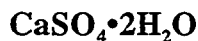
Tschermigite?



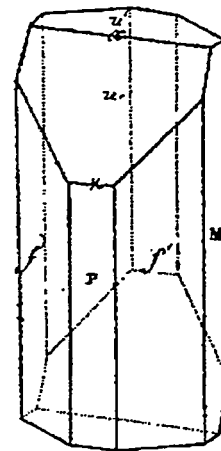
Tiny ($\sim 200 \mu\text{m}$) sharp clear colorless octahedra and cubooctahedra were tentatively identified as an alum group mineral from their morphology and general appearance. A typical example (Figure 5) had $\text{S}:\text{Al} \approx 2:1$ as expected, *but no K was present*. The tentative identification of this material as tschermigite is consistent with these observations.



Gypsum



The morphology of gypsum at Alum Cave ranges from the fairly typical bladed shape, to a more acicular habit that a casual observer could mistake for one of the hair salts. An example of gypsum in the acicular habit is shown in Figure 6.



Epsomite



Epsomite forms glassy-clear fibrous to columnar masses, as well as some euhedral prismatic terminated crystals to $5 \mu\text{m}$ (resembling commercial Epsom salt), Figure 7. Under dry conditions epsomite irreversibly loses up to $1 \text{H}_2\text{O}$, altering to hexahydrate [8].

Melanterite **$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$**

Melanterite ranges from pale-green to colorless, euhedral crystals to "ram's horn" fibers, rounded masses, and coatings, Figure 8. Melanterite alters to opaque white pseudomorphs (the pentahydrate or lower hydrates) in dry air [8].

Apjohnite **$(\text{Mn,Mg})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$**

Clear needles and silky masses of typical hair-salt appearance, Figure 9, were very common. Most specimens of hair salt were identified as magnesian apjohnite by semiquantitative XRF analysis (most analyses showed $\text{Mn} > \text{Mg}$, with little or no Fe).

Pickeringite? **$(\text{Mg,Mn})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$**

Pickeringite forms a solid solution series with halotrichite and apjohnite, and is distinguishable with certainty only by analysis. The hair salt samples analyzed in this study were much more frequently apjohnite; even many samples intimately associated with epsomite proved to have $\text{Mn} > \text{Mg}$. Some XRF analyses of hair salt showed approximately equal amounts of Mg and Mn, with Mg slightly greater than Mn, but a definite confirmation of pickeringite will require a more quantitative analysis.

Halotrichite **$\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$**

Silky white to yellowish fibrous masses and free-standing acicular crystals with no visible terminations are shown in Figure 10. The halotrichite was associated with melanterite, and its identity was confirmed by XRF. With pickeringite and apjohnite, gave name to locality ("iron alum").

Alunogen? **$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$**

Colorless to grayish very thin plates with elongated pseudo-hexagonal outline (micaceous habit), Figure 11, ~100-300 μm , associated with magnesiocopiapite on rock surfaces and crevices. Identification of this specimen as alunogen is highly speculative at this time; it is consistent with semiquantitative XRF analysis (only Al and S detected; $\text{S} > \text{Al}$), but one would normally expect alunogen to be fibrous. As noted in Dana [9], however, "Crystals [are] small and rare; prismatic $\{001\}$ or $\{010\}$ with a six-sided outline about $[010]$." So it is conceivable that the micaceous crystals in Figure 11 are indeed alunogen.

“Jarosite” (probably Ammoniojarosite) $(\text{NH}_4)\text{Fe}^{+3}(\text{SO}_4)_2(\text{OH})_6$

Crusts of minute yellow to red-brown crystals (pseudocubic or flattened rhombohedron and pinacoid) to about 200 μm , Figures 12 and 13. First identified as jarosite-group mineral from color, habit, and insolubility [6]; the present identification is based on XRF (no K or Na was detected in any samples analyzed). Some jarosite and/or natrojarosite could be present at Alum Cave, although neither was present in the five “jarosites” analyzed by XRF.

Aluminite? $\text{Al}_2\text{SO}_4(\text{OH})_4 \cdot 7\text{H}_2\text{O}$

Masses of snow-white to yellow-stained matted fibers ($\sim 2 \times 20 \mu\text{m}$), Figure 14, associated with gypsum and iron oxide. Tentatively identified by XRF ($\text{S}:\text{Al} \simeq 1:2$) and by the acicular/fibrous habit.

Basaluminite? $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$

Creamy-white, very fine-grained crystalline masses were associated with gypsum. At very high magnification, SEM shows well-crystallized material in very thin foliated crystals, Figure 15. Tentatively identified as basaluminite by XRF ($\text{S}:\text{Al} \simeq 1:4$).

Botryogen? $\text{MgFe}^{+3}(\text{SO}_4)_2(\text{OH}) \cdot 7\text{H}_2\text{O}$

Very tiny rosettes of bladed pale-orange crystals, Figure 16, have a radiating habit that is not inconsistent with a tentative identification as botryogen. XRF analysis supports this as well, showing $\text{S}:(\text{Fe}+\text{Mg}) \simeq 1:1$, although the spectrum suggests some substitution of Fe^{+2} for some of the Mg, which is well known in this mineral [10].

Slavikite $\text{MgFe}^{+3}_3(\text{SO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$

Sharp euhedral glassy-clear greenish-yellow (fresh) to translucent orange (altered) crystals of tabular habit with a combination of rhombohedron and pinacoid, sometimes modified by minor rhombohedra, Figures 17 and 25, about 100 to 300 μm , were originally identified by as slavikite by (powder) X-ray diffraction [11]. This appears to be the only known North American locality [6]. The formula given is that of Gordon [12] on the only other (comparatively) large crystals, from Argentina. XRF analysis of the Alum Cave Bluff material showed a trace of Mn but did not detect sodium; however, the type material from Bohemia may have contained impurities. A trace of manganese was also found. The crystals from Alum Cave Bluff show a slight pearly luster on the basal pinacoid, suggesting the existence of a perfect basal cleavage which has not been recorded in earlier descriptions. The SEM photographs, Figure 17, clearly show the crystals splitting into thin flexible lamellae along this cleavage, suggesting that slavikite may have a sheet sulfate structure akin to that of spangolite, langite, etc. [6].

Magnesiocopiapite $\text{MgFe}^{+3}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$

Crusts and masses of tiny yellow flakes, Figure 18, illustrate the characteristic habit of magnesiocopiapite. Copiapite $[(\text{Fe},\text{Mg})\text{Fe}^{+3}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}]$ is probably also present at Alum Cave, but all of the samples analyzed in this study have significant Mg and are properly classed as magnesiocopiapite.

Diadochite $\text{Fe}^{+3}_2(\text{PO}_4)(\text{SO}_4)(\text{OH}) \cdot 6\text{H}_2\text{O}$

Buff to salmon masses of minute powdery (few tens of microns) crystals to rare tiny (100 μm) blocky euhedral crystals, Figures 19 and 20, were identified by XRD and XRF. The diadochite crystals occurred in and on rock in soil associated with acicular gypsum crystals, and in soil salts [6]. The formula presented here, with six waters of hydration instead of five, has been determined recently by a crystal-structure analysis [13].

Coskrenite-(Ce) $(\text{Ce},\text{Nd},\text{La})_2(\text{SO}_4)_2(\text{C}_2\text{O}_4) \cdot 12\text{H}_2\text{O}$

Tiny (<800 μm) squarish to wedge-shaped platy crystals, commonly with lozenge-shaped cross section, Figures 21 and 22, were analyzed by XRF and provided the first surprising evidence of rare earth minerals at Alum Cave. The spectrum showed only rare earth elements (REE) and sulfur, from which it was surmised that the mineral was a REE sulfate (a REE sulfide would not be stable under the conditions at Alum Cave and would likely not be transparent). This mineral occurs in association with apjohnite and epsomite, and sometimes with slavikite, jarosite, tschermigite, and the two related minerals levinsonite and zugshunstite described below. Some is in radiating masses completely embedded in hair salt. A few crystals are cream-colored; most, however, are pale pink under incandescent lights, pale blue-gray under fluorescent light, and nearly colorless in sunlight. (It is well known that in glasses [14], as well as in many host crystals [15], the very sharp absorption bands of Nd^{+3} make the observed color particularly dependent on the spectral energy of the illuminating light. Gemologists often refer to this phenomenon as color-change or "alexandrite effect", although in alexandrite REE ions are not responsible for the coloration.) Formal descriptions of this and the two following REE minerals are in progress and the names have been approved by the International Mineralogical Association; the formulas given here are based mostly on completed structure analyses and electron microprobe analyses [13], with REEs determined partly by XRF analysis. Coskrenite, levinsonite, and zugshunstite are the first naturally-occurring rare-earth sulfates or oxalates, and the first minerals that contain both oxalate and another anion (sulfate in the present case) [6].

Levinsonite-(Y) $(Y,Nd,Ce)Al(SO_4)_2(C_2O_4) \cdot 12H_2O$

The second REE mineral forms sharp euhedral colorless to white prismatic crystals with orthorhombic aspect (but true symmetry is monoclinic [13]). Tiny rectangular prisms with transverse striations, to several hundred μm , are shown in Figure 23. A second habit is slightly elongated rectangular tablets, Figures 24 and 25. This mineral has somewhat lower solubility than that of the hair salts and can be exposed by partially dissolving the hair salts with water. This mineral and the following one have the same formula except for the nature of the dominant REE. Both minerals are present within a centimeter of each other in one specimen, and this occurrence may represent a rare example of the stable coexistence of Ce- and Nd-dominant minerals, although the yttrium ion, which is smaller than neodymium, may be necessary to stabilize levinsonite-(Y).

Zugshunstone-(Ce) $(Ce,Nd,La)Al(SO_4)_2(C_2O_4) \cdot 12H_2O$

The third new mineral forms sharp glassy-clear crystals with blocky habit, monoclinic in aspect, Figures 26 and 27. The mineral shows the same colors (and color-change effects) as coskrenite, but slightly paler. Only a few specimens of this mineral, with several crystals, were found in soil salts [6].

6. DISCUSSION

Many of the sulfates illustrated in this report are highly soluble in water. Exceptions are jarosite and diadochite (nearly insoluble); gypsum (slightly soluble); and slavikite (slowly soluble with decomposition). Some of the minerals are unstable and normally dehydrate under dry conditions as noted in the descriptions. The present study is not exhaustive; moreover, the minerals present at any one time are subject to change, depending on the temperature and humidity. It should be noted that Mount LeConte receives 80-100 inches of rainfall annually [16]. It is perhaps surprising that such a productive soluble-salt locality should exist in one of the wetter places in the country.

The surprising discovery of three rare-earth-element sulfate-oxalates identified in this study may have significant implications for our understanding of rare-earth geochemistry. Minute amounts of these minerals have been found as tiny crystals in masses of hair salt (apjohnite) in the soil. The rare-earth elements were presumably leached from the Anakeesta; it is surprising that the REE concentration in the leachate was high enough to precipitate these remarkable minerals. No REE analyses are available for the Anakeesta, but REEs are ubiquitous in nature in trace amounts. A part of the explanation may be in the efficient mobilization of REEs through oxalate chelation. The oxalate ion no doubt originated from the leaching of decaying organic material in the overlying soil and forest litter. The existence of these minerals in the absence of other oxalate minerals at the site might imply that oxalate has a great affinity for REEs or that REE oxalates are less soluble than other oxalates. Further study of these interesting species will contribute to our understanding of the mobility of REEs under weathering conditions.

The radii of the REE ions are much larger than the radii of the other trivalent ions at the locality (Al^{+3} and Fe^{+3}), and the REEs are therefore unsuitable for substitution into the structures of the other salts at the locality. The low formation temperature (probably the lowest temperatures for any known REE minerals) further lowers the tolerance of the structures for foreign ions. Moreover, the low temperature should permit a more complete fractionation of the REEs between minerals, a prediction supported by the preliminary data afforded by the XRF analyses.

7. COLLECTION OF SECONDARY SULFATES AT ALUM CAVE

Alum Cave Bluff is within a National Park; therefore, collection of mineral specimens or other disturbance of the site is not generally permitted. Unauthorized collecting may be prosecuted under Title 36, Code of Federal Regulations.

The samples used in this study were obtained under a collecting permit for scientific research. Our future plans are to study the distribution of minerals throughout the site in a systematic way, to determine if/how the mineral assemblages vary with local microclimate and with seasonal weather conditions.

8. ACKNOWLEDGEMENTS

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Thanks are due to the administration of Great Smoky Mountains National Park, for permission to collect specimens at the Alum Cave site. Kathleen Manscill, Museum Curator for Great Smoky Mountains National Park, provided historical information. The author is grateful to Prof. Donald R. Peacor for permission to use names and preliminary data on the new REE sulfates, now being studied by his group at the University of Michigan.

The illustrated specimens were collected by A. D. McMillan (Oak Ridge National Laboratory), T. D. Coskren (Geo-Marine, Inc.), and the author. Photographs of the site (Figures 1-3) were taken by Roni McMillan. The manuscript was reviewed by Arvid Pasto and Claudia Rawn. Cathy Cheverton prepared the manuscript for publication.

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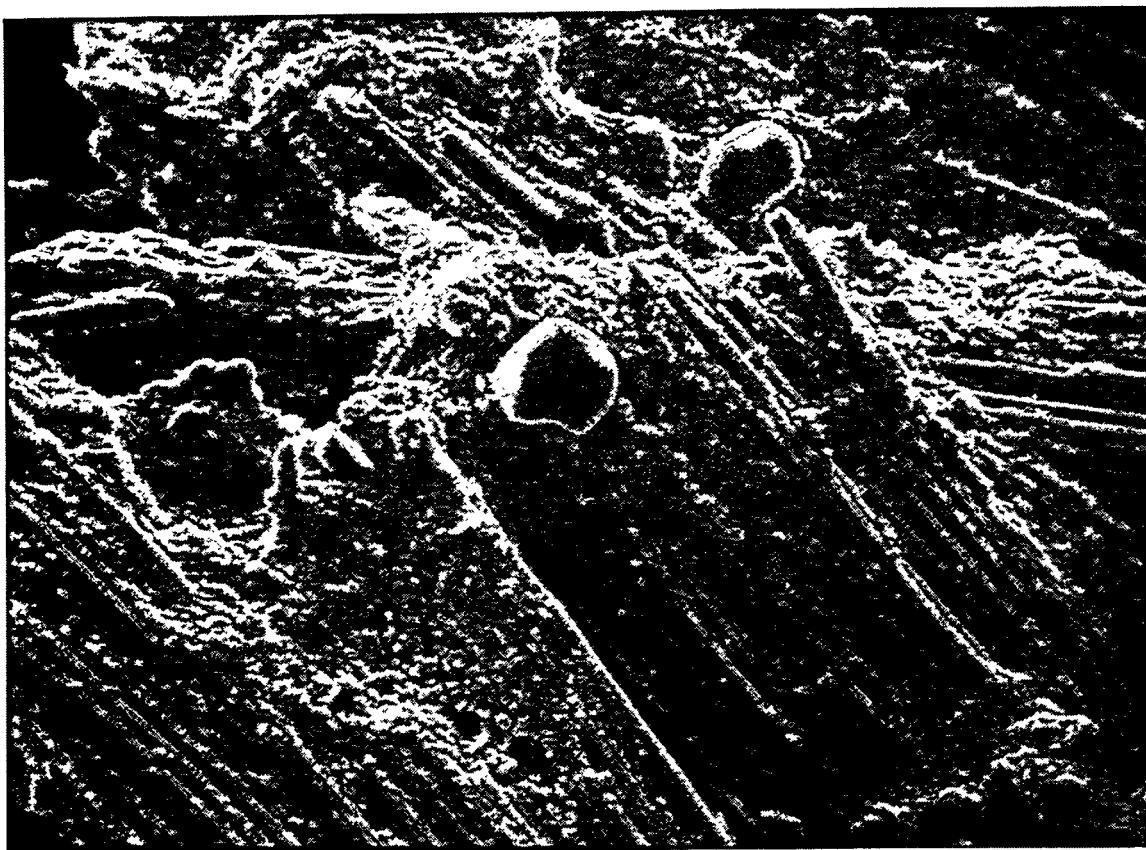


Figure 4. Small rounded crystals of native sulfur on hair salt (apjohnite). The sulfur crystals are about 100 μm in diameter.



Figure 5. Crude octahedral crystals $\sim 50\text{-}100\ \mu\text{m}$ presumed to be tschermigite.



Figure 6. Acicular gypsum crystals $\sim 25\ \mu\text{m}$ diameter, which to the unaided eye might appear to be hair salt. The terminations visible at this magnification are characteristic of gypsum, and the chemical analysis confirms the identification.

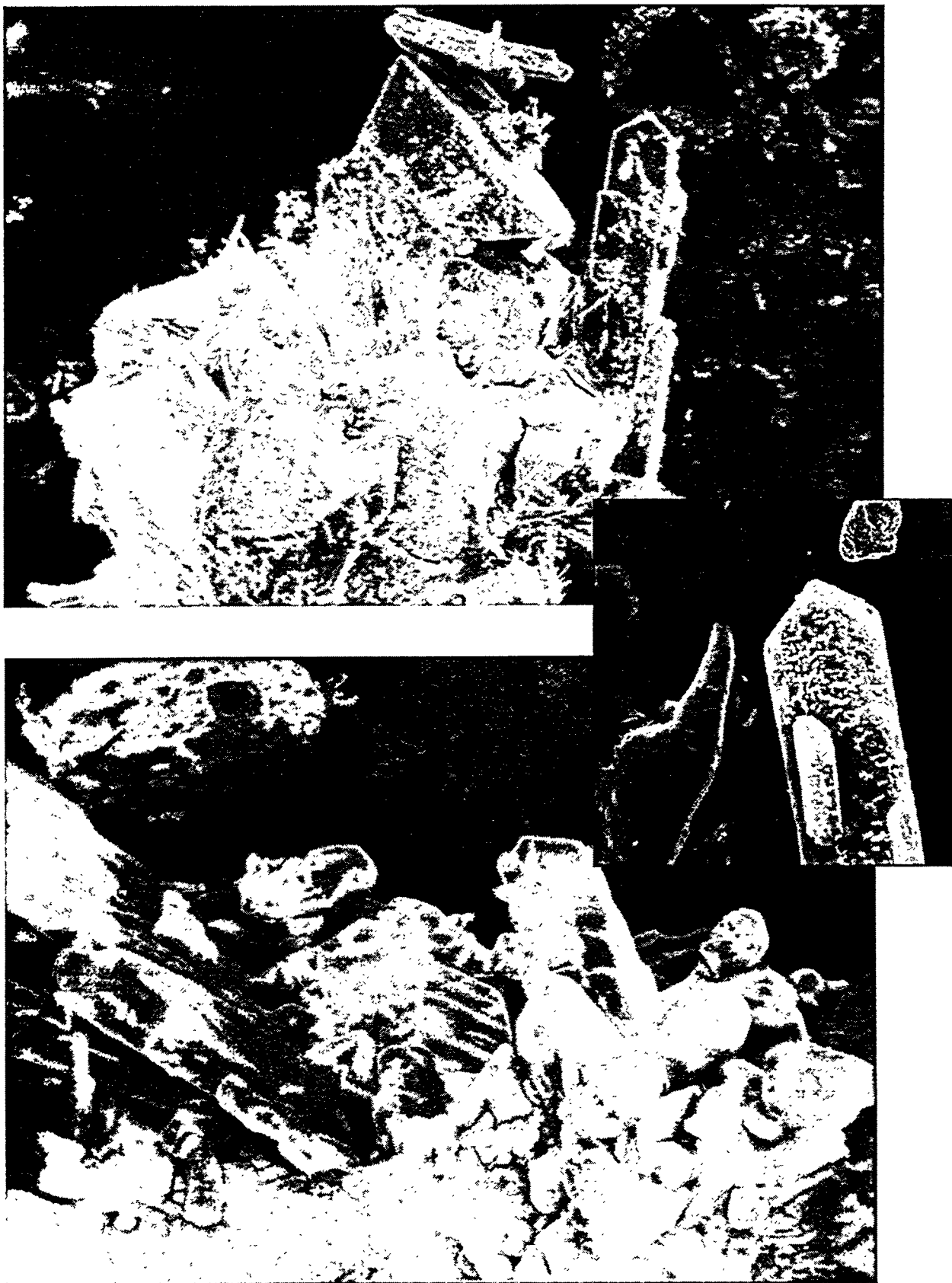


Figure 7. Epsomite crystals. Top: crystal on matrix from Alum Cave. Bottom: glassy, rounded crystals on rock fragment collected in soil during rainy conditions. Inset: commercial Epsom salt.

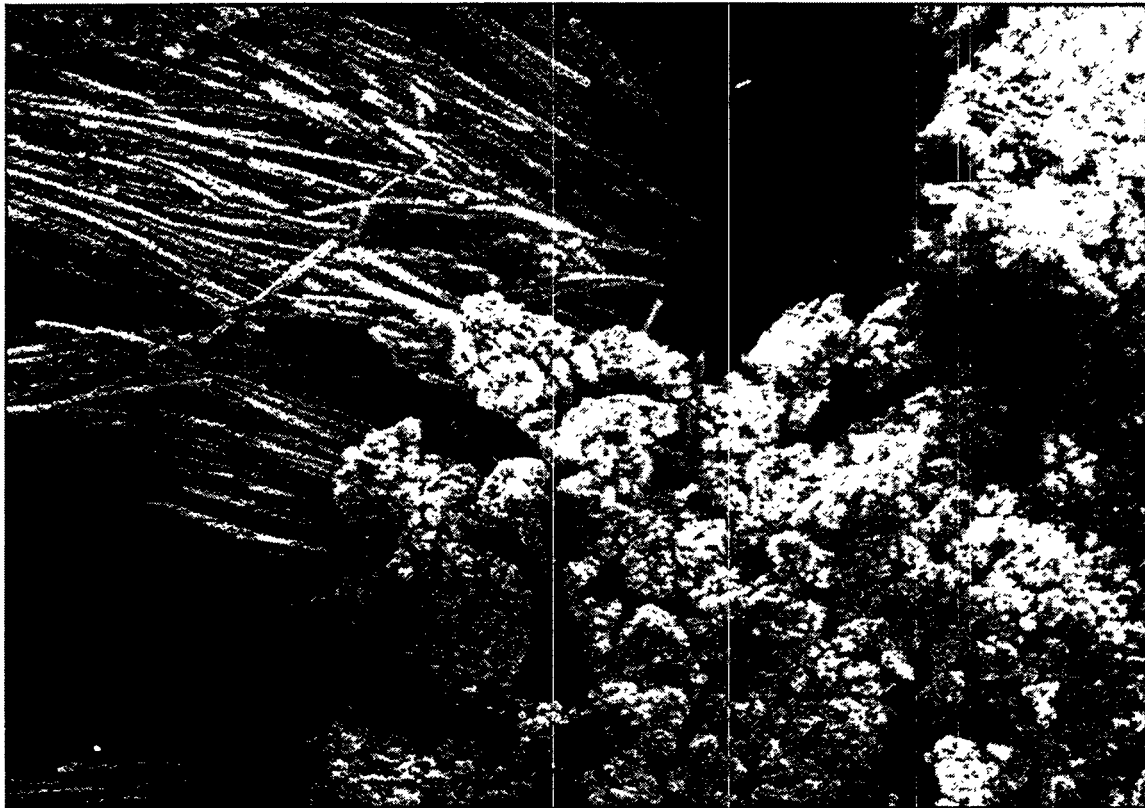
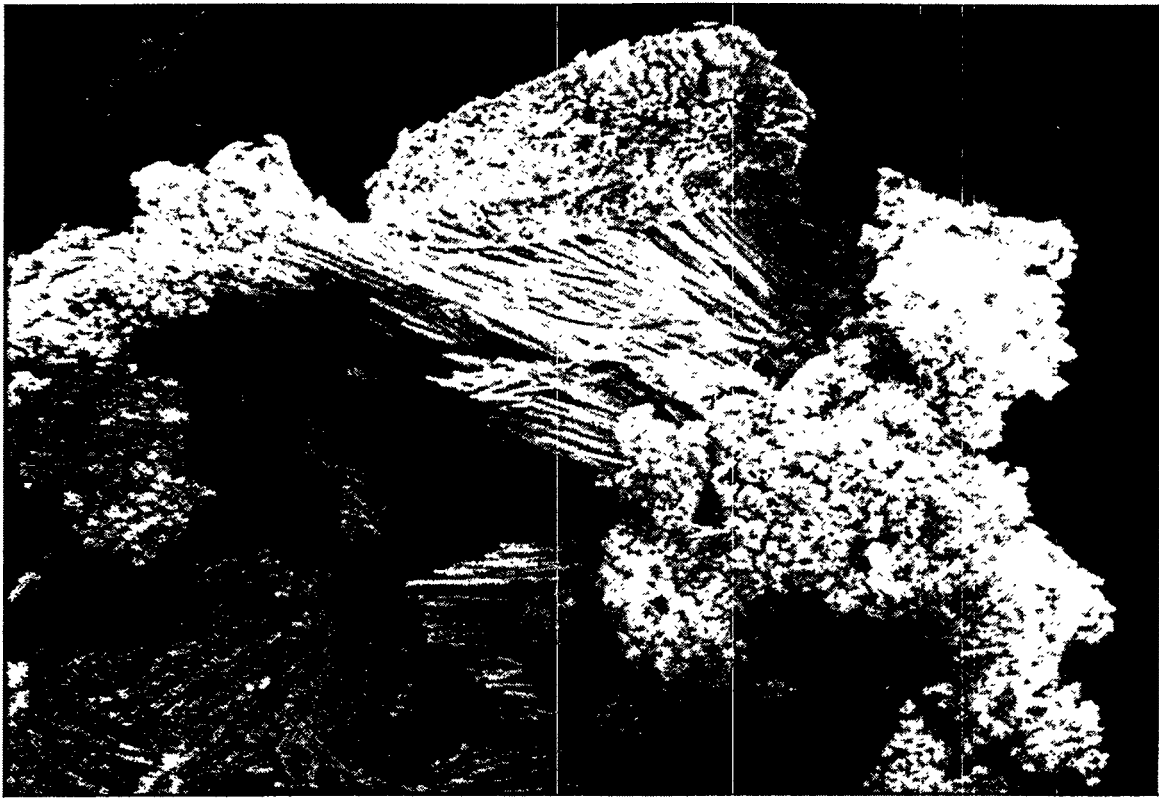


Figure 8. Top: 300 μm aggregates of melanterite forming cauliflower-like masses on halotrichite. Bottom: detail of melanterite aggregate.

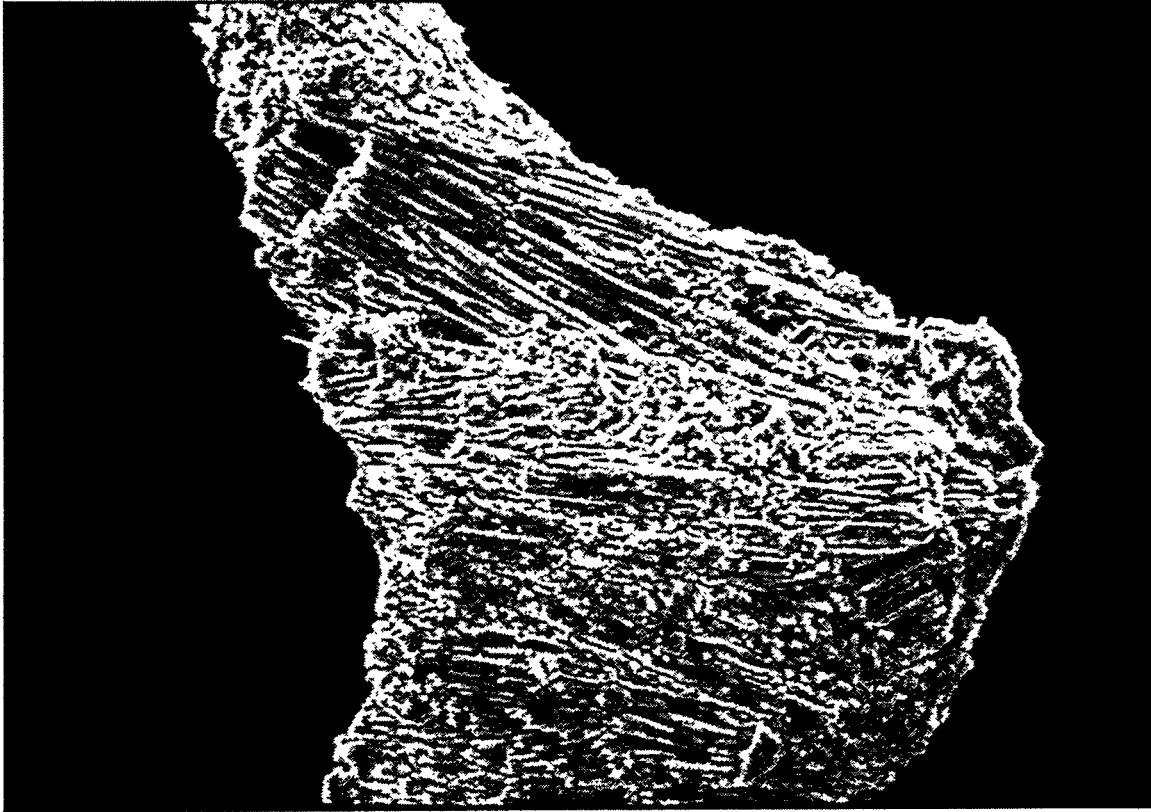


Figure 9. Acicular crystals of apjohnite, one of the “hair salts” showing characteristic subparallel needles forming a solid mass.



Figure 10. Slightly curved fibrous crystals of halotrichite, another of the "hair salts".



Figure 11. Micaceous plates $\sim 100\ \mu\text{m}$ diameter, of an aluminum sulfate (possibly alunogen). If the sample is indeed alunogen, it is a fairly uncommon habit for the mineral, which is more typically fibrous [8].



Figure 12. A jarosite group mineral, presumably ammoniojarosite.



Figure 13. Another “jarosite” from a different sample.



Figure 14. Minute fibers with S:Al \approx 1:2, presumed to be aluminite.



Figure 15. Foliated crystals with S:Al \approx 1:4, consistent with the composition of basaluminite.



Figure 16. A 100 μm rosette of bladed crystals whose composition suggests a slightly ferroan botryogen.

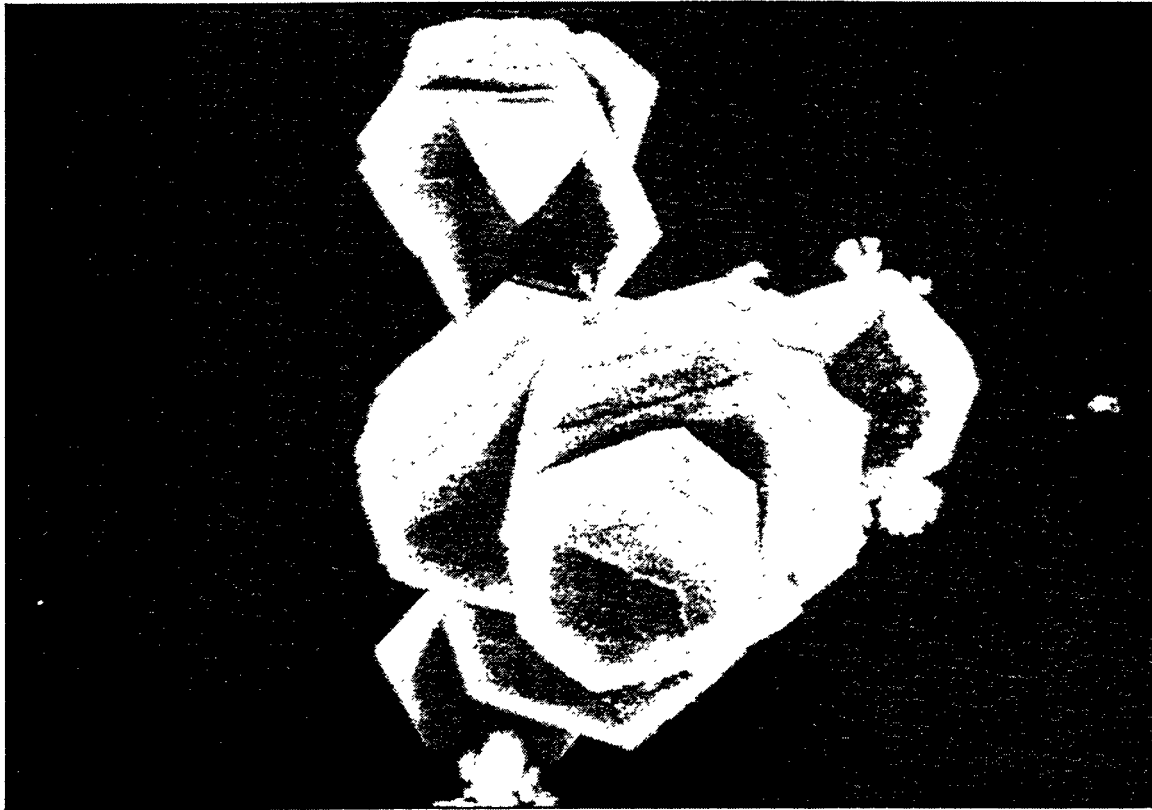


Figure 17. Top: A small group of slivkite crystals (largest is about 70 μm across). Bottom: Slivkite crystal separating along basal cleavage into laminae about 2 μm thick.



Figure 18. Tabular 5 μm crystals of magnesiocopiapite. Top: View of sample showing arrangement of crystals in a scaly mass. Bottom: Another sample with individual crystals showing prominent cleavage.



Figure 19. Euhedral diadochite crystals about 10 x 20 μm on massive earthy material.

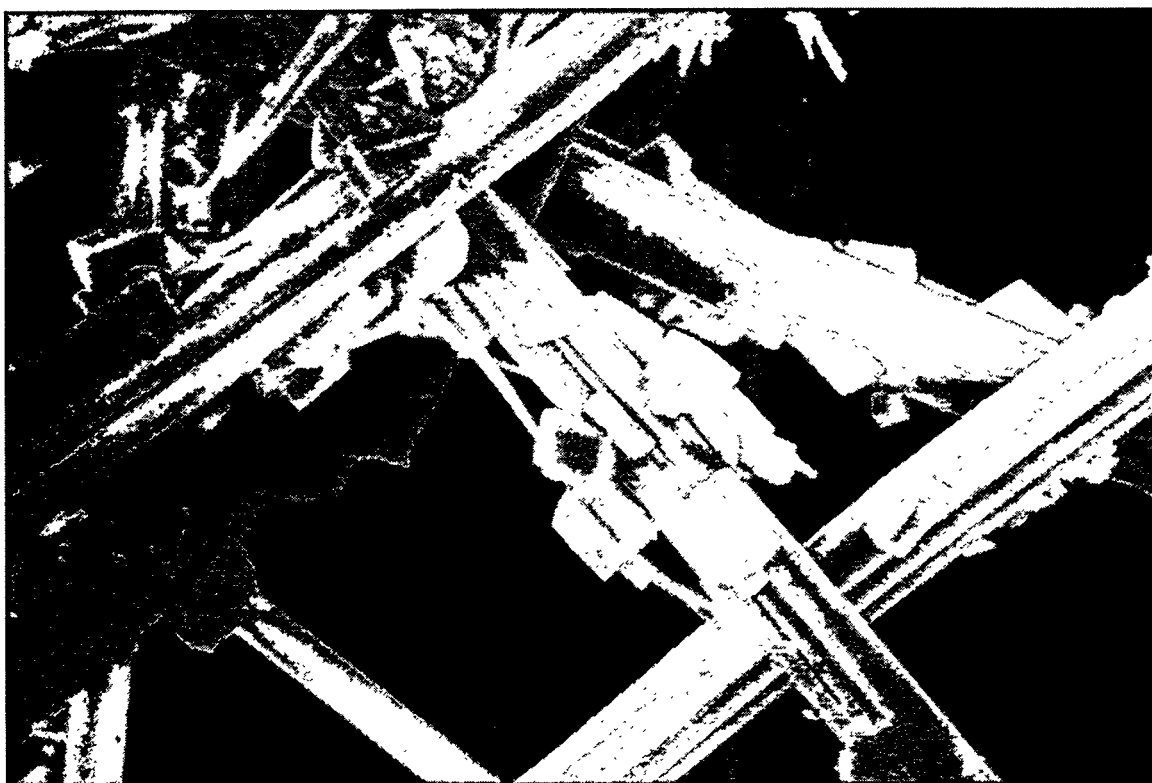


Figure 20. Diadochite crystals similar to those in Figure 19 but growing in clusters on acicular gypsum.

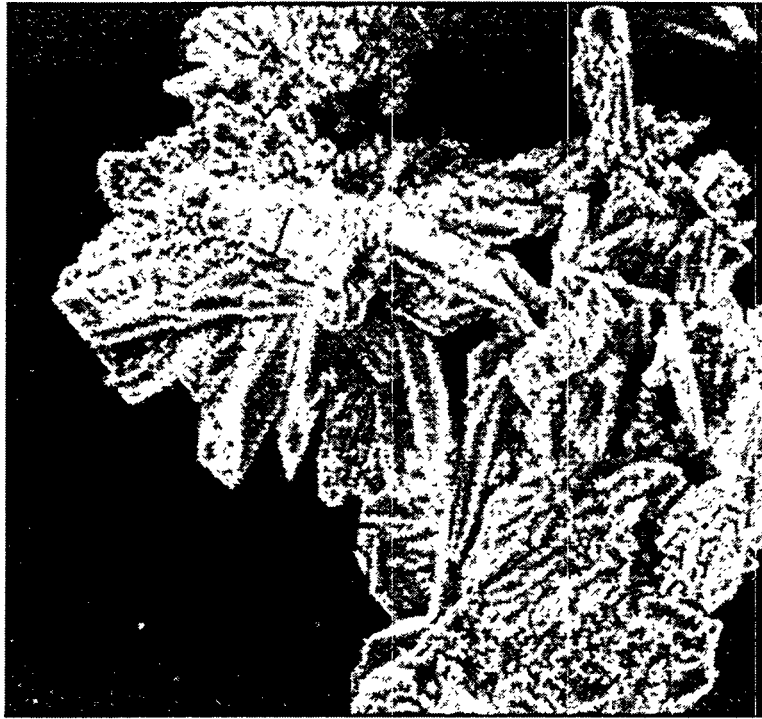


Figure 21. Platy crystals of coskrenite-(Ce), the largest of which are about 100 μm long, forming radiating clusters. These particular crystals were cream-colored in natural light. XRF showed $\text{Ce} > \text{Nd} > \text{La}$ and $(\text{Ce} + \text{Nd} + \text{La}) : \text{S} \approx 1 : 1$.

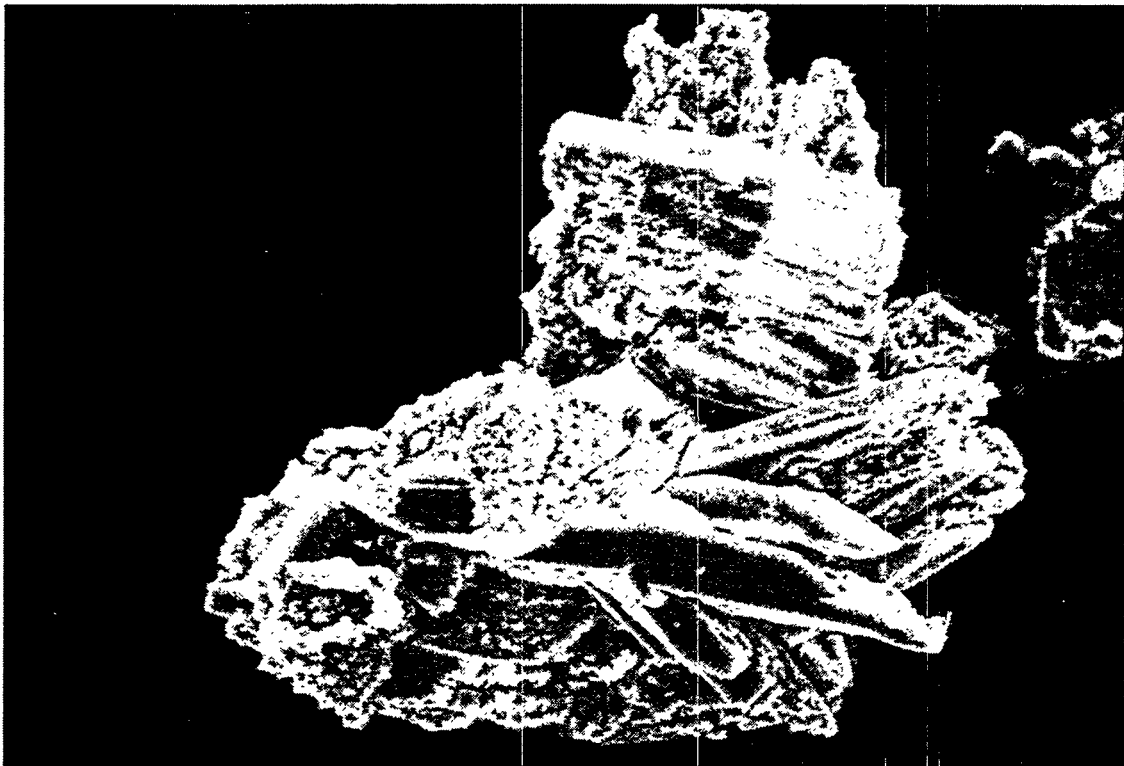


Figure 22. Another sample of coskrenite-(Ce); although these crystals were pink, the XRF data showed no discernable difference from the composition of the cream-colored crystals shown above.

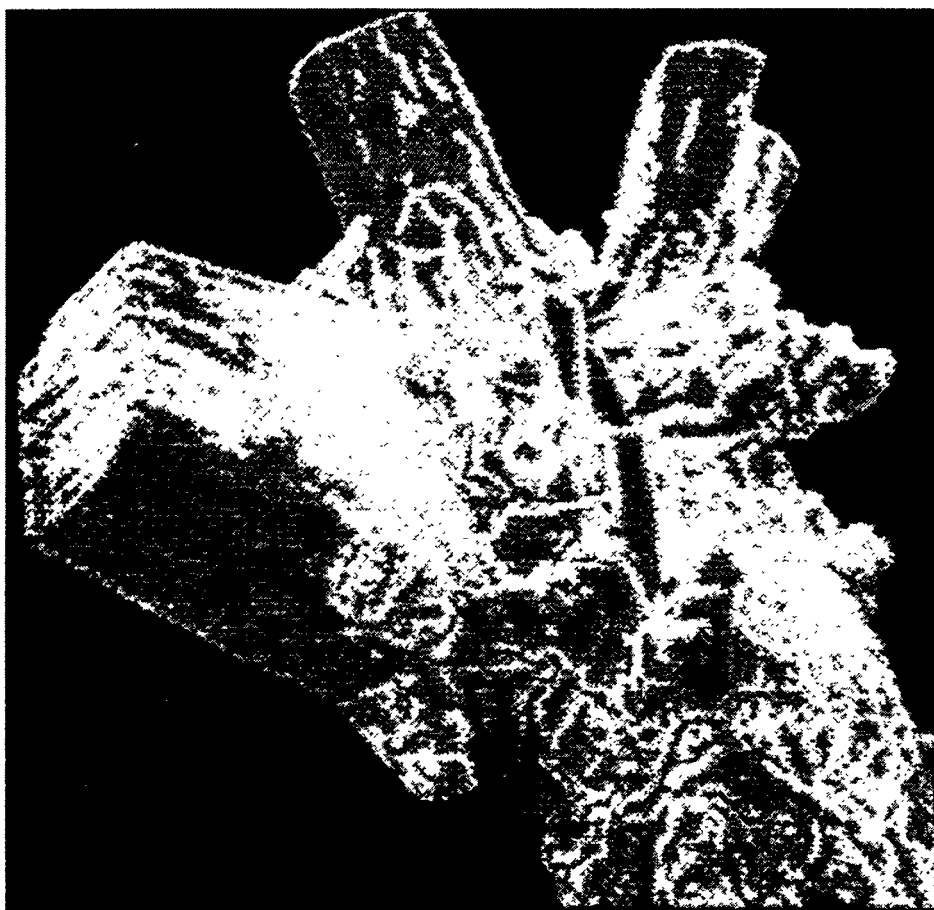


Figure 23. Euhedral crystals of levinsonite-(Y), the largest of which is about 75 x 100 x 150 μm .



Figure 24. A crystal of levinsonite-(Y) in the form of a simple elongated tablet.

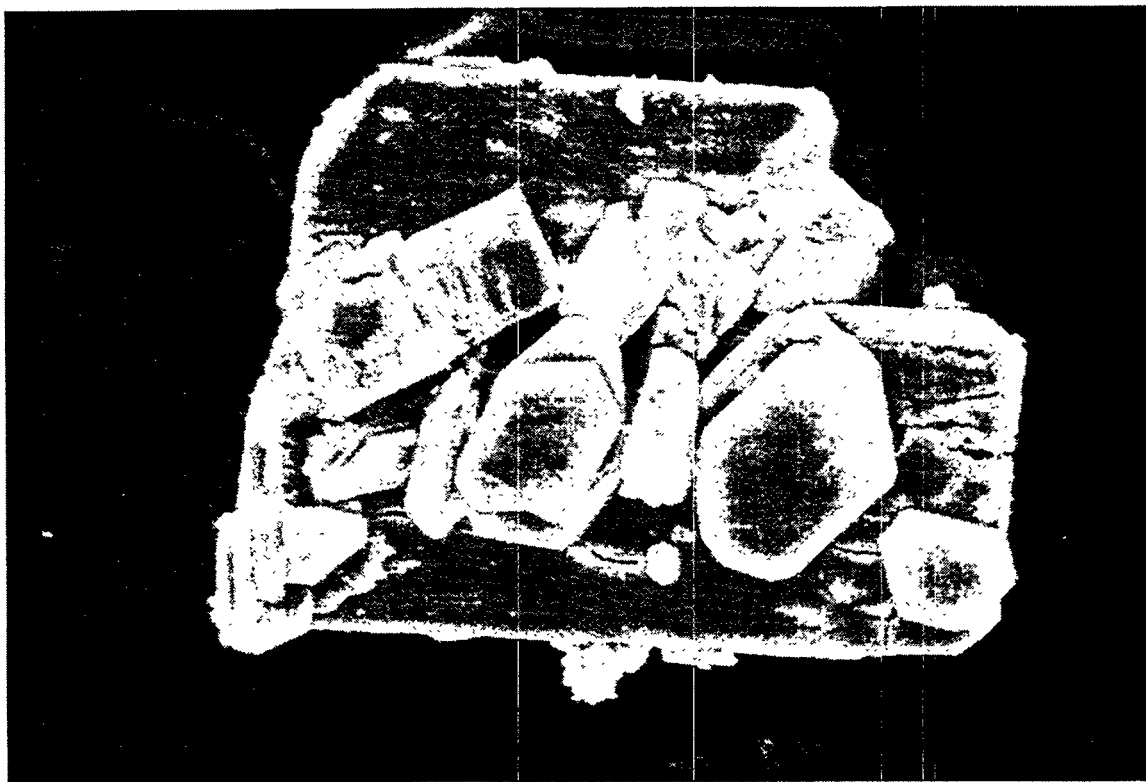


Figure 25. Slavikite crystals attached to a crystal of levinsonite-(Y).



Figure 26. Blocky crystals of zugshunsite-(Ce), the largest of which is about 250 μm .



Figure 27. Single crystal of zugshunsite-(Ce) with a habit very similar to epsomite.

APPENDIX A
Selected X-ray Fluorescence Spectra

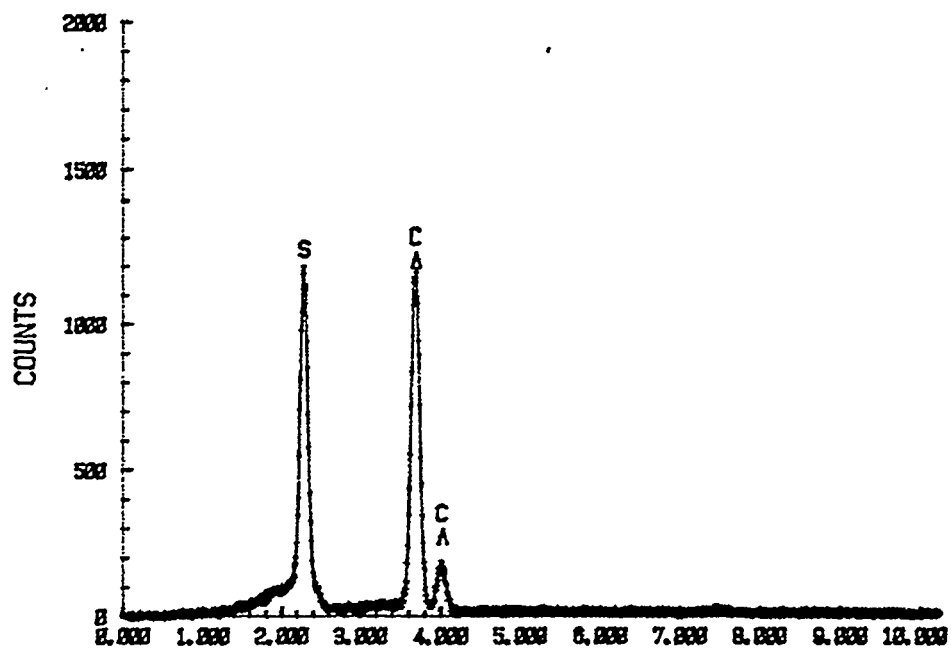


Figure A-1. Gypsum

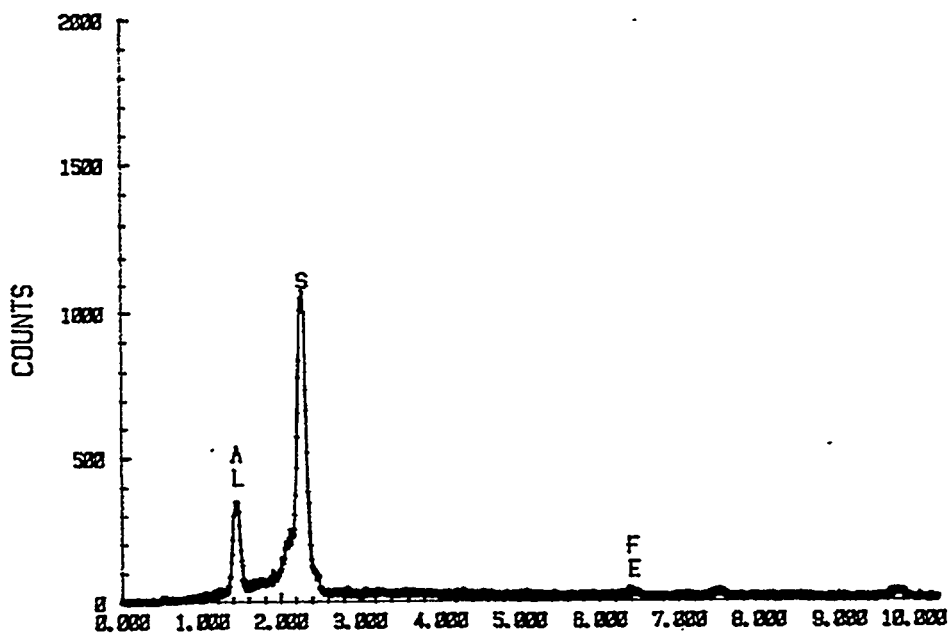


Figure A-2. Tschermigite

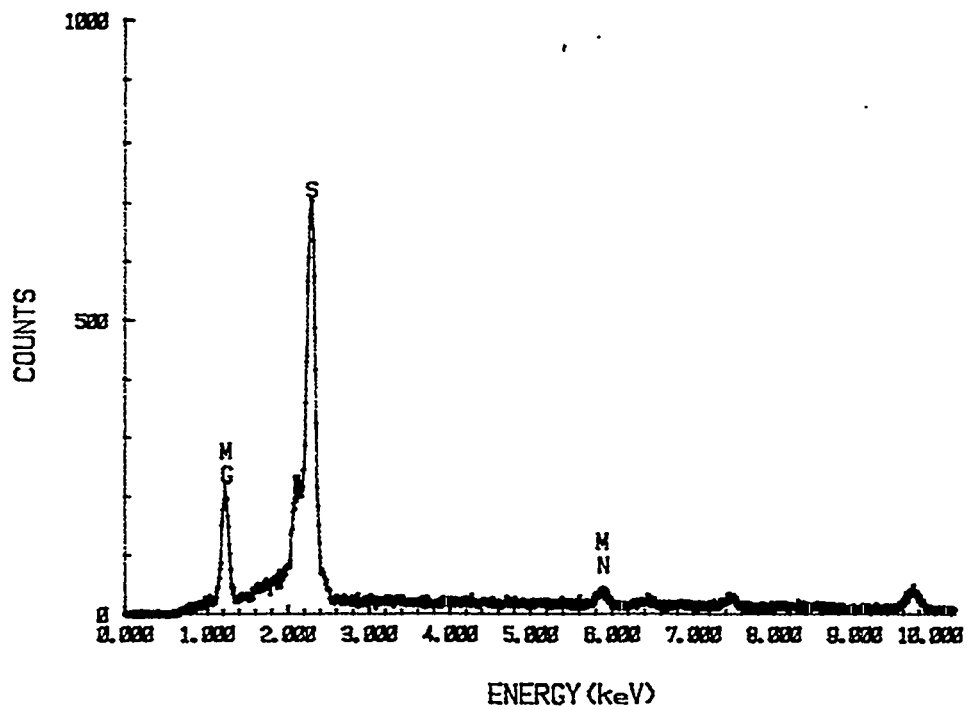


Figure A-3. Epsomite

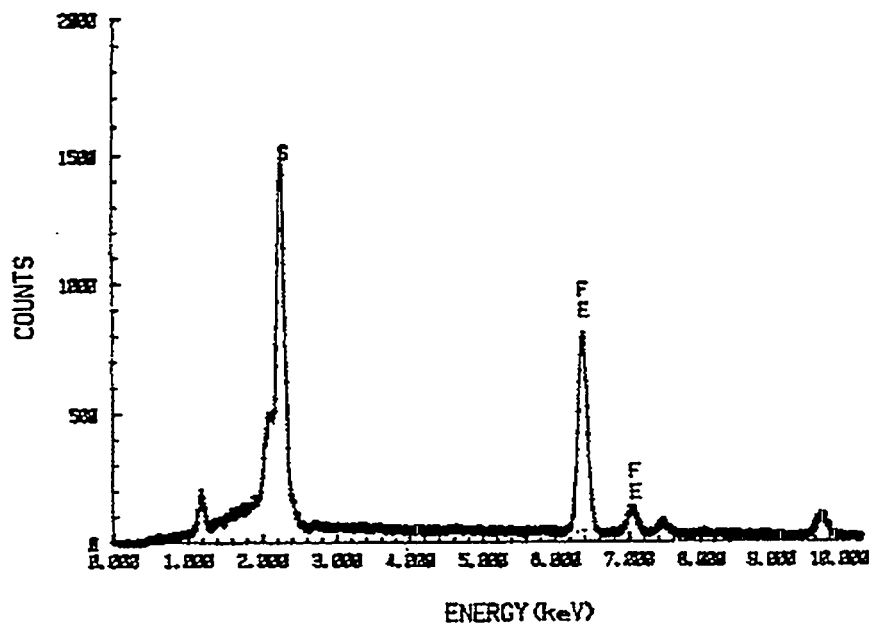


Figure A-4. Melanterite

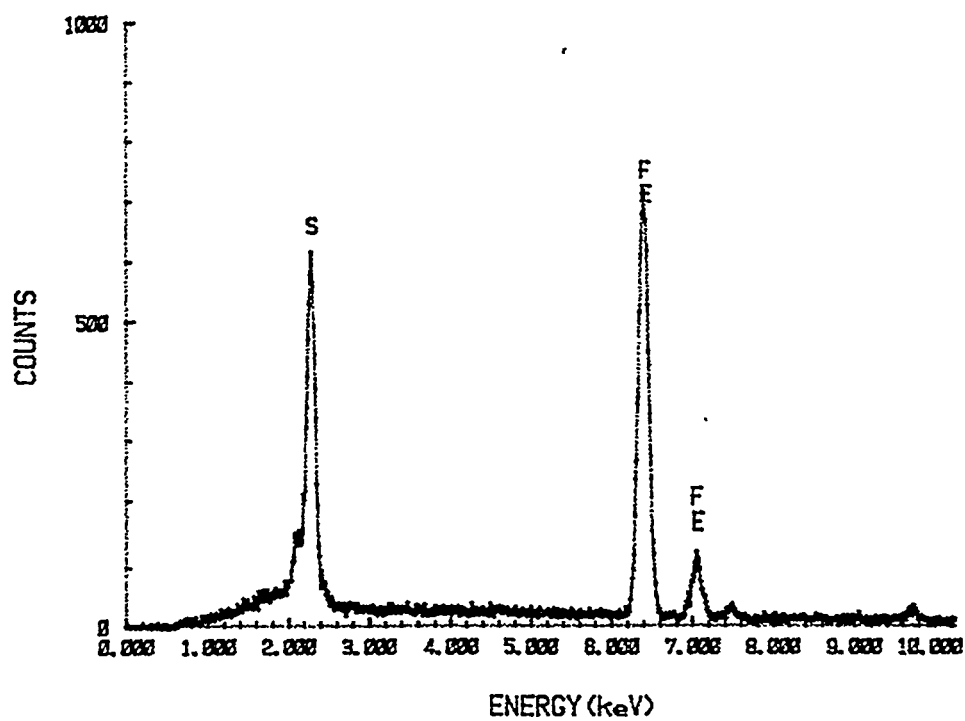


Figure A-5. Ammoniojarosite

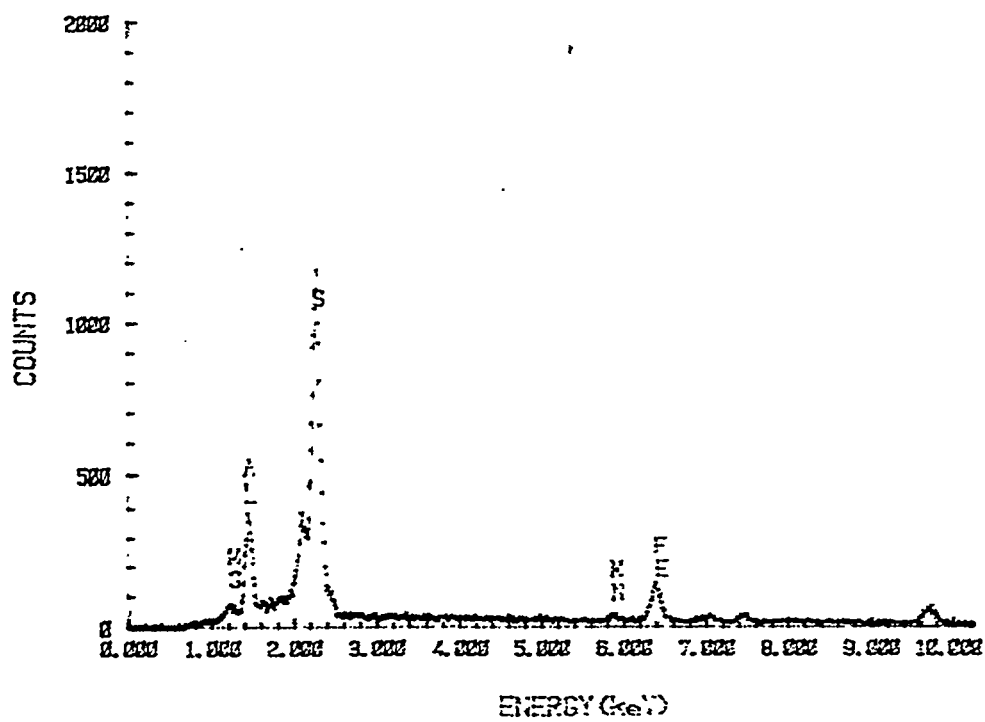


Figure A-6. Halotrichite

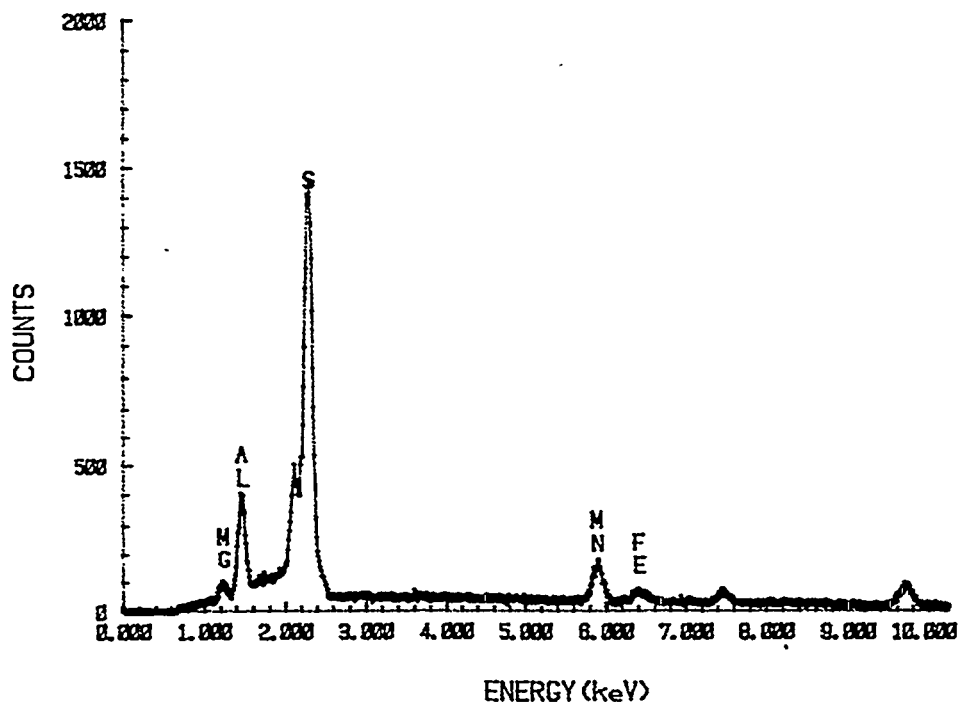


Figure A-7. Apjohnite

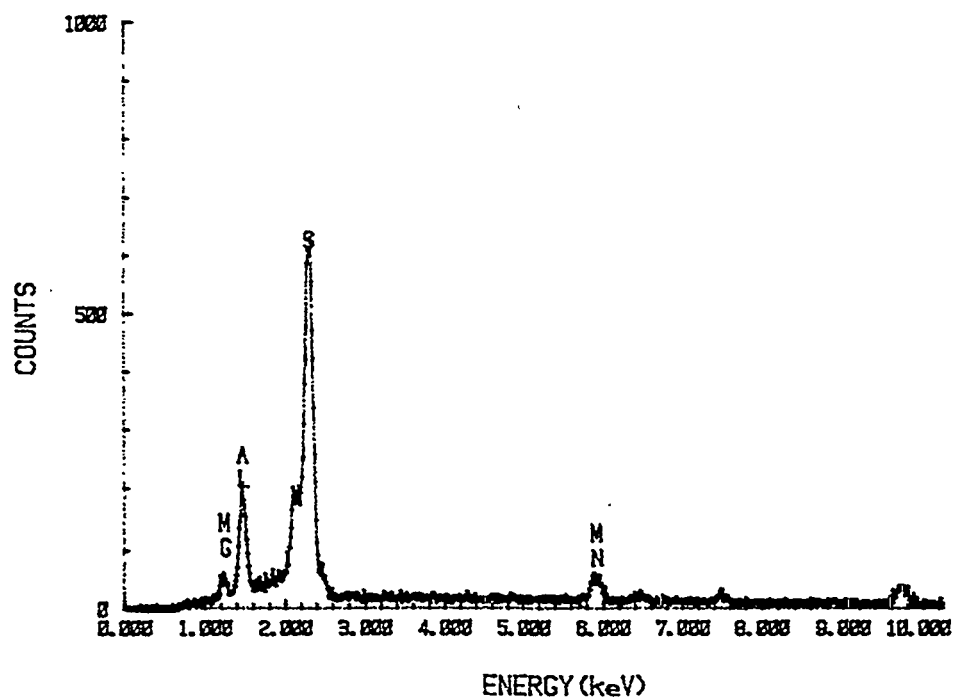


Figure A-8. Pickeringite (?)

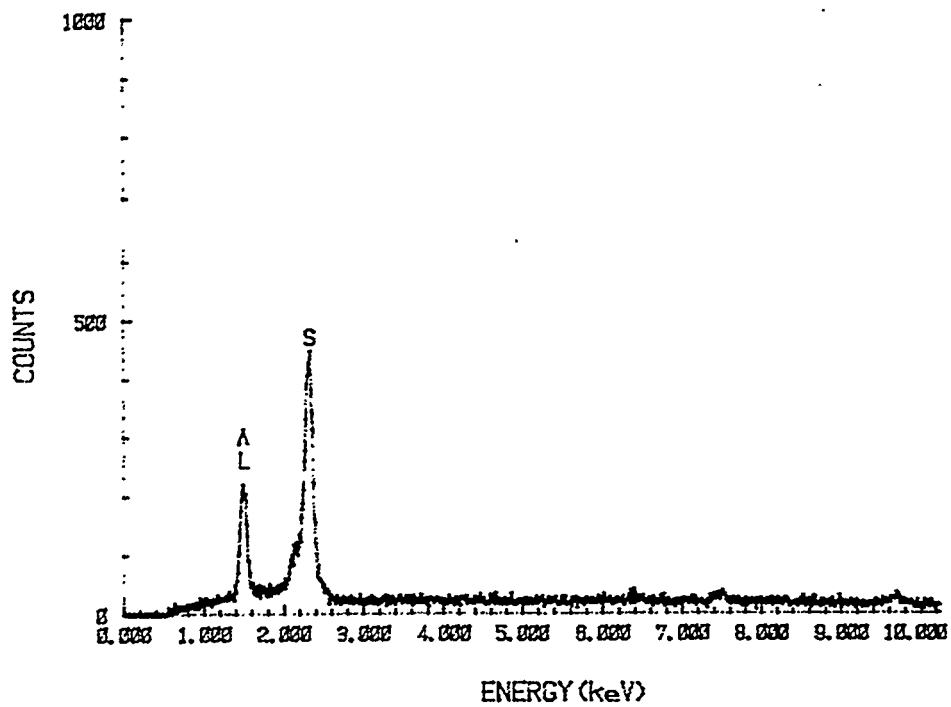


Figure A-9. Alumnogen (?)

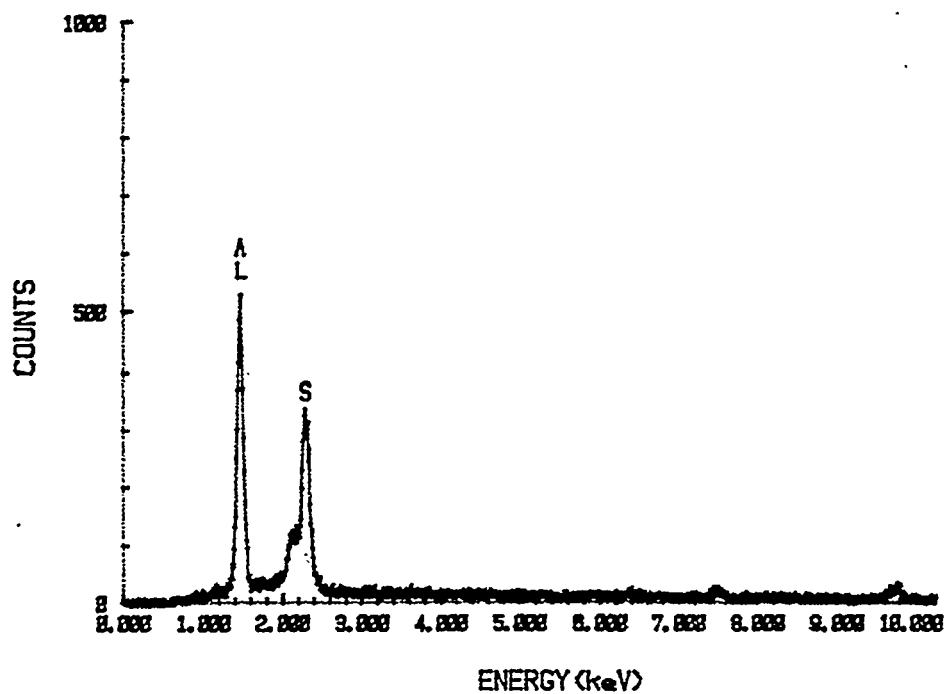


Figure A-10. Aluminite(?)

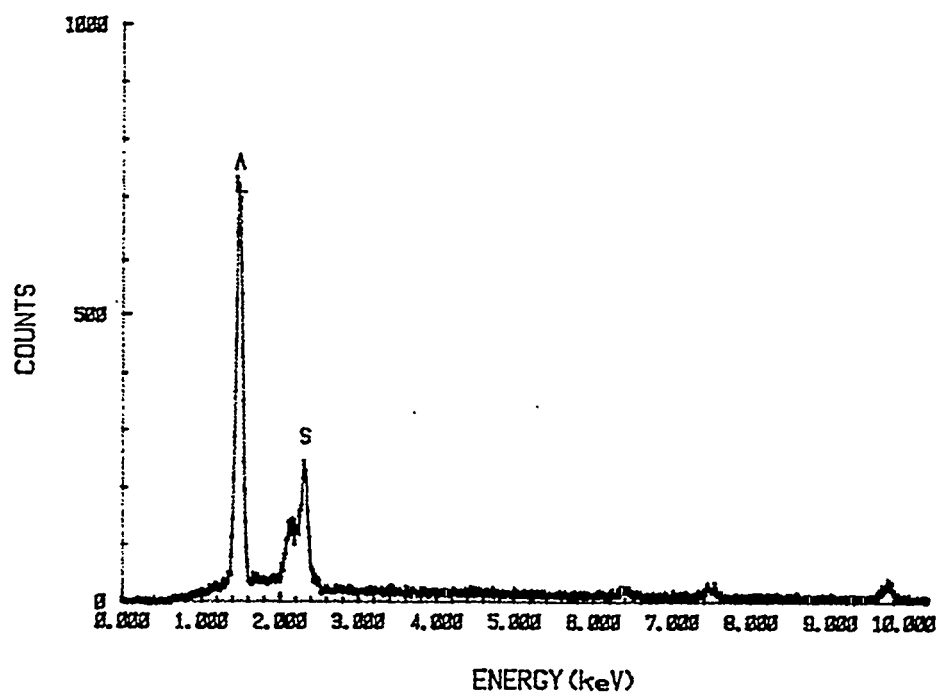


Figure A-11. Basaluminite (?)

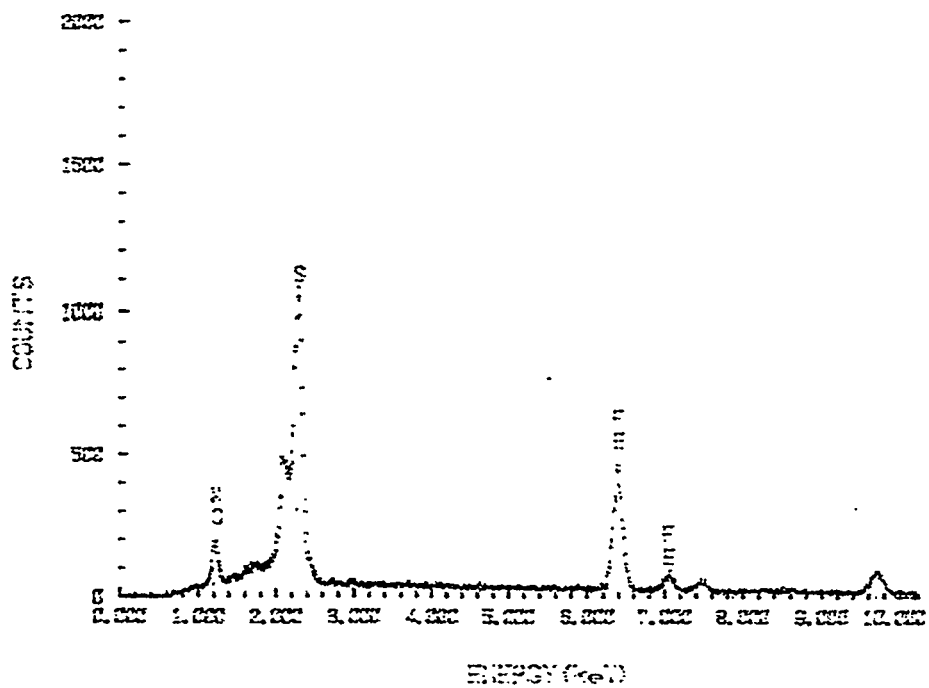


Figure A-12. Botryogen (?)

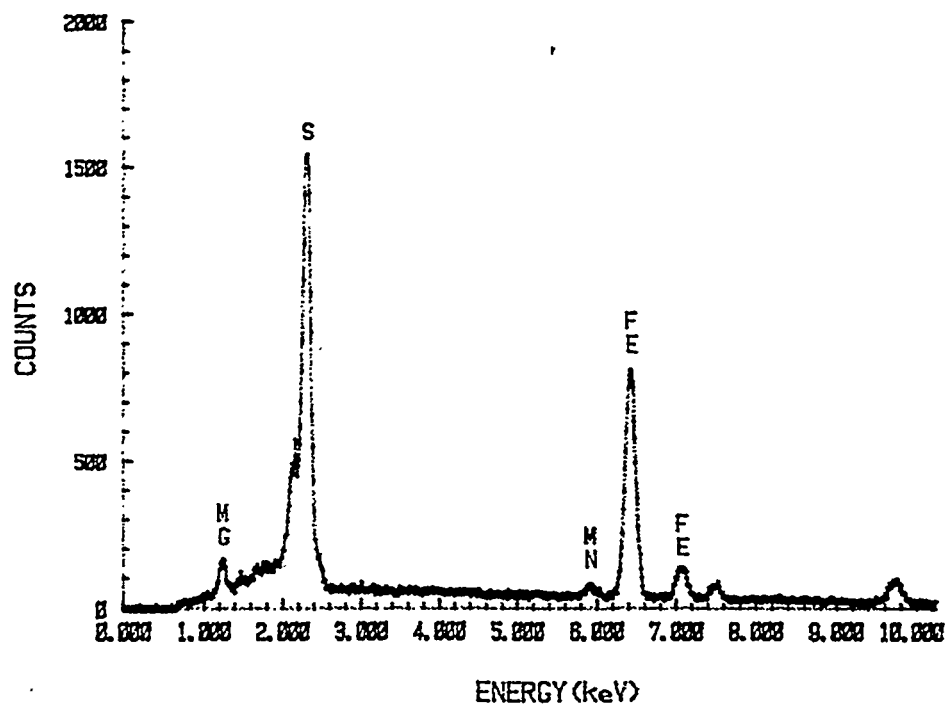


Figure A-13. Slavikite

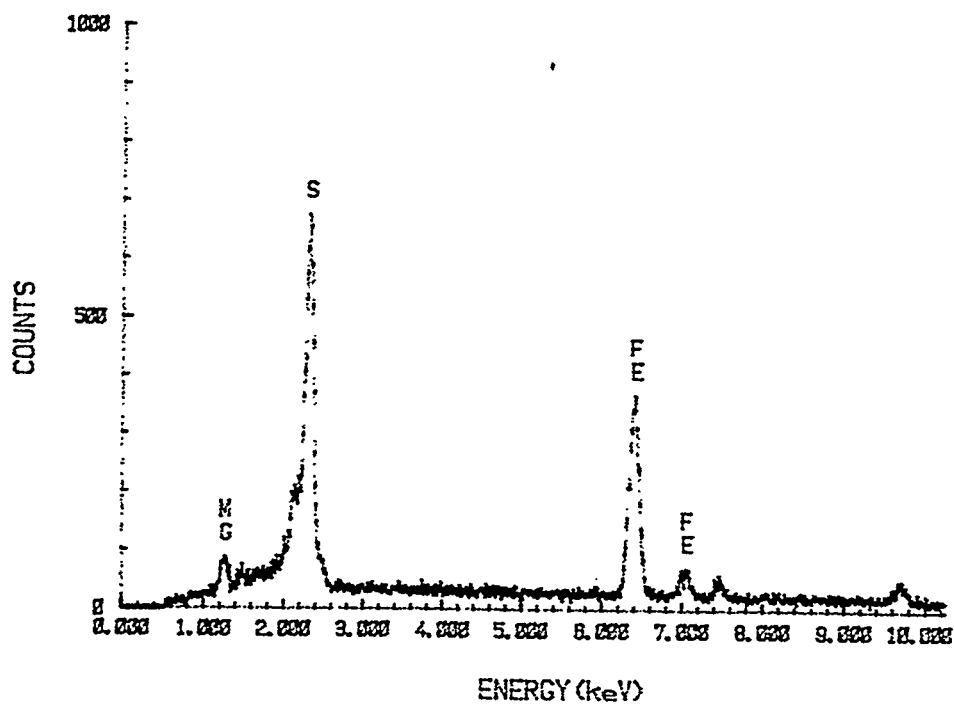


Figure A-14. Magnesiocopiapite

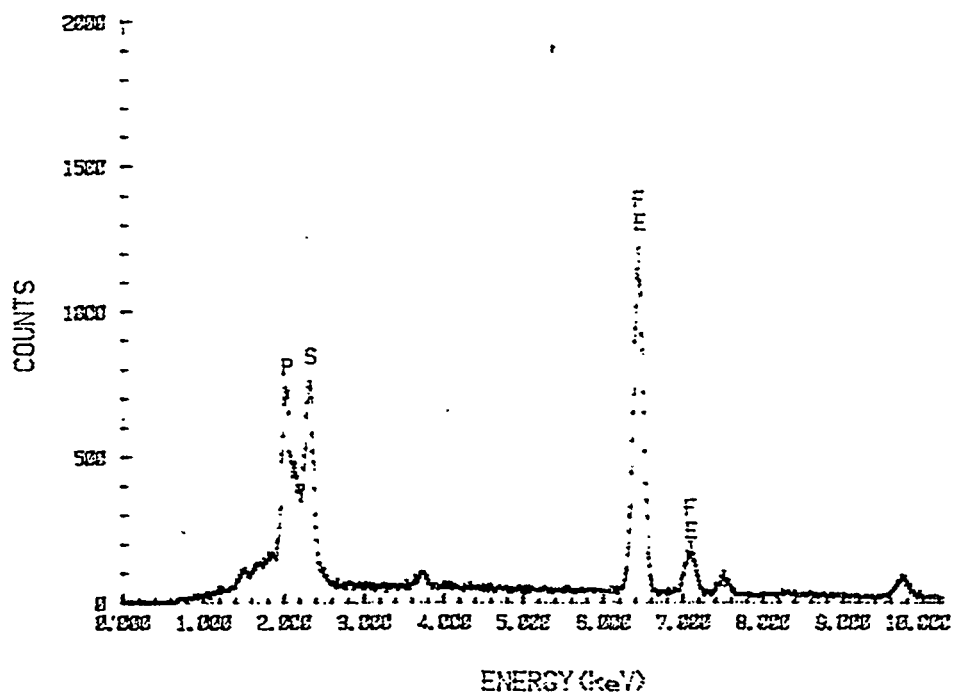


Figure A-15. Diadochite

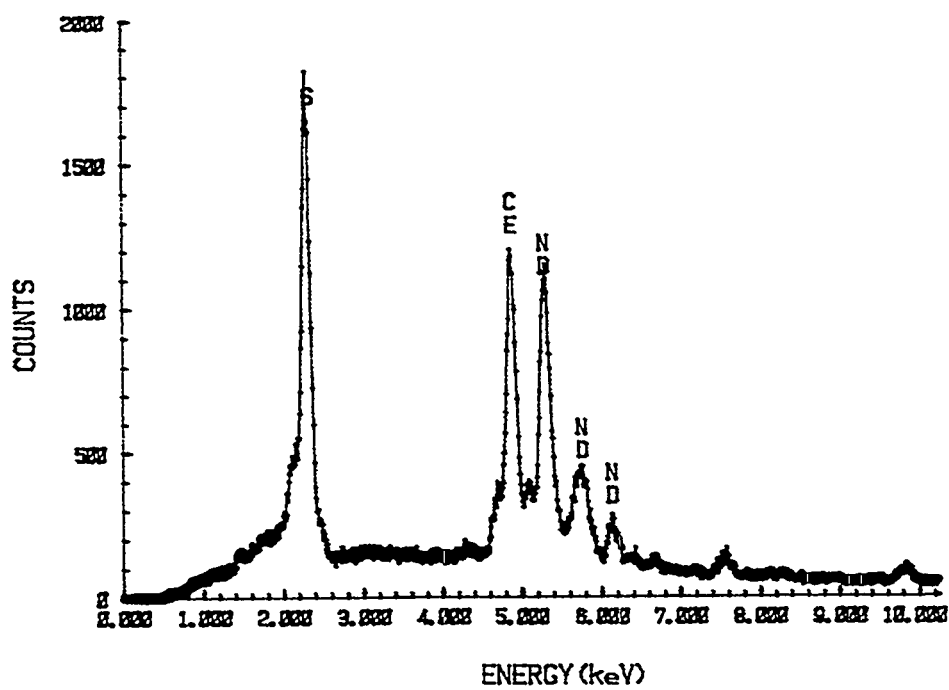


Figure A-16. Coskrenite - (Ce)

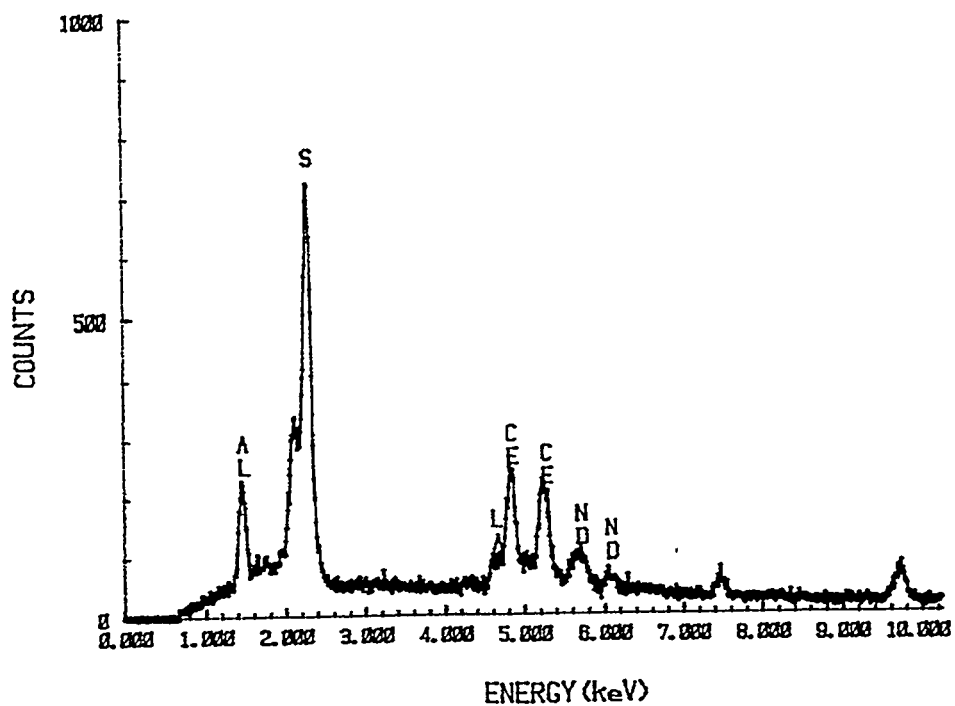


Figure A-17. Zugshunstite - (Ce)

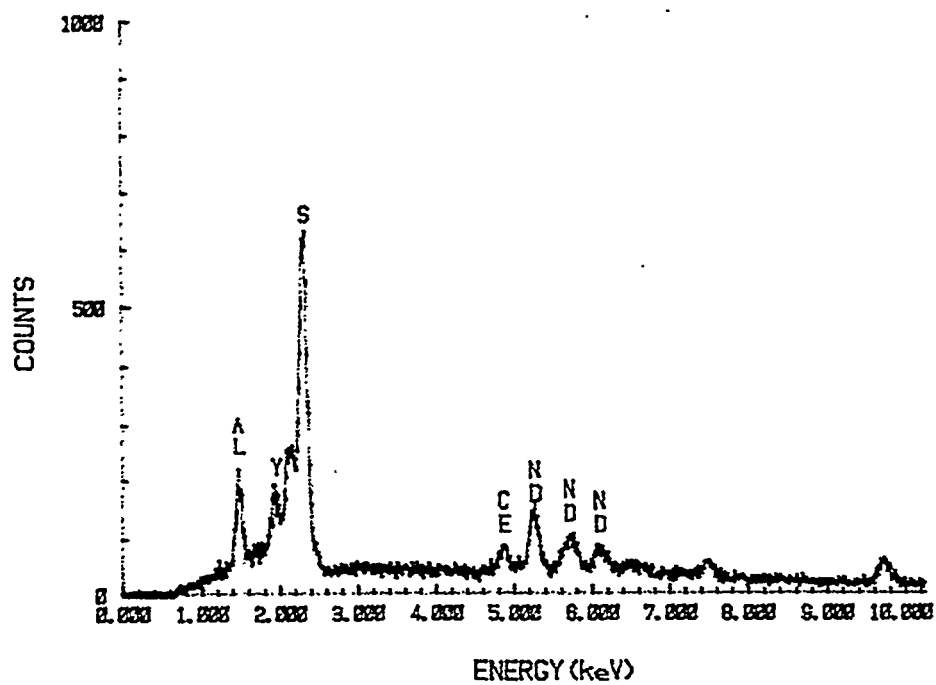


Figure A-18.
Levinsonite - (Y)

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