APPLICATION OF THE ELECTRON MICROSCOPE TO MINERALOGIC STUDIES*

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Abstract

A discussion of the use of the electron microscope in mineralogic studies and of sample preparation is followed by a series of electron photomicrographs showing the size, shape, and crystal habit of fine fractions of some uranium-bearing minerals from the Colorado Plateaus, lignite from North and South Dakota, phosphate minerals from Florida, and minerals synthesized in the laboratory. The information obtained from these photographs is useful in establishing paragenetic relations of associated minerals in uranium deposits, in supplementing mineralogic descriptions, and in guiding and checking separation techniques.

Introduction

This report is an outgrowth of mineralogic investigations conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission. Electron photomicrographs (Figs. 1–8) that were taken as part of these investigations reveal the size, shape and crystal habit of fine-grained minerals and sediments occurring in or associated with uranium deposits. These include sooty pitchblende, carnotite, tyuyamunite, and related vanadates of the Colorado Plateaus area; ultrafine fractions of lignite separates; leached-zone material and "slimes" from the Florida phosphate deposits; and schroeckingerite from Wyoming. Micrographs of synthetic minerals prepared in connection with studies of the torbernite and apatite groups are also shown. Photographs of surface features of polished and etched carbonate-fluorapatite sections, as revealed by the replica technique, suggest another approach to high-resolution study of compact minerals not easily disaggregated and dispersed for electron-microscope examination.

Electron micrographs of earthy hematite and wad, both showing a habit somewhat similar to that of pitchblende, and a mixture of descloizite and montmorillonite are also included.

Electron-diffraction patterns were made of many of the specimens examined in the electron microscope to build up a library of electron-diffraction patterns and to aid in the identification of these and other specimens.

The writers are indebted to fellow geologists who submitted material for electron-microscope examination, for their description and identification of samples, and for their aid in the interpretation of micrographs. Thanks are due to George Jansen for his assistance in the electron-

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microscope laboratory in sample preparation and examination of his synthetic uranium minerals.

HISTORY

The use of the electron microscope as a tool in scientific research has become increasingly important during the past 12 years. Technical journals have carried many reports on its application to problems involving the study of materials in the submicroscopic and colloidal size range. Most of these studies have been in the fields of biology, chemistry, and metallurgy, but some applications have been made in mineralogy. The most significant application has been in the investigation of clay minerals that occur in the particle size range especially suitable for electron-microscope examination. Using the electron microscope the mineralogist can see individual clay particles that are irresolvable in the petrographic microscope. Humbert and Shaw (1941) presented a series of micrographs contrasting the crystalline plates of kaolinite with the apparently amorphous, fluffy particles of montmorillonite. Marshall, Humbert, and Caldwell (1942) presented results of their work on fractionation of beidellite, nontronite, magnesium bentonite, and attapulgite. These studies were followed by those of Kelley and Shaw (1942) on hydrodynamic considerations in relation to shape of particles, wherein electron micrographs afforded a direct measurement of two dimensions of particles, calculation of the third, and determination of the specific surface of various clay species.

Humbert (1942) reported on the particle shape and behavior of kaolinite- and montmorillonite group minerals and commercial deposits of fire clay and attapulgite. He suggested that the electron microscope be used as a rapid means of selecting raw materials for certain types of ceramic ware. Bates (1947) used the electron microscope in his investigation of slate to provide additional data on recrystallization of "illite" to larger plates or flakes and reorientation to parallel alignment, thus accounting for slaty cleavage. Ross and Hendricks (1945) in their work on minerals of the montmorillonite group used electron micrographs of hectorite, bentonite, and nontronite to show significant morphological differences in structurally similar minerals.

Perhaps the most comprehensive report on the application of the electron microscope to geologic research was made by Bates (1949), who illustrated specific applications and indicated new methods of approach to current geologic and mineralogic problems. A detailed study of the morphology of endellite and halloysite with the electron microscope was reported by Bates, Hildebrand, and Swineford (1950). Davis and others (1950) presented a collection of micrographs of clay minerals and related species.

DESCRIPTION OF INSTRUMENTS

The electron microscope used in these studies is the research type designed for study of particulate matter in the range of 0.001 to 10 microns. The range of magnification obtainable with the electron microscope is 1,000 to 22,800 times. Individual fields of view may be enlarged photographically to 100,000 times; this is generally accepted as the limit of useful magnification. For a more complete description of the electron microscope—its history, development, and modifications, discussion of electron lenses and image formation, and applications to scientific research—the reader is referred to an article by Zworykin and Hillier (1950).

Although the electron microscope may be used as a diffraction camera, a separate electron-diffraction unit is also used at the Geological Survey. This unit was designed specifically for work with powder mounts, single crystals, and reflection diffraction of polished and mineral surfaces. It may be used as a shadow microscope with magnifications from 500 to 1,000 times.

A third high-vacuum apparatus, the metal-evaporation unit, is used primarily to "shadow" specimens for electron micrography, and also to check experimentally the behavior of hydrated salts in high vacua, to prepare metallic standards for the calibration of the diffraction unit, and to deposit thin uniform metallic reflecting surfaces.

ADVANTAGES AND LIMITATIONS OF THE ELECTRON MICROSCOPE

The advantages and limitations of the electron microscope as applied to mineralogic investigations were evaluated by Bates (1949) and are considered briefly here. The chief advantage of the electron microscope is its increase in resolving power over the light microscope. The accepted value for the limit of resolution in the light microscope is 0.2 micron. A value of 0.001 micron or 10 angstrom units has been reached in high-resolution studies with the electron microscope, but in normal operation 0.01-micron particles can be readily resolved.

The biggest disadvantage of electron radiation is the very low penetrating power. No set value for maximum thickness can be given because the density of the material under examination must be considered. Thin platelets of micaceous minerals or asbestiform fibers are penetrable, whereas uranium minerals of approximately equal thickness appear opaque. To offset the lack of penetrating power of the electron beam the replica technique can be used for study of surface features of cleavage fragments, fracture surfaces, and etched polished sections.

Energy absorption of electrons by matter and resultant high temperatures lead to further difficulty in observing some mineral species. Intensity of the illumination must be kept at a minimum in order to avoid a change in the specimen, which would complicate interpretation of the resultant micrograph. The optical properties of minerals as determined in the petrographic microscope are, of course, not applicable when the minerals are imaged by electron radiation.

In general, then, the electron microscope can be expected to provide data on size, shape, and crystal habit of those minerals whose particle size is 0.001 to 10 microns. To a limited extent relative density and fusibility are indicated.

Sample Preparation

The support for electron-microscope mounts is a standard-mesh, $\frac{1}{8}$-inch diameter, stainless-steel or copper grid covered with a thin film of collodion. The film must be strong enough to support dispersed particles on its surfaces in a uniform plane and thin enough to avoid excessive scattering of transmitted electrons. These blank mounts are prepared by placing four or five drops of a 5-to-1 mixture of amyl acetate and collodion in the center of a large evaporating dish filled with distilled water. After the solvent evaporates, a thin film of collodion forms on the surface. The 200-mesh grids are placed on the film within an area the size of a glass microscope slide and picked up by cutting through the film in a downward motion and entrapping the grids between the film and a slide. After drying, these blanks are ready for sample preparation.

The specimen material may be dispersed on the surface by collecting it as dust or smoke; or it may be rolled on gently with a cotton swab. For a more uniform dispersion of fine particles, however, a wet method is generally used. The technique consists in disaggregating the sample in a mechanical mixer of the "blender" type in distilled water. After several minutes the suspension is poured into a tall vessel and allowed to settle until it assumes a slightly murky appearance. Droplets of the suspension are then pipetted from several depths in the vessel and transferred to the collodion-covered grids. After evaporation of the water the mounts are ready for examination in the microscope, or they may be placed in the metal evaporation unit for coating with some heavy metal such as chromium or uranium. This technique of coating with a metal in a high vacuum at a computed oblique angle enhances contrast in the specimen, gives a direct measure of the height of the particle, and—because of the relatively great depth (10–25 microns) of focus of the electron microscope—portrays the general shape of the particle.

In the study of compact and dense materials it is necessary to resort to a replica technique to ascertain fine structural detail. One of the quickest methods is to flood a polished, etched, or cleavage surface of a mineral with a 7-to-1 amyl acetate collodion solution, and after evaporation of the solvent, to float the replica film on the surface of distilled water. This film may then be picked up by the 200-mesh grids in a method similar to that for preparing blank mounts. Because the film lacks contrast, it is metal-shadowed in the evaporation unit to emphasize depressions and ridges in the original surface. Although this is a negative replica technique, the true nature of the sample surface is revealed when the finished micrographs are viewed under appropriate incident light. A discussion and evaluation of other replica methods can be found in the manual edited by Drummond (1950).

Artifacts introduced into the sample during preparation make interpretation of finished micrographs difficult. Therefore great care must be taken to avoid contamination of the sample. The distilled water must be fresh to avoid bacterial development. Chemical dispersants and aerosols or wetting agents are rarely used. Whenever feasible certain samples are prepared by wet- and dry-mounting methods, although uniform dispersion is not generally attained by dry mounting. Rupturing of the film substrate, the effects of heating the mount in the evaporation unit, and the electron beam itself also give rise to artifacts that must be recognized as not inherent in the specimen.

Because sample preparation requires extreme caution, the trial of various techniques, and the necessity of reproducing the results before the characteristics of the material under examination are established, the electron microscopist must devote at least 60 per cent of his time to sample preparation.

CONCLUSIONS

In the study of lignite, phosphates, and uranium and vanadium minerals, data on the shape, particle size, and crystal habit of these materials in 10-micron range have been obtained and many more data are readily available. This information may prove helpful in supplementing mineralogic description, in guiding and checking separation techniques, and in establishing paragenetic relations of associated minerals in uranium deposits.

The clays and related species are particularly suitable for electron-microscope examination. Presence of attapulgite in the Florida phosphate deposits has been reported for the first time, and continuing *x*-ray spectrometer study of phosphorites by Z. S. Altschuler of the Geological Survey reveals that it is a major constituent in a zone of alteration at the top of the Hawthorn formation in the Land-Pebble field.

In connection with synthesis work, particle size and homogeneity of resultant products are readily determined by the electron microscope.

The application of the electron microscope to mineralogic studies has given other workers in related fields investigating similar materials a clearer insight into actual particle shape and size of some of the uranium-bearing minerals and associated sedimentary rocks.

Although the applications of the electron microscope to mineralogic investigation cited in this report are general in nature, they suggest that more exhaustive and detailed studies of the fine fractions of uranium-bearing minerals and sediments are warranted.

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DESCRIPTION OF PLATES

In all the following illustrations the scale marker equals 1 micron or 0.001 mm. and represents both the magnification of the specimen in the original electron micrograph and photographic enlargement. Some of the specimens have been shadowed with chromium in the evaporation unit to enhance contrast and indicate particle thickness. Shadow areas appear light in these photomicrographs.

Identification of the material examined is based on petrographic or x-ray methods except where otherwise noted.

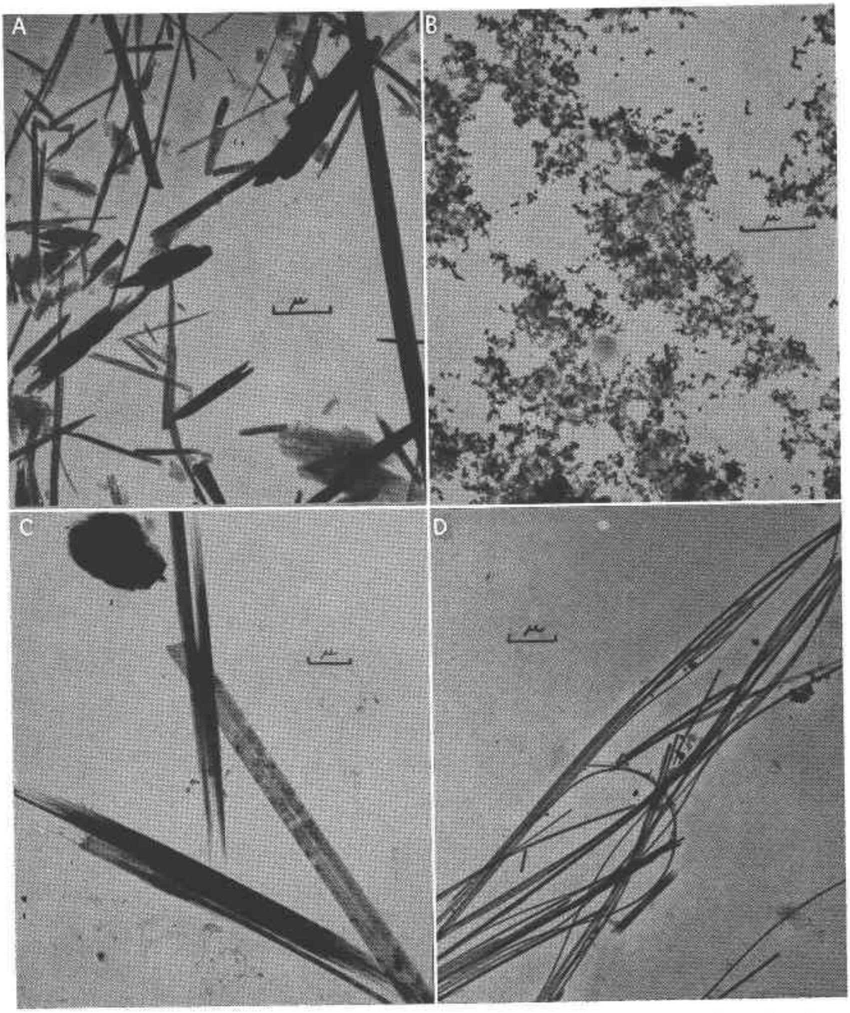

FIG. 1. (*A*) Iron vanadate, Jo Dandy mine, Montrose County, Colo. This mineral, as yet undescribed, shows a fibrous to lathlike habit different from the hewettite in *D* and also from the metahewettite of *C*, another related vanadate. Platy aggregates associated with the specimen probably belong to the montmorillonite group. (*B*) Schroeckingerite, Red Desert, Wyo. A well-dispersed mount showing particles of about 0.01 micron. The plate consists of material assumed to be recrystallized from solution. (*C*) Metahewettite, Matchless mine, Mesa County, Colo. A hydrated calcium vanadate with distinctly different morphology. The frayed hairlike terminations of the laths are characteristic of this mineral. Individual "hairs" are approximately a few hundred angstroms in thickness and are readily distinguishable from the hewettite fibers. The mottled effect on the lower lath is due to a moderately prolonged exposure to the beam. Further heating of the specimen leads to skeletalizing and fusion. Width of particles is 0.7 to 1 micron; maximum length is 15 microns. (*D*) Hewettite? Jo Dandy mine, Montrose County, Colo. This specimen shows a characteristic fibrous habit not unlike that of asbestiform serpentine. The fibers may be tubular in end section.

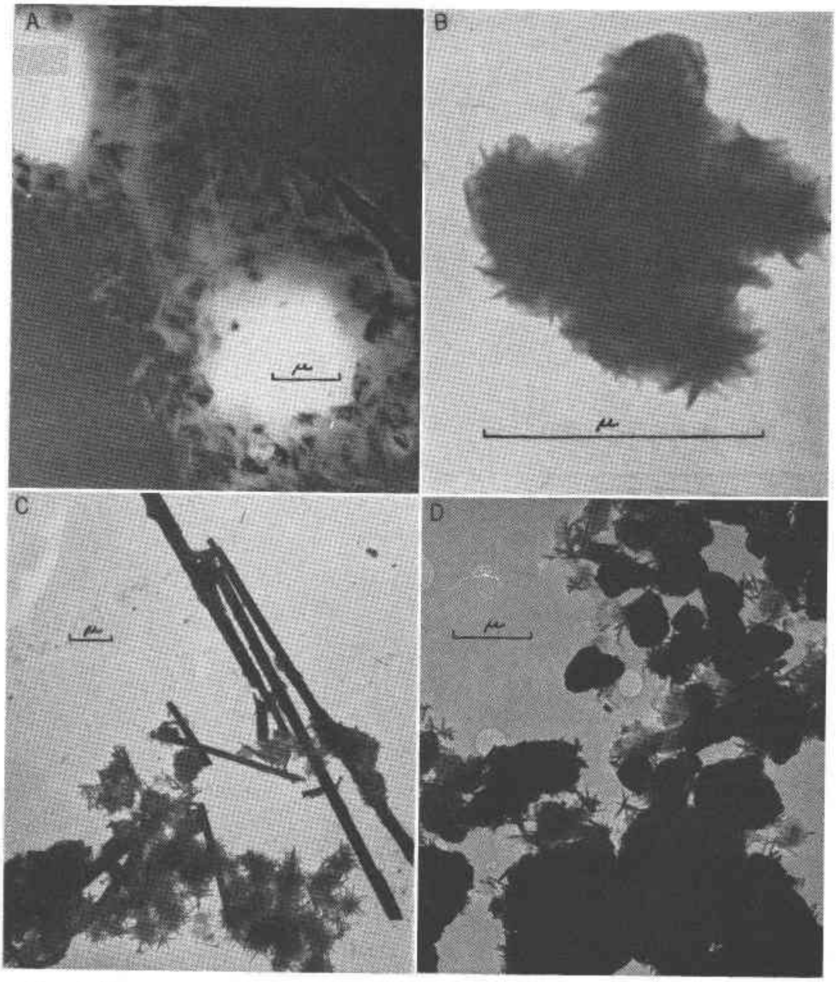

FIG. 2. (*A*) Sooty pitchblende (?) 300-foot level, Prospector mine, Piute County, Utah. This material shows a platy to lathlike character where individual particles are separated from the aggregate. Significance of the dark blebs associated with the particles has not been established. (*B*) Material presumed to be pitchblende from San Juan County, Utah. The width of the fibrous projection from the main mass of material is 100 to 200 Å. The density of the pitchblende is apparent from the relative opacity of the specimen to the electron beam. There is some suggestion of twisting and curling in the aggregate. (*C*) Wad (manganese oxides). This micrograph of supposedly amorphous material reveals the presence of two distinct morphological forms—the elongate laths and spherical clusters of short fibers. The individual needles comprising the aggregates are about 500 Å or 0.05 micron in thickness. The laths range in length up to 16 microns. (*D*) Hematite (earth). This material shows a habit similar to that of manganese oxides of the previous figure and sooty pitchblende. It is hoped that further study of apparently amorphous, natural, metal oxides will prove significant in mineralogic description of these minerals and related hydrates. Individual fibers are slightly coarser than those of the manganese oxides in *C*.

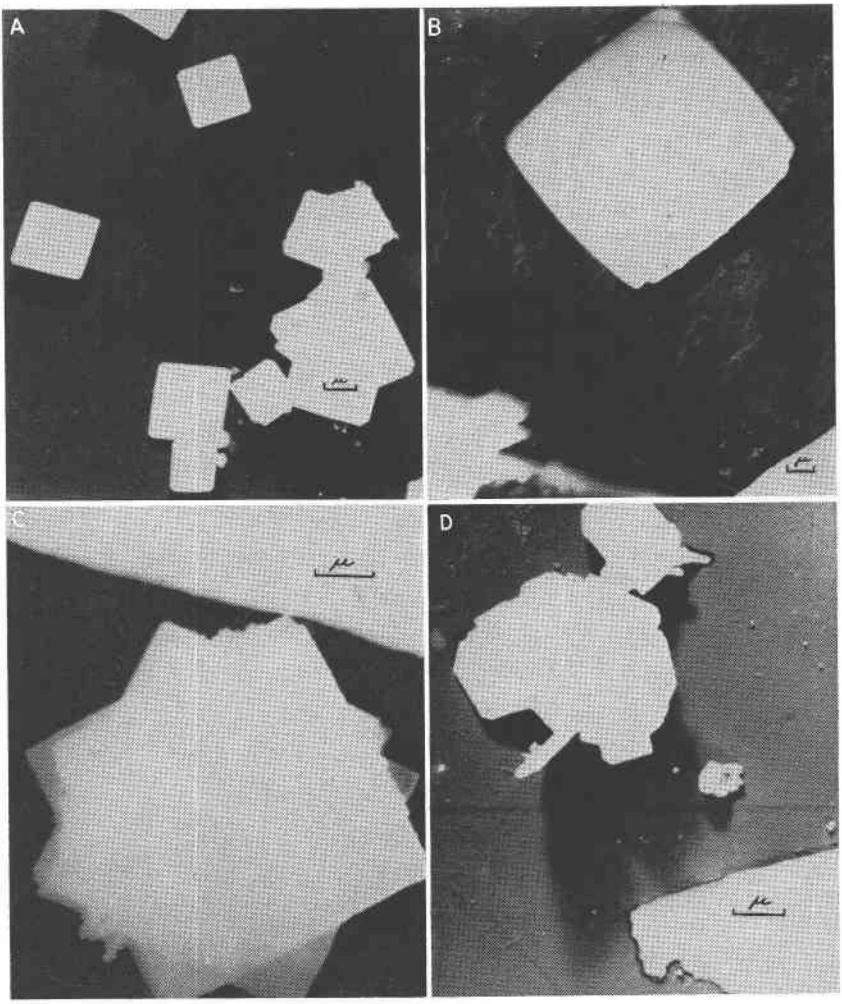

Fig. 3. (*A*) Synthetic uranocircite. This micrograph shows a well-crystallized synthetic product prepared by George Jansen of the Geological Survey. The mineral was identified by its *x*-ray diffraction pattern. Chromium shadowing shows that the material develops as thin tablets characteristic of the uranite group. Crystals vary in size from 1.5 to 3.5 microns along one edge. (*B*) Synthetic autunite. This mineral shows a square platy habit with particles as much as 8.5 microns along one edge. Its *x*-ray pattern is similar to that of autunite. Background irregularities are due to distortion of the film. (*C*) Synthetic parsonsite. Several square tablets of the synthetic product superimposed on one another. Crystals are about 5 microns along one edge. *X*-ray study shows a pattern similar to that of parsonsite with slightly larger spacings. (*D*) Synthetic bassetite. Electron-microscope examination shows a coarsely crystalline product essentially homogeneous with a pronounced development of prism faces. Size ranges from about 2 microns to particles greater than 15 microns. Product was identified by its *x*-ray diffraction pattern.

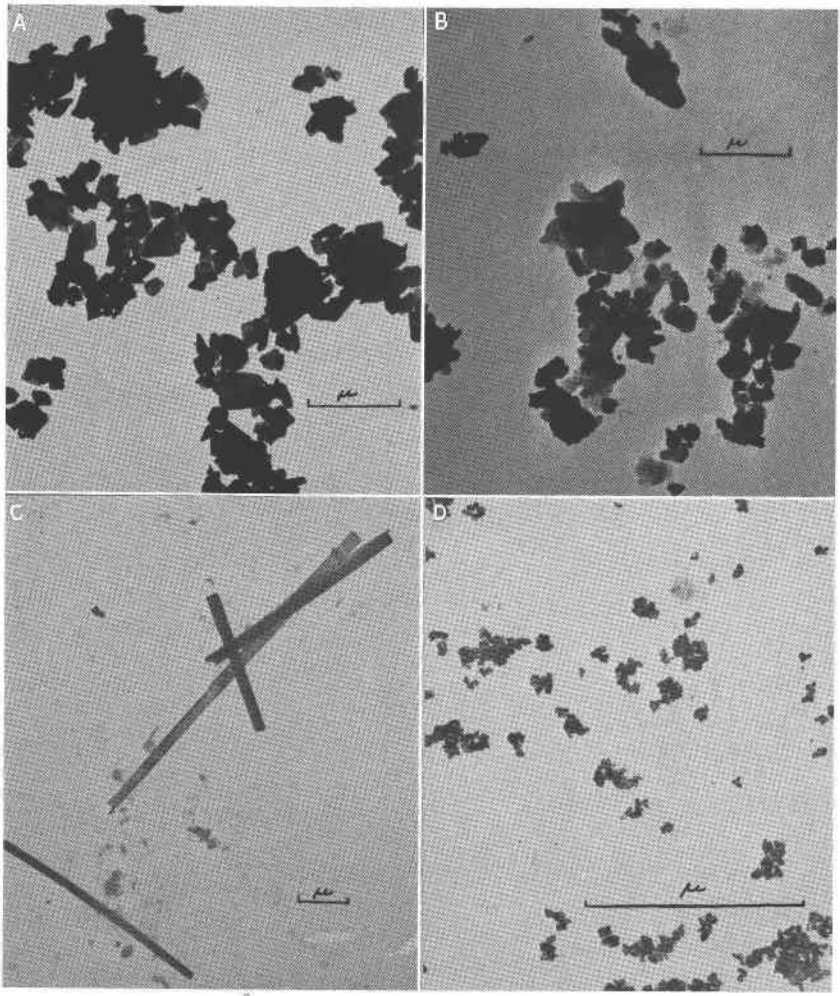

FIG. 4. (*A*) Synthetic carnotite. A micrograph showing a homogeneous product closely resembling natural carnotite in size and morphology. Compare with *B*. (*B*) Carnotite, Mine D, Yellow Bird group, Montrose County, Colo. Subhedral to euhedral overlapping plates of carnotite. Size of particles varies from 0.16 to 1.0 micron in longest dimension. The transparent platy material may be an admixed montmorillonite clay. (*C*) Synthetic α tricalcium phosphate prepared at Bureau of Plant Industries, U. S. Department of Agriculture. Material is lathlike in habit, approximately 0.25 micron in width, and as much as 5 microns long. (*D*) Synthetic hydroxylapatite, prepared at the Bureau of Plant Industries, U. S. Department of Agriculture. A homogeneous product examined at the Survey in connection with synthesis of apatite group members. Particle size 0.04 to 0.06 micron.

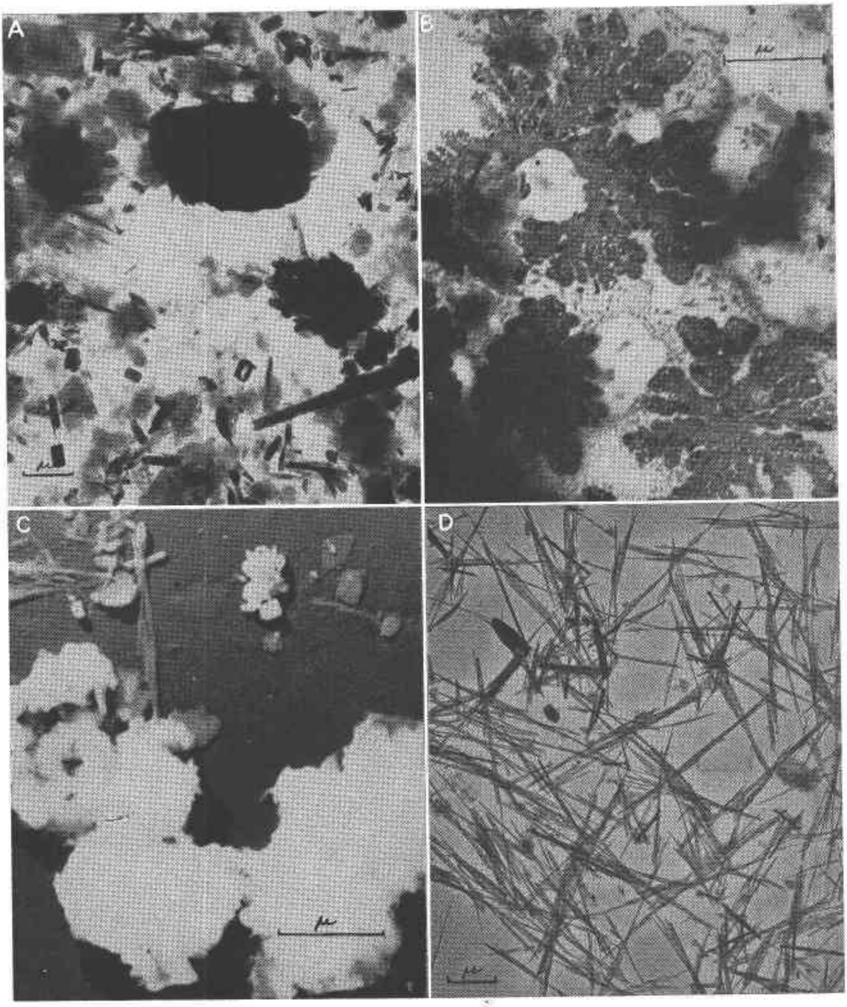

Fig. 5. (*A*) Fine fraction of phosphorite, Florida. The intimate mixture of distinct mineral species is indicated by the variety of crystal habit of the particles. Study of the picture reveals well-defined hexagons of kaolinite; lathlike, rod-shaped, and fibrous particles; euhedral to subhedral rhombs and cubes; fluffy aggregates, presumably phosphorite; and remnants of organic structure. Particle size ranges from 0.03 to 3.5 microns. (*B*) Material from phosphorite fines, Florida. This plate illustrates the difficulty encountered in interpretation of micrographs. This material occurs sparingly in phosphorite fines. It may be an artifact introduced in sample preparation, a collapsing envelope of some minute organism or a recrystallized water-soluble mineral. Substances such as this are generally micrographed for future reference. (*C*) "Slimes" from phosphorite wastes, Florida. This material taken from the −150-mesh waste product of phosphate mining operations is, as expected, similar to the extremely fine material encountered in the examination of the phosphorite and leached-zone samples depicted in previous figures. (*D*) Attapulgite from leached-zone material, Florida. Initial examination of this material showed a surprising similarity to attapulgite. It was subsequently identified by E. B. Jaffe, U. S. Geological Survey, from its electron-diffraction pattern as attapulgite and marks a new occurrence of the mineral already reported from Attapulgus County, Ga., and Quincy, Fla. The more opaque lathlike particles may be wavellite or pseudowavellite.

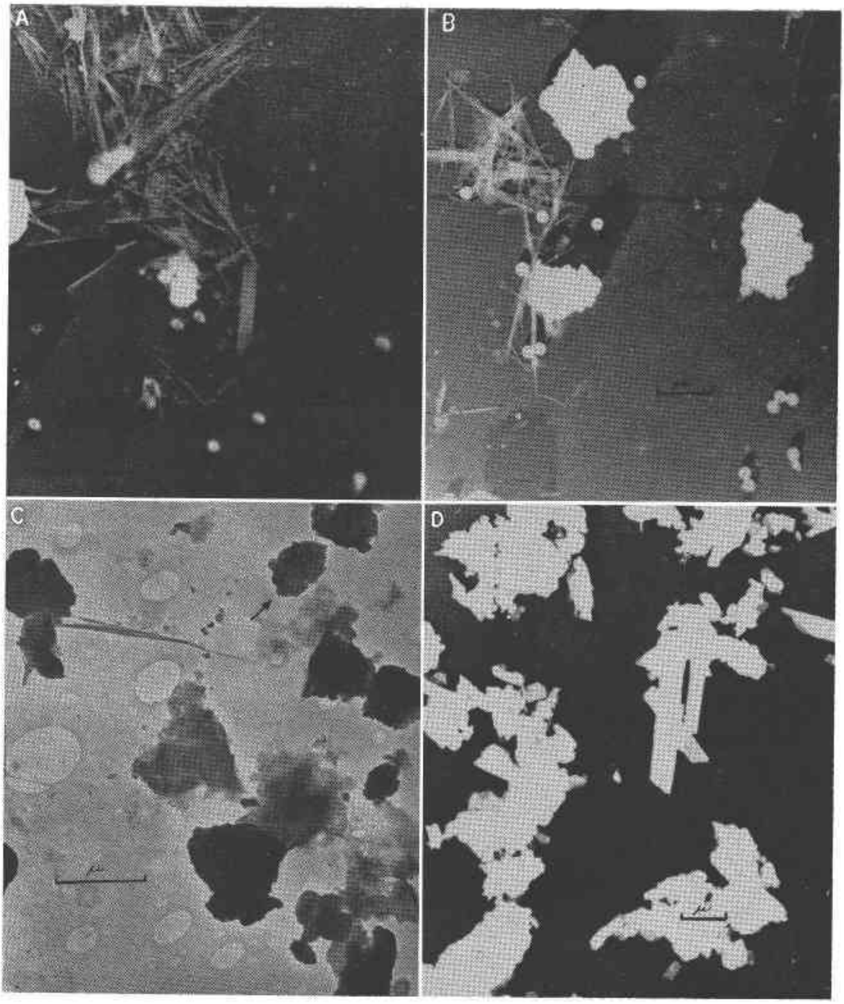

FIG. 6. (*A*) Ultrafine fraction of lignite separate, Medicine Pole Hills area, Bowman County, N. Dak. This micrograph, though not representative of the material, is included to show presence of matted fibrous material similar in crystal habit to that of attapulgite. The small cubes may be pyrite, and the platy euhedral aggregate is suggestive of kaolinite. The large opaque shapeless mass is typical of the bulk of the sample. The distorted polystyrene latex particles with attendant shadows are used for internal calibration of particle size. The spheres are approximately 0.25 micron in diameter. (*B*) Ultrafine fraction of lignite separate, Medicine Pole Hills area, Bowman County, N. Dak. More of the same material shown in *A*. Polystyrene latex particles provide an internal calibration for particle-size determination. (*C*) Ultrafine fraction of lignite separate, Medicine Pole Hills area, Bowman County, N. Dak. An unshadowed mount showing carbonaceous particles up to 1.2 microns in size and admixed clay mineral with shape similar to that of montmorillonite. The platy euhedral aggregate indicated by arrow is suggestive of kaolinite. A few fibrous particles are probably similar to those shown in *A* and *B*. (*D*) Tyuyamunite, San Rafael Swell, Utah. Aggregates of tyuyamunite crystals showing a more elongate habit than that of carnotite in Figure 4*B*. Distinct prismatic terminations are evident in some of the crystals. Shadowing indicates a lathlike habit. Size of largest laths in the elongate directions is 3 microns.

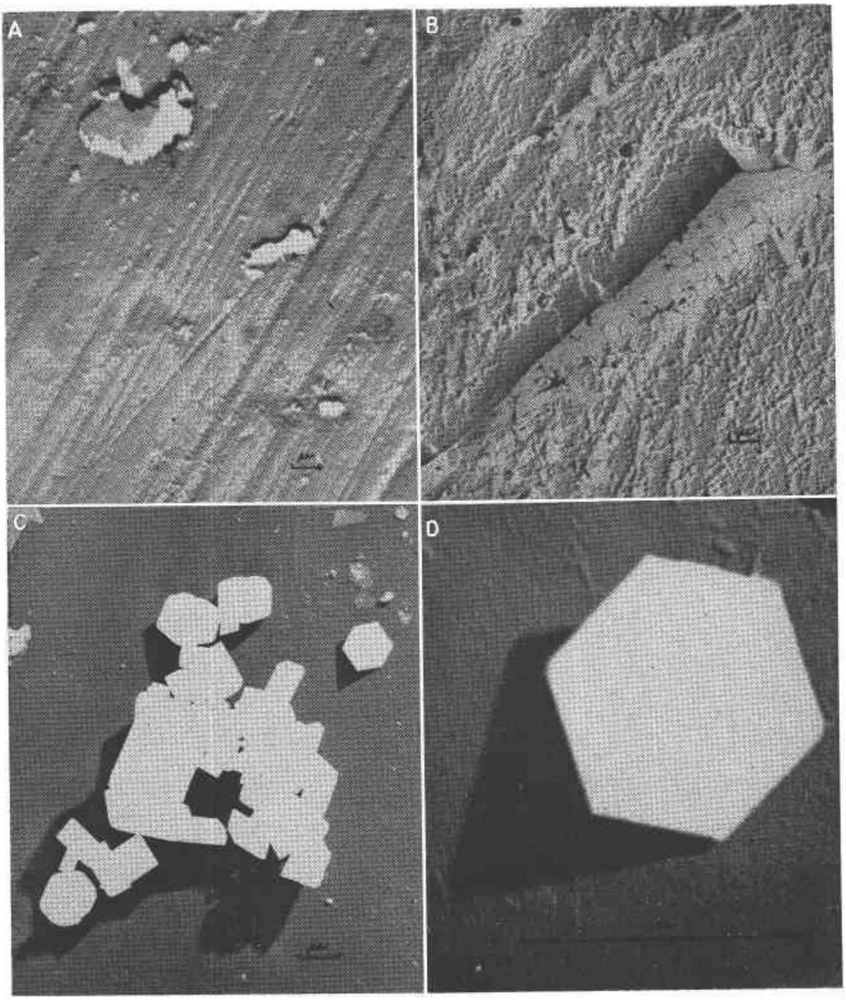

FIG. 7. (*A*) Staffelite, Staffel, Germany. This is a replica of a polished surface of staffelite prepared by the collodion technique. The reader is urged to allow incident light to fall on the micrograph from such a direction that the scratch marks appear as depressions. This micrograph is characteristic of the surface before treatment with triammonium citrate, a preferential etchant for calcium carbonate. (*B*) This is a similar polished surface of staffelite after an hour's immersion in triammonium citrate. Etching is noticeable over the entire surface and is more evident along scratch marks. The large pit in the center of the micrograph may represent solution of calcium carbonate, or a void in the original surface. Preliminary investigation seems to warrant application of the replica technique as a means of affording additional data on problems such as the carbonate-fluorapatite problem. Sound interpretation of this micrograph can come, however, only after more detailed study of surfaces at different orientations, recognition and elimination of possible artifacts, study of other minerals of the apatite group and synthetic products, and employment of other replica methods permitting greater resolution. (*C*) Jarosite from weathered lignite collected from the Mendenhall strip mine near Slim Buttes, Harding County, S. Dak. The jarosite is pulverulent. No euhedral crystals could be observed with the optical microscope but this micrograph shows readily the typical crystallinity exhibited by this sample of jarosite. (*D*) Jarosite. Enlarged from *C*.

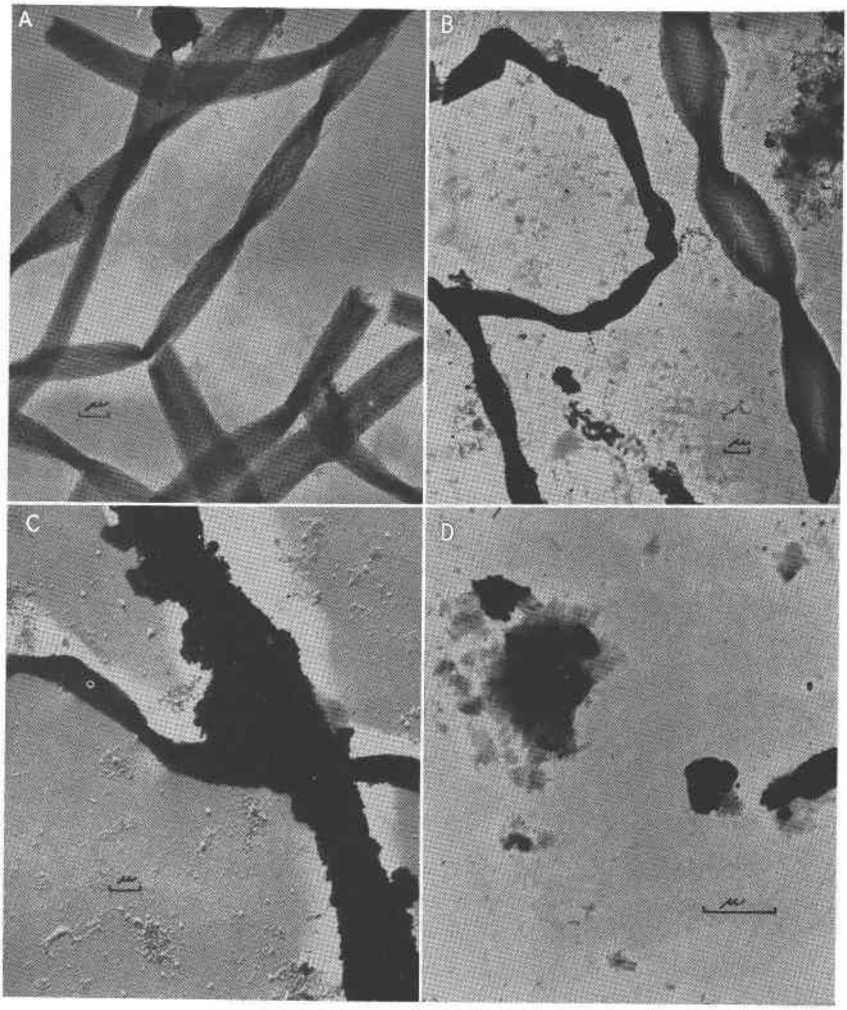

FIG. 8. (*A*) *Gallionella ferruginea* Ehrenberg, collected from a bog iron deposit from the Montezuma area, Summit County, Colo., by Maurice Deul. Newly formed filament of hydrous ferric oxide showing fibrous nature of the twisted filaments. This is an unshadowed picture but the density of the image is due to the composition of the filaments. (*B*) *Gallionella ferruginea* Ehrenberg, gradual fossilization of filament on right and more complete fossilization on left. This sample was collected from sludge from the bottom of a stream. (*C*) *Gallionella ferruginea* Ehrenberg, a fossil filament showing thicker crusts of limonite. (*D*) Descloizite and montmorillonite, Montrose County, Colo. This micrograph illustrates the application of the microscope in confirming the results obtained by *x*-ray diffraction and chemical analyses. Chemical analysis of an apparently homogeneous sample of montmorillonite showed an unusually high lead content. An *x*-ray powder mount yielded a good montmorillonite pattern. Close inspection of the pattern revealed a few faint lines with spacings similar to descloizite. Examination in the electron microscope showed thin transparent laths and aggregates suggestive of a montmorillonite group species and subhedral dense particles presumed to be descloizite. The latter particles were fused readily on exposure to the more intense electron beam, a property characteristic of descloizite.