

# ELECTRON MICROSCOPY AS A METHOD OF IDENTIFYING CLAYS

BY THOMAS F. BATES \*

## ABSTRACT

Electron microscope studies show that most of the clay minerals have morphological characteristics which can be effectively used to aid in their identification. In addition, detailed studies at high magnification have provided structural information not obtainable by other means.

In the kaolinite group each of the common minerals has a clear-cut and diagnostic morphology. However, much more work is needed on flint clays and the kaolins in soils before the same can be said of these varieties. Continued study of halloysite reveals significant details pertinent to the form and structure of the tubular crystals.

Illites from different sources show interesting differences in form which reflect variation in the degree of crystallinity. An illite from the Ordovician Oswego formation shows an unusual development of narrow to broad lath-shaped crystals. Except for lower content of iron and magnesium the material has all the characteristics of other illites. The thinnest laths are of the same order of thickness as the flakes of more common illites. Certain mixed-layer minerals are identical in morphology with some varieties of illite.

The minerals of the montmorillonite group have been the most difficult of the clay minerals to characterize on the basis of morphology. The lath-shaped crystals of certain beidellites, saucornite, nontronite, and hectorite are diagnostic. The metal shadowing technique shows that many of the laths approach one unit cell in thickness.

The morphology of many montmorillonites is dependent upon the mode of sample preparation. The replica method offers a means of studying clay particles in their natural state but this technique is still in the early stages of development as it relates to the clay minerals.

*Introduction.* The method of electron microscopy relies for its chief advantage over other techniques upon the application of the well-worn principle that "seeing is believing." Two clays may give the same X-ray pattern, the same differential thermal curve, and so on, but if they look different, we know that something either of a fundamental nature or related to environment, growth, and possibly subsequent alteration has resulted in the morphological traits which now distinguish them.

In the electron micrographs which follow, significant details of morphology will be pointed out, and those which aid in distinguishing one clay material from another will be emphasized.

In general, the method of preparation of the material to be photographed was the simplest possible. A small amount of clay was mulled in distilled water, the suspension diluted the proper amount, and a drop allowed to evaporate upon a substrate of polyvinyl formal (formvar) which was supported by the usual disc of 200-mesh screen. Most of the pictures were taken on a model EMU electron microscope by Mr. Joseph Comer, electron microscopist of the College of Mineral Industries at the Pennsylvania State University. Most of our work on the morphology of fine-grained minerals has been supported by a Penrose Grant from the Geological Society of America and a contract with the Geophysics Branch of the Office of Naval Research.

The electron micrographs included here were chosen either because they are representative of a particular variety of clay or because they illustrate some significant morphological feature. With two exceptions our own pictures were used, chiefly because it was convenient to do

so. There is no intent to minimize the very important contributions made in this field by other laboratories. Except where noted otherwise, the scale on all figures represents one micron.

*Kaolinite Group.* The first electron micrograph (figure 1) is that of kaolinite from the Woodbury clay deposit near Huntingdon, Pennsylvania. The difference between thin and thick crystals (*A* and *B* respectively) can be distinguished by variation in density. This picture shows the difference in appearance of single crystals as opposed to oriented aggregates. Studies of kaolins found in fireclay, flintclay and soils are more difficult, less satisfying, but of considerable importance. The relatively small amount of electron-microscope work that has been done on these materials shows that discrete particles and aggregates are in some instances flaky but do not commonly show the perfection of crystal habit illustrated by the china clay type of kaolinite pictured in figure 1.

Figures 2 and 3, which show a mixture of halloysite and kaolinite from the Maria Elizabeth bauxite deposit in British Guiana, illustrate several interesting points. The large tubes are not typical of most halloysites but were chosen to illustrate certain interesting features which are not apparent in smaller crystals. Evidence obtained by several workers indicates that kaolinite plates, if thin enough, will curl at the edges and possibly roll up into tubes. This is consistent with the theory that curvature results from the misfit of the tetrahedral and octahedral layers and the presence of weak interlayer bonds (Bates, Hildebrand, and Swineford 1950; Bates 1951).

In figure 2 the crystal marked *A* might either be an endellite tube unrolling or kaolinite rolling up. The hexagonal character of the plates suggests the latter. The tube at *B* also has hexagonal terminations and in this respect is not typical of halloysite tubes in general.

Figure 3 is a composite of three electron micrographs of material from British Guiana. An interesting difference may be noted in the morphology of the cross sections shown in the top and bottom portions of the figure. That at *A* gives the appearance of overlapping plates, while at *B* the exterior of the tube appears smooth. In both cases the polygonal rather than truly circular aspect of the sections is of interest. The difference in thickness along the center tube at Point *C* represents a change of wall thickness of 100 Å.

Figure 4 is of a more typical halloysite from Alexander, North Carolina. Here a large number of the tubes have unrolled, giving rise to flakes of irregular shape.

Anauxite (figure 5) is another mineral of the kaolinite group which needs more study. Like dickite it commonly occurs in crystals somewhat large for electron microscope investigation. Figure 5 shows how much some of the material from the Ione formation of California resembles kaolinite.

*Illite Group.* The clay minerals in the illite group are not as photogenic as those described above; nevertheless they have distinctive and interesting morphological characteristics.

\* Professor of Mineralogy, The Pennsylvania State University, State College, Pennsylvania.

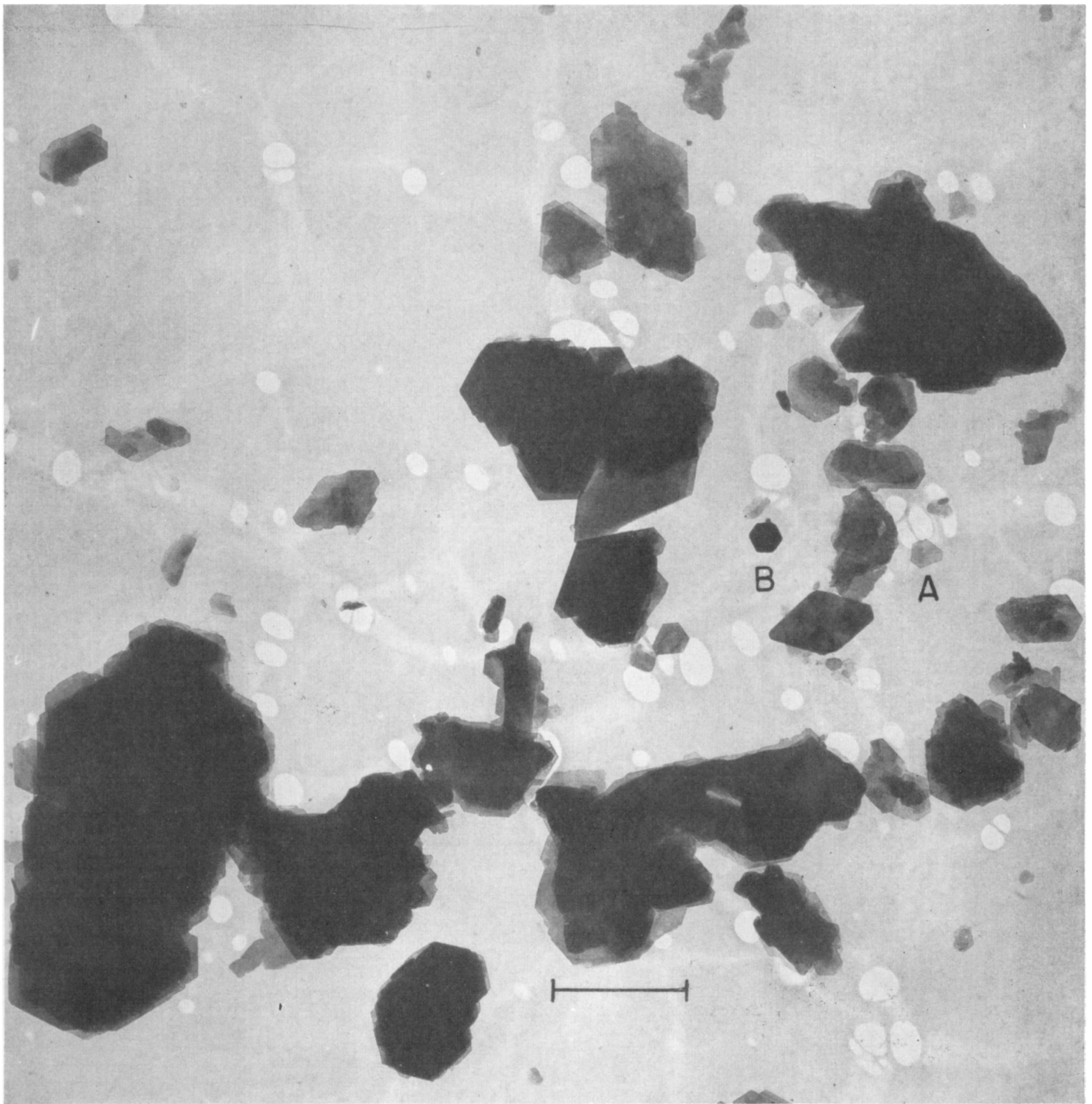


FIGURE 1. Kaolinite from Woodbury clay deposits, Huntingdon, Pennsylvania. *A*, thin, and *B*, thick single crystals. Graphic scale represents one micron.

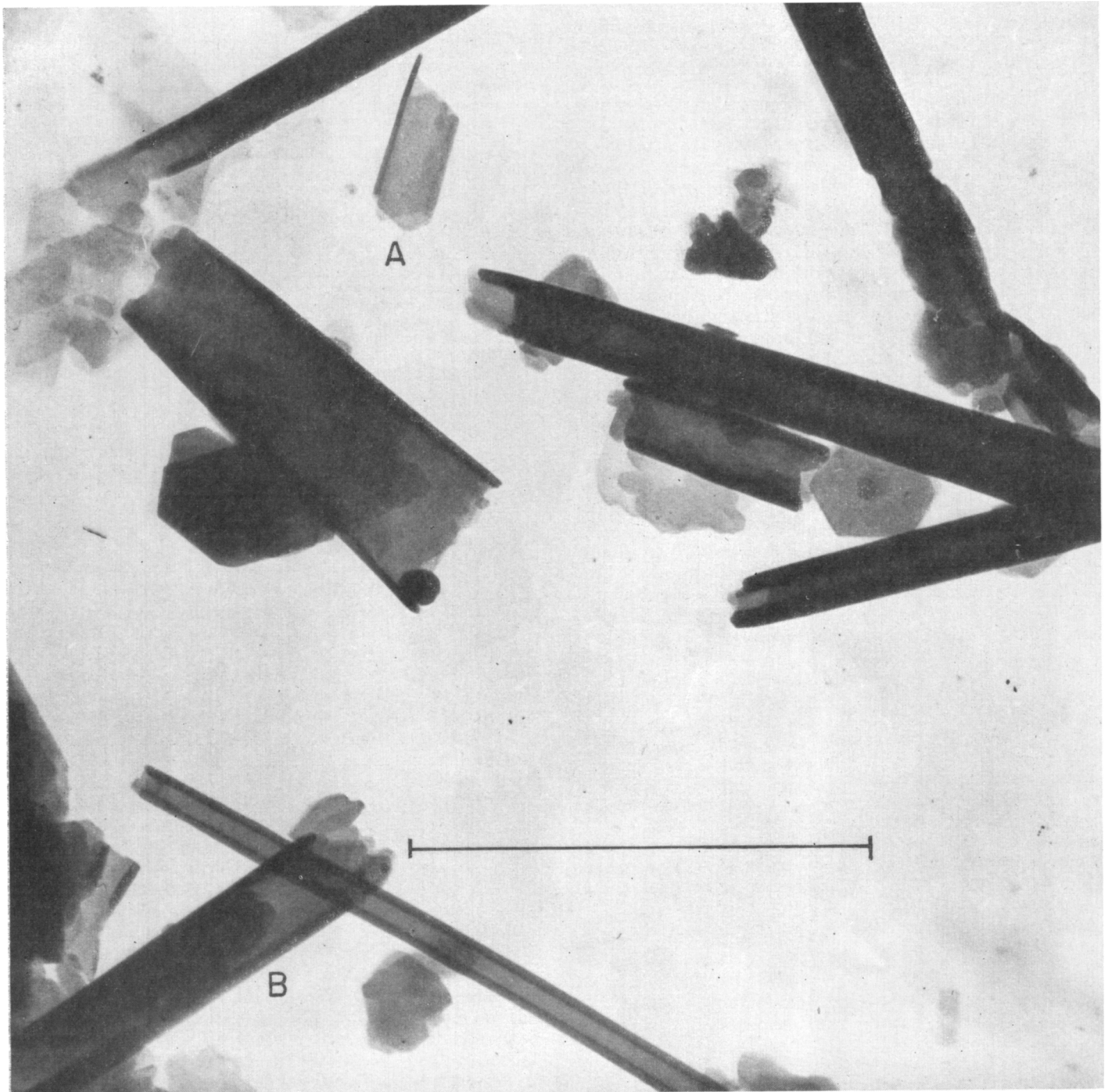


FIGURE 2. Kaolinite, halloysite mixture from Maria Elizabeth bauxite deposit, British Guiana. *A*, flake with rolled edge; *B*, tube with hexagonal terminations. Graphic scale represents one micron.

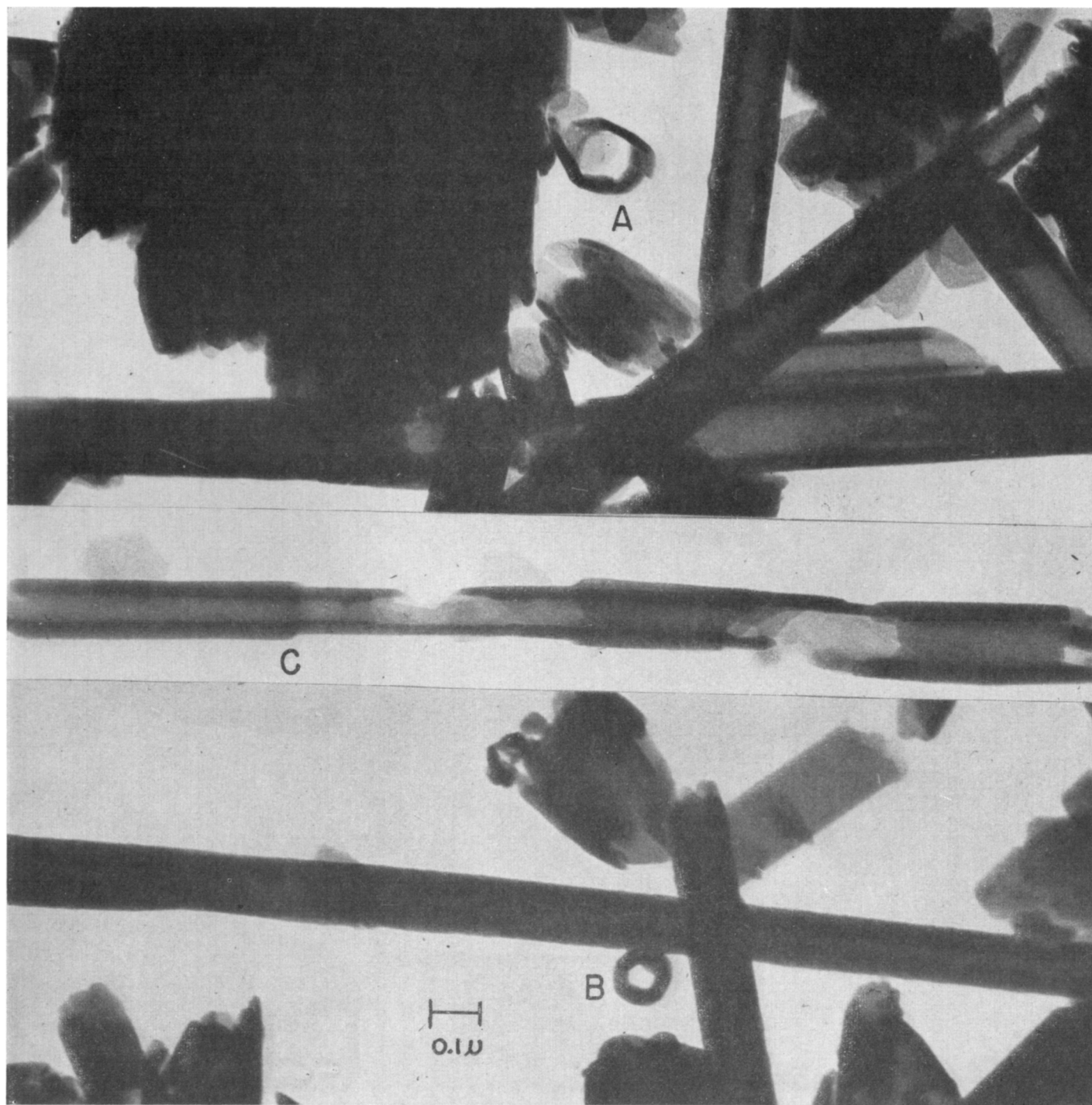


FIGURE 3. Same sample shown in figure 2. *A*, tube showing overlapping effect; *B*, another end view of a tube; *C*, 100Å increase in wall thickness. Graphic scale represents 0.1 micron.

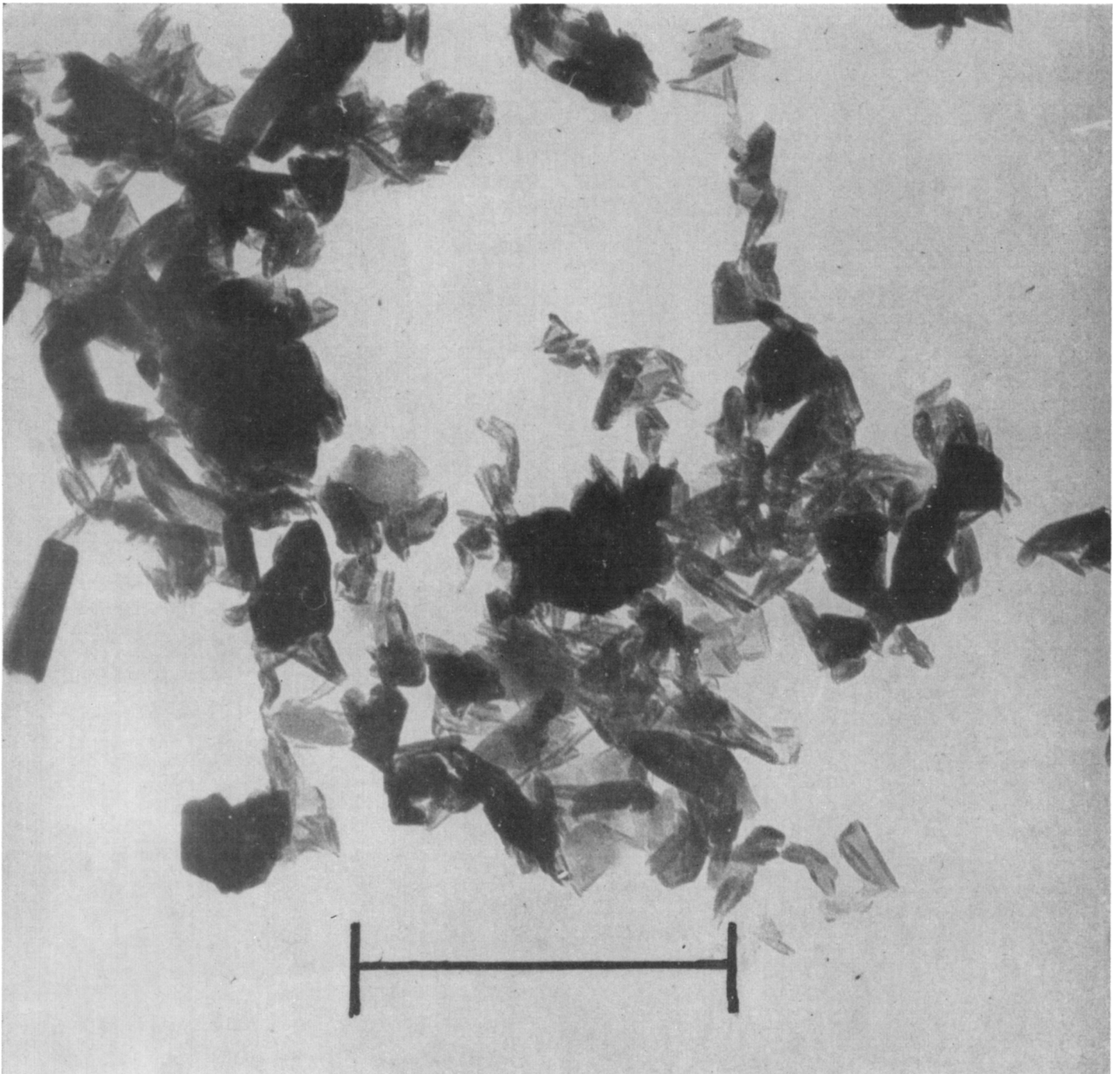


FIGURE 4. Halloysite from Alexander, North Carolina. Graphic scale represents one micron.

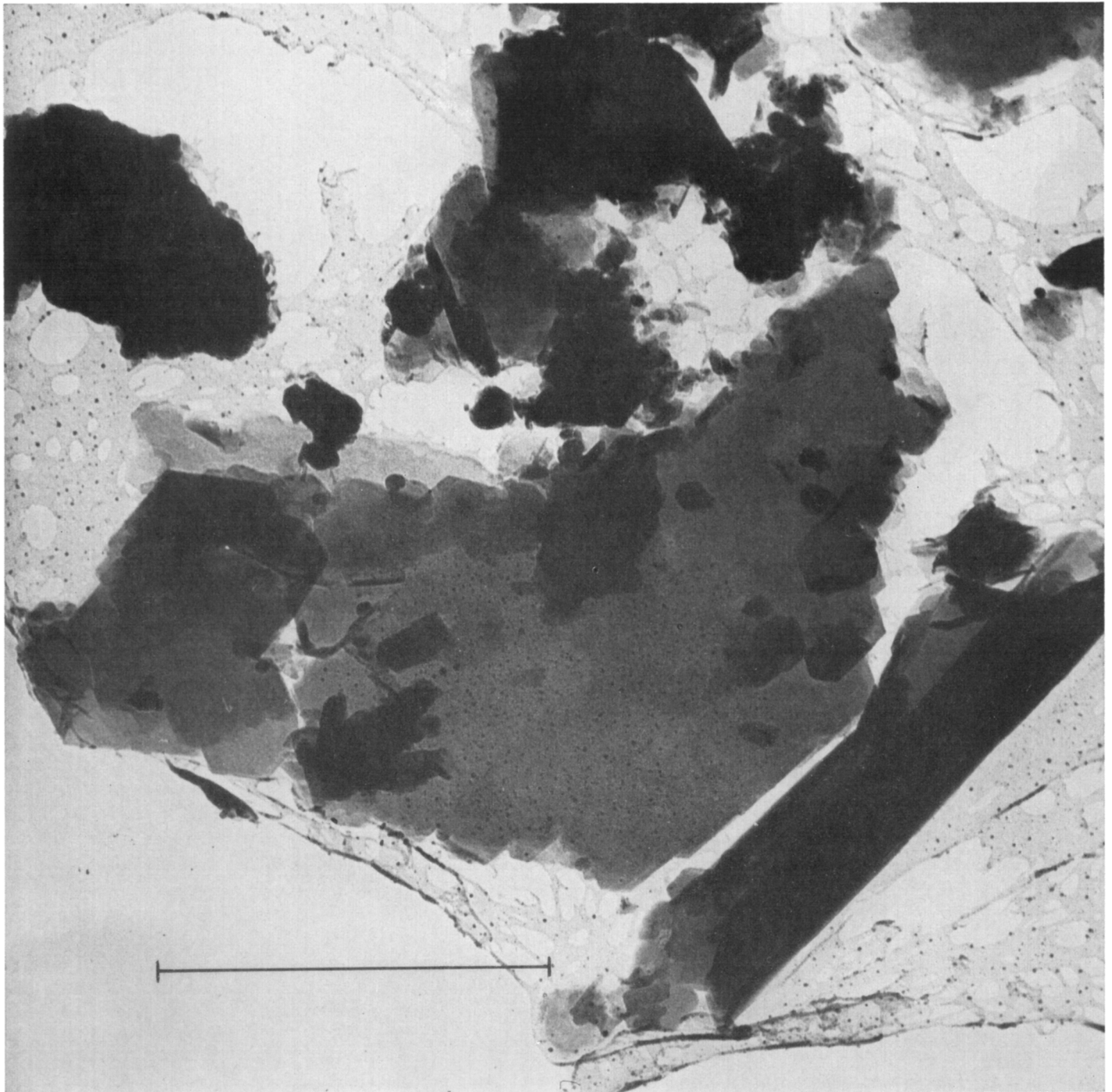


FIGURE 5. Anauxite from Ione, California. Breaking of substrate has probably caused apparent rolling up of large particles at lower right. Graphic scale represents one micron.

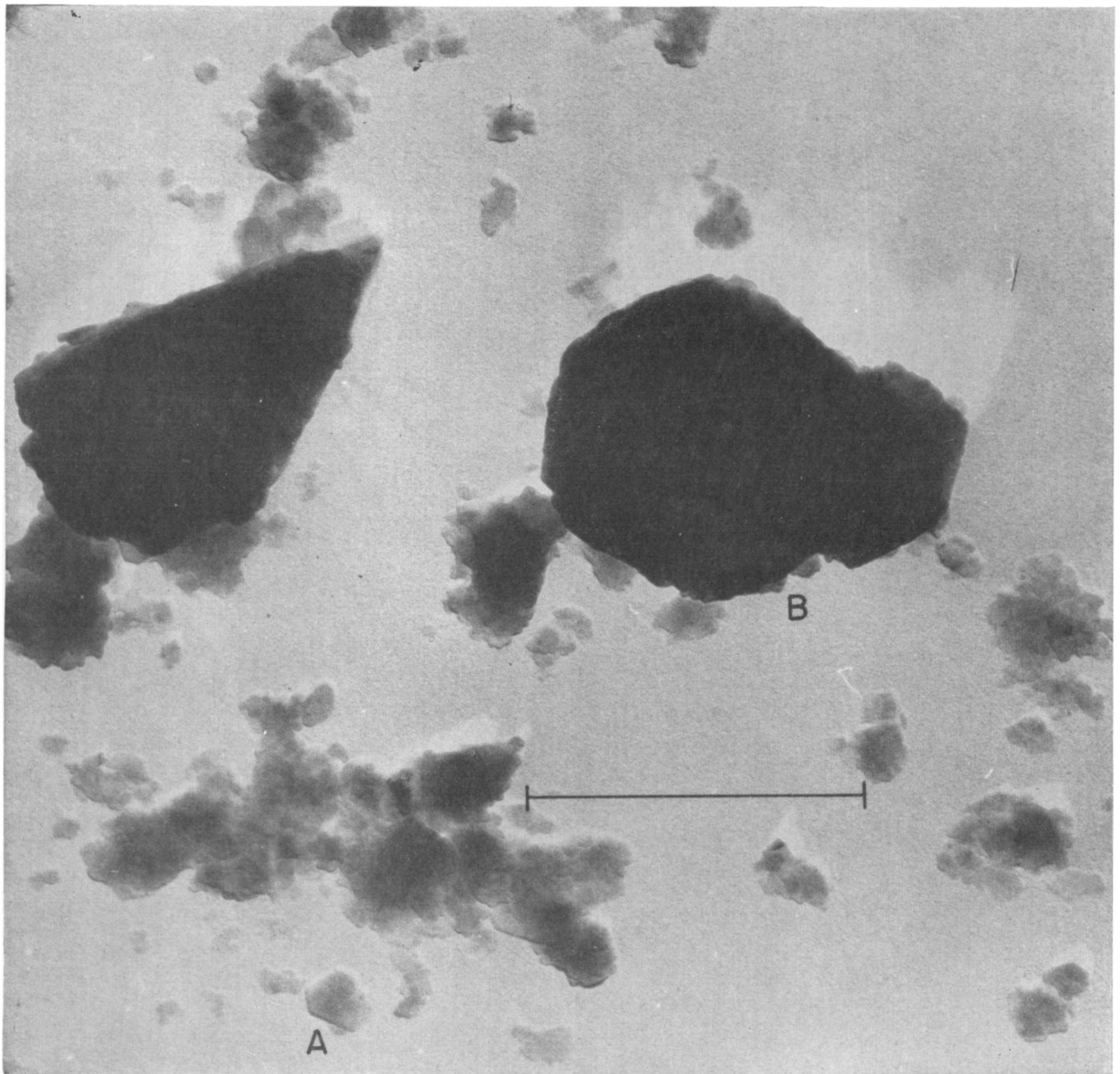


FIGURE 6. Illite from Fithian, Illinois. *A*, flake with hexagonal outline; *B*, hexagonal-appearing aggregate. Metal shadowed with Pt.-Pd. Graphic scale represents one micron.

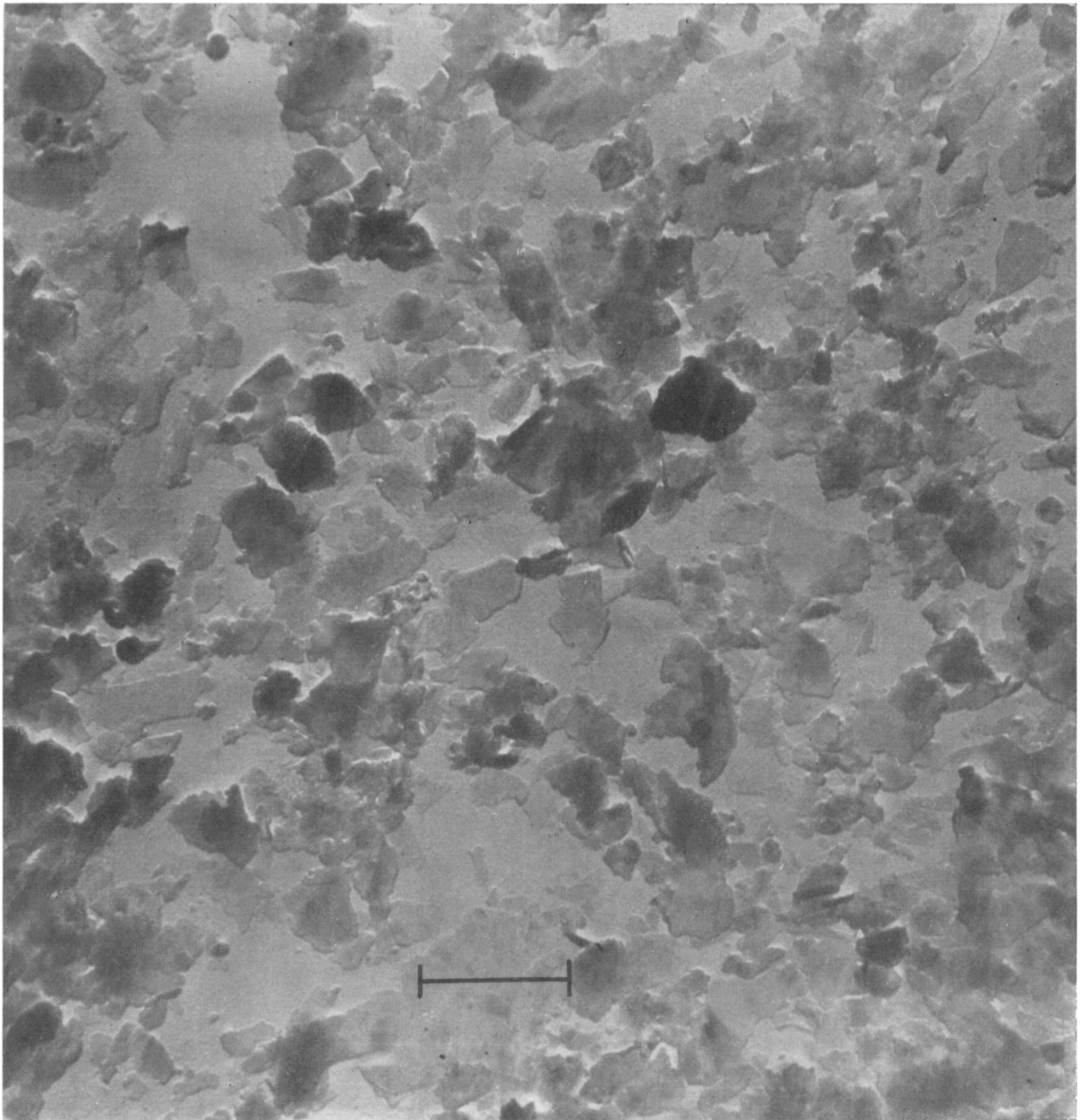


FIGURE 7. Illite from Juniata formation, Milesburg, Pennsylvania. Cr-shadowed. Graphic scale represents one micron.



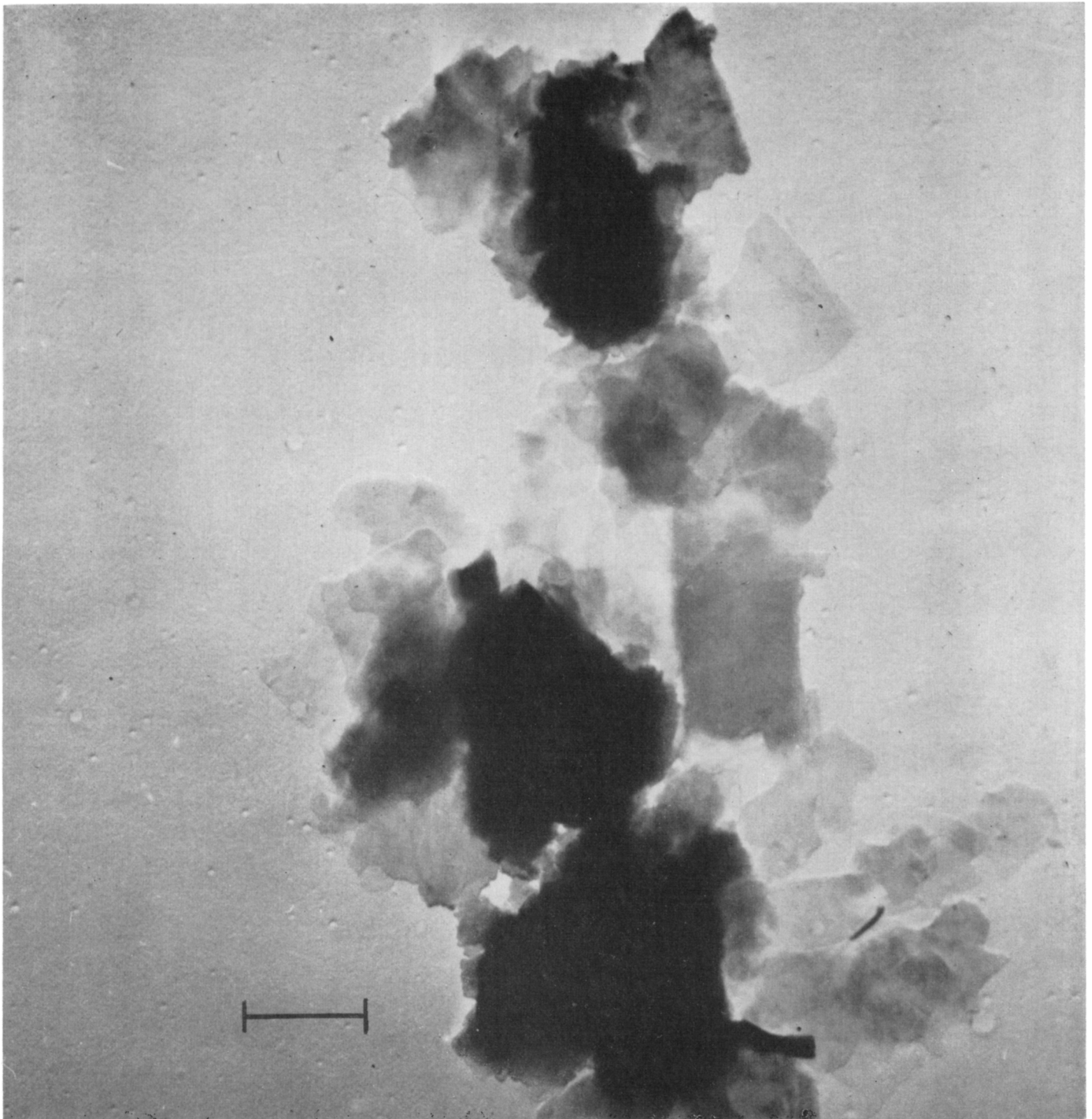


FIGURE 8. Brammallite, from Coal Measures of South Wales. Cr-shadowed. Graphic scale represents one micron.

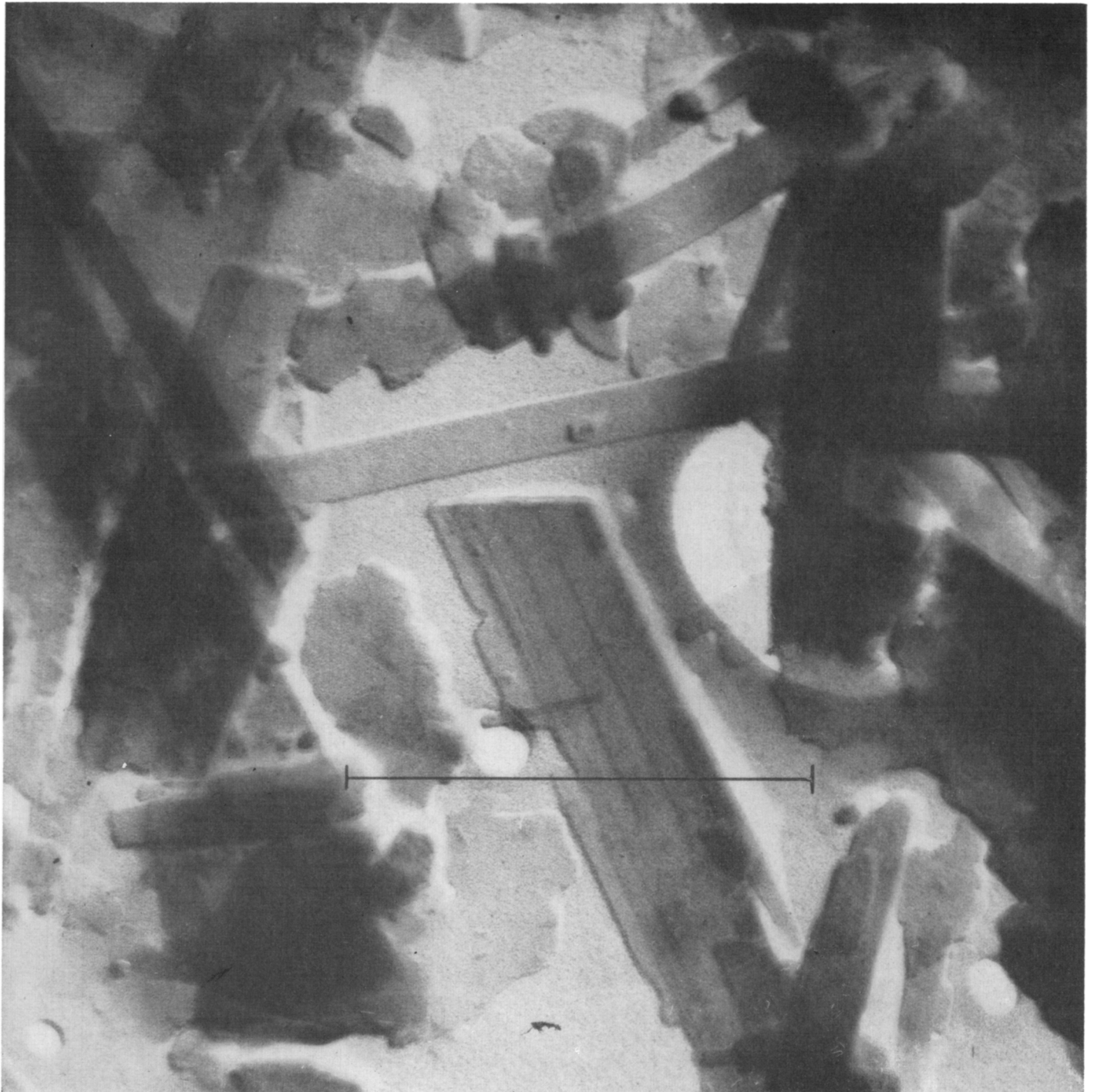
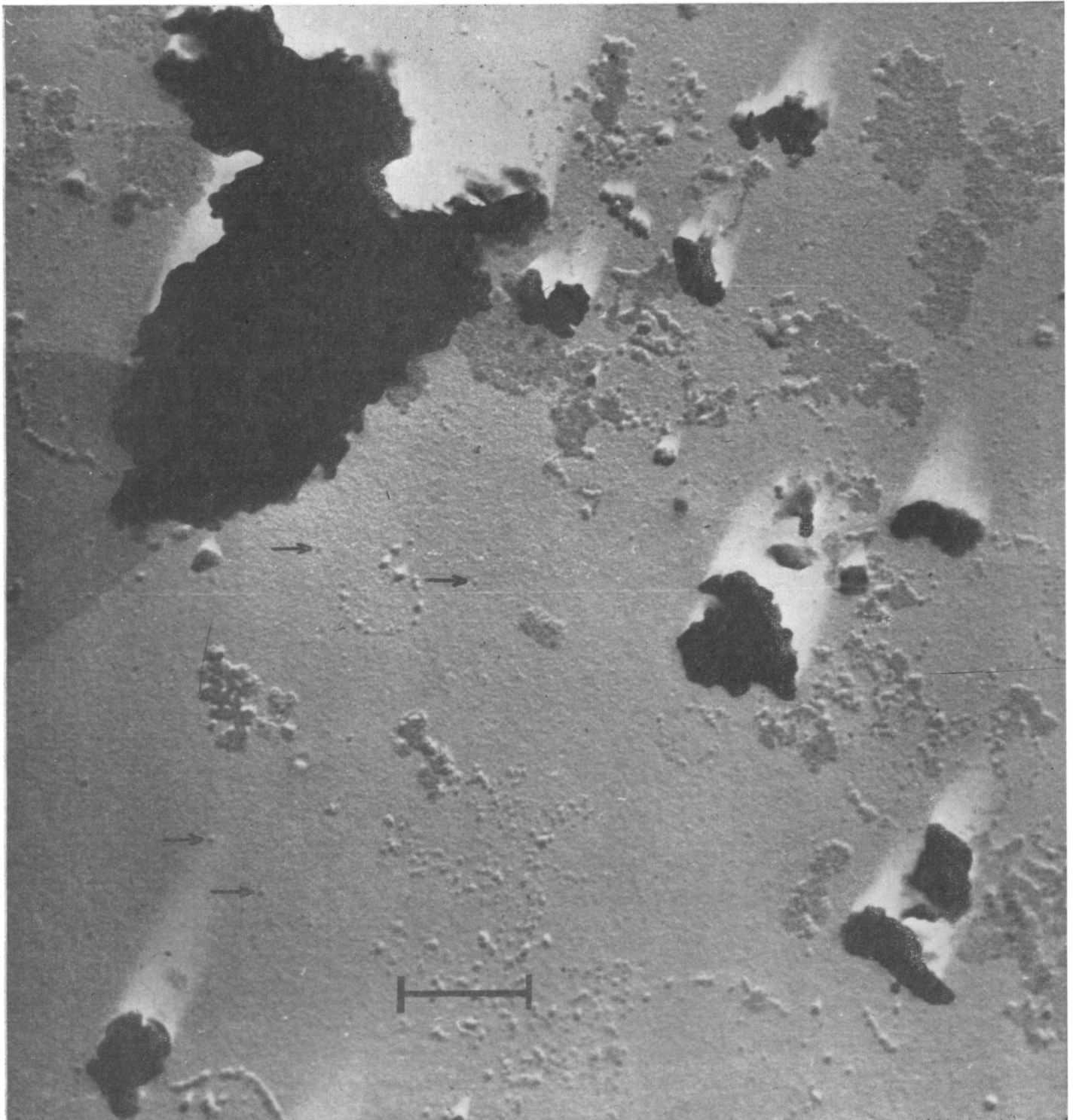


FIGURE 9. Illite from Oswego formation, State College, Pennsylvania. Pt-Pd shadowed. Graphic scale represents one micron.



**FIGURE 10.** Fullers earth from Surrey, England, Ba-saturated. Arrows indicate tiny spherical units which form larger two- and three-dimensional aggregates. Cr-shadowed. Graphic scale represents one micron.

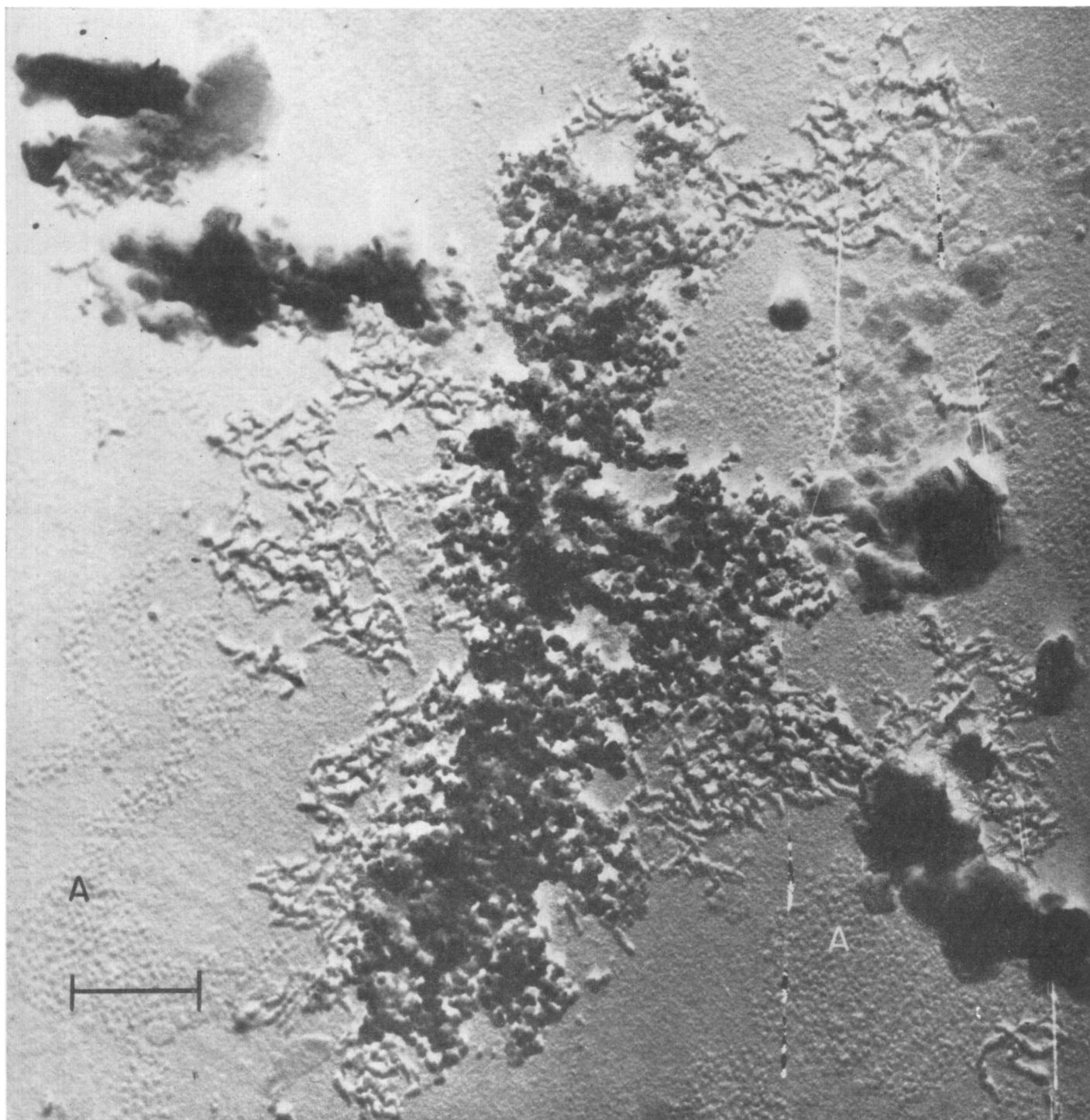


FIGURE 11. Montmorillonite from West Side, Oregon. Thread-like aggregates of spherical units clustered at A. Cr-shadowed. Graphic scale represents one micron.

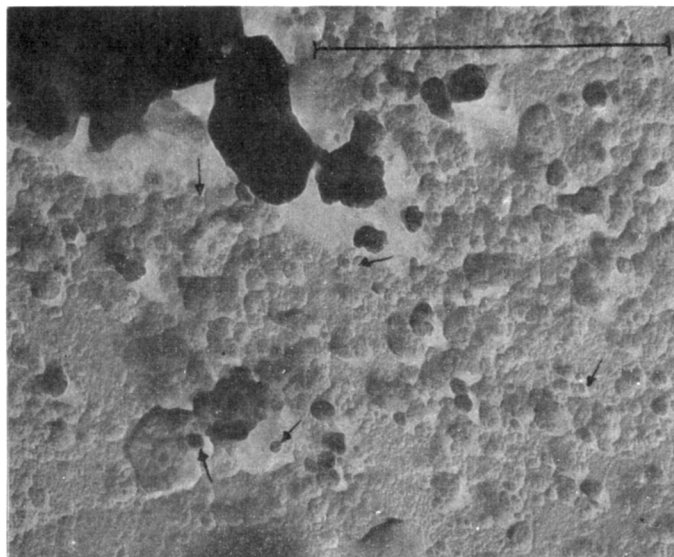


FIGURE 12. Montmorillonite from Camp Berteaux, France. H-saturated. Graphic scale represents one micron. From Mathieu-Sicaud, Méring, and Perrin-Bonnet 1951; reproduced by permission of the authors.

Figure 6 shows some of the illite from Fithian, Illinois, originally described by Grim, Bray, and Bradley (1937). Here the clay particles have been metal shadowed with Pt-Pd at an angle of incidence of  $20^\circ$ . The length of the shadows indicates that the thinnest flakes are about 50 Å thick. Flake edges are discrete and in this particular specimen often intersect at suspiciously hexagonal angles. Figure 6 shows a small crystal (*A*) and an interesting looking aggregate (*B*) which possess this tendency.

The morphology just described is not as typical of the illites we have studied as that shown in figure 7 which pictures the illite from the Juniata graywacke, exposed at Milesburg, Pennsylvania. The flakes are about the same thickness, but are larger, have better defined edges, and are very irregular in shape. Still larger illite plates of the same general shape make up the bulk of the fine fraction of the slate of northeastern Pennsylvania (Bates 1947). The morphology shown in figure 7 is not only typical of many illites but also of certain mixed-layer clays comprising Ordovician K-bentonite beds of the Appalachian region.

Figure 8 shows brammallite (Na-illite) from the Coal Measures of South Wales. Here again are found thin irregular but discrete, equidimensional plates similar to those just described.

A marked departure from the morphology typical of the usual illite is that of the clay shown in figure 9. A paper by C. E. Weaver (1953) describes this material. The mineral is characteristic of certain portions of the Oswego formation of Ordovician age. X-ray and differential thermal analysis patterns are similar to those of other illites. Chemical analysis, however, indicates an unusually low iron and magnesium content (2.96 percent  $\text{Fe}_2\text{O}_3$ , 1.09 percent MgO) and it is suggested that the well-developed crystals may result from the absence of the strain normally caused by larger amounts of these irons. The thinnest laths are once again about 50 Å thick.

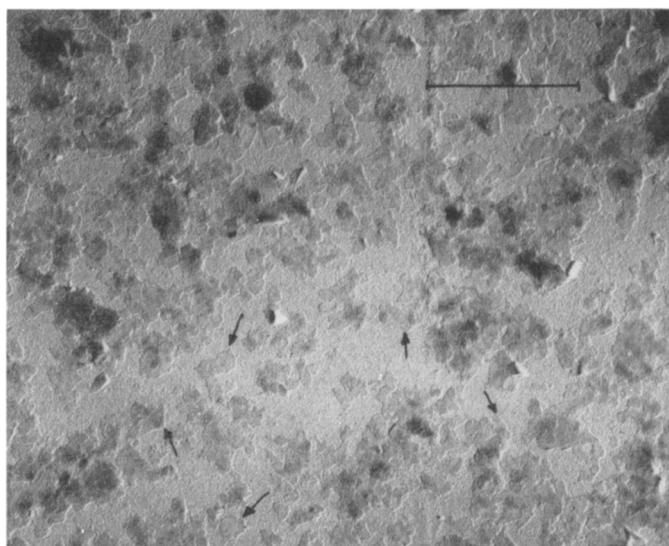


FIGURE 13. Same material shown in figure 12;  $\frac{1}{8}$  of the base-exchange positions are saturated with calcium. Graphic scale represents one micron. From Mathieu-Sicaud, Méring, and Perrin-Bonnet 1951; reproduced by permission of the authors.

*Montmorillonite Group.* As we proceed now to the minerals of the montmorillonite group the problems become more complicated, more difficult, and more challenging. Montmorillonite itself is a very difficult clay mineral to study because the morphology depends upon the manner in which the material is prepared. The nature of the dispersing agent, the cation on the clay, the grinding procedure, all have their effect on morphology. Figures 10 to 13 illustrate some of the complexities.

Figure 10 is an electron micrograph of the famous fullers earth from Surrey, England. The material was prepared in the usual manner following saturation of the exchange positions with barium. The particles run the gamut from large nondescript aggregates to small units, such as those marked by arrows, which appear nearly spherical. The latter are referred to by Mathieu-Sicaud, Méring, and Perrin-Bonnet (1951) as single crystals. The patches at upper right in the figure are essentially two dimensional aggregates of these fundamental units. Electron micrographs of many montmorillonites show the range of particle size illustrated here.

In figure 11 the aggregates of tiny particles (seen in clusters at points marked *A*) take another form. Here, apparently as the result of flocculation, they have joined in thread-like aggregates. This material is montmorillonite from West Side, Oregon, dispersed in distilled water.

The article by Mathieu-Sicaud et al. represents some of the best work on the morphology of montmorillonites that has been done to the present time, and figures 12 and 13 are reproduced from this paper with the kind permission of the authors. Figure 12 shows montmorillonite from Camp Berteaux, France, as it appears when H saturated. The fluffy appearance is very typical of both H- and Na-saturated expanding clays. Figure 13 shows the same material after an eighth of the base-exchange positions were saturated with Ca. The effect on the morphology is obvious. The arrows in the micro-

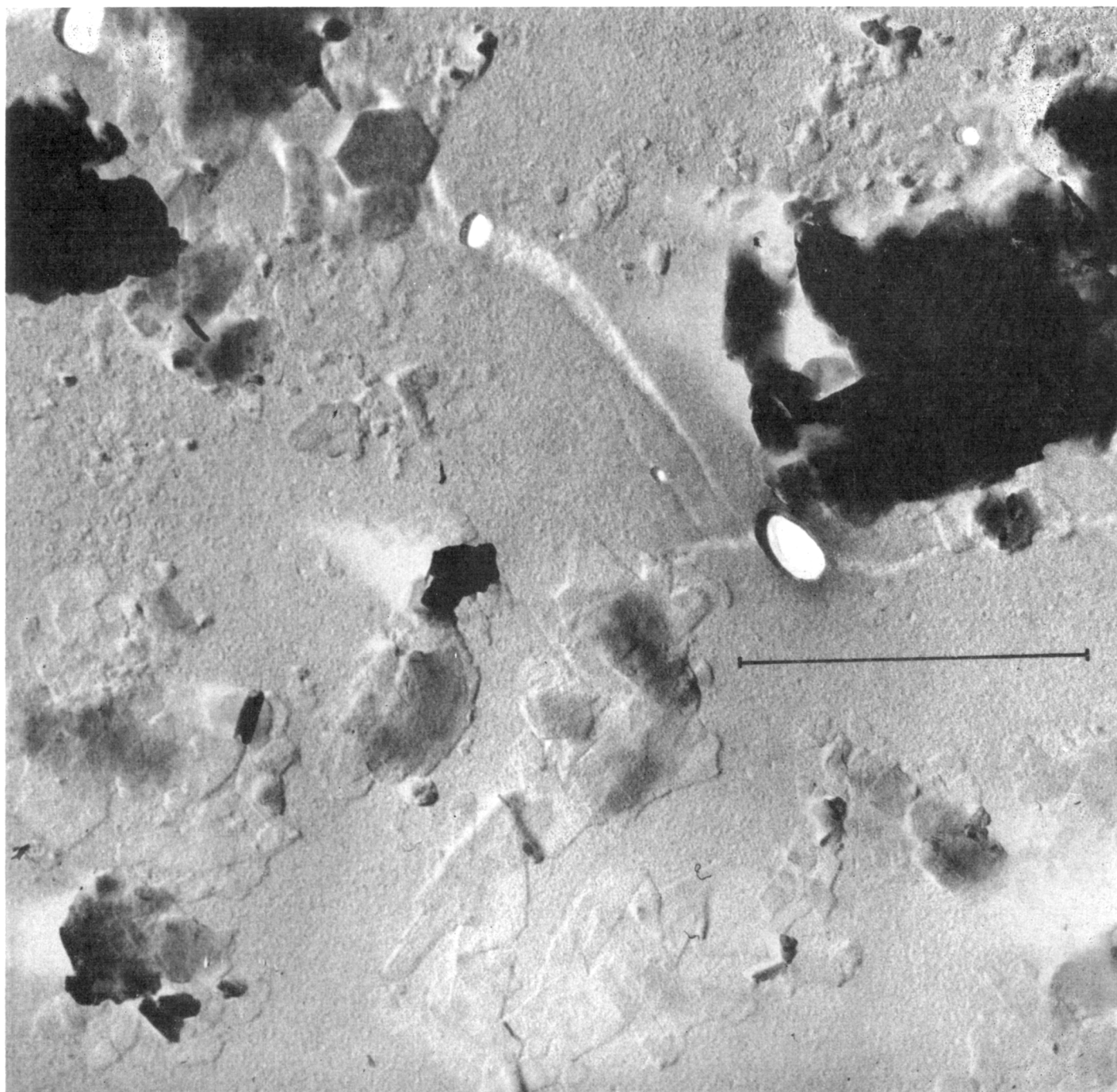


FIGURE 14. Sauconite from Friedensville, Pennsylvania. The hexagonal flake at upper left may be a kaolinite impurity. Pt-Pd shadowed. Graphic scale represents one micron.

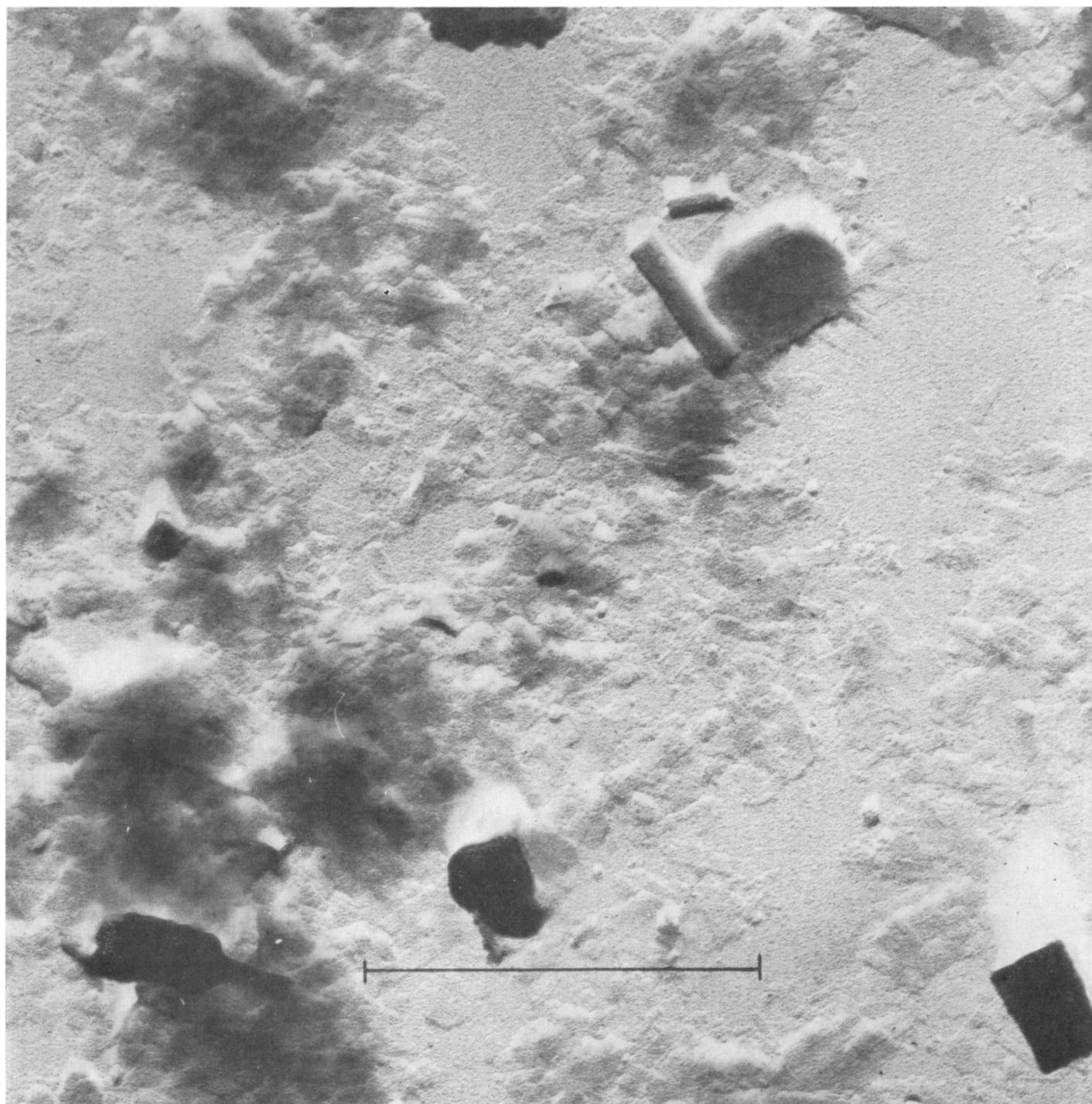


FIGURE 15. Beidellite from Wagon Wheel Gap, Colorado. The crystal at lower right may be fluorite, as this mineral occurs with the clay at this locality. Graphic scale represents one micron.

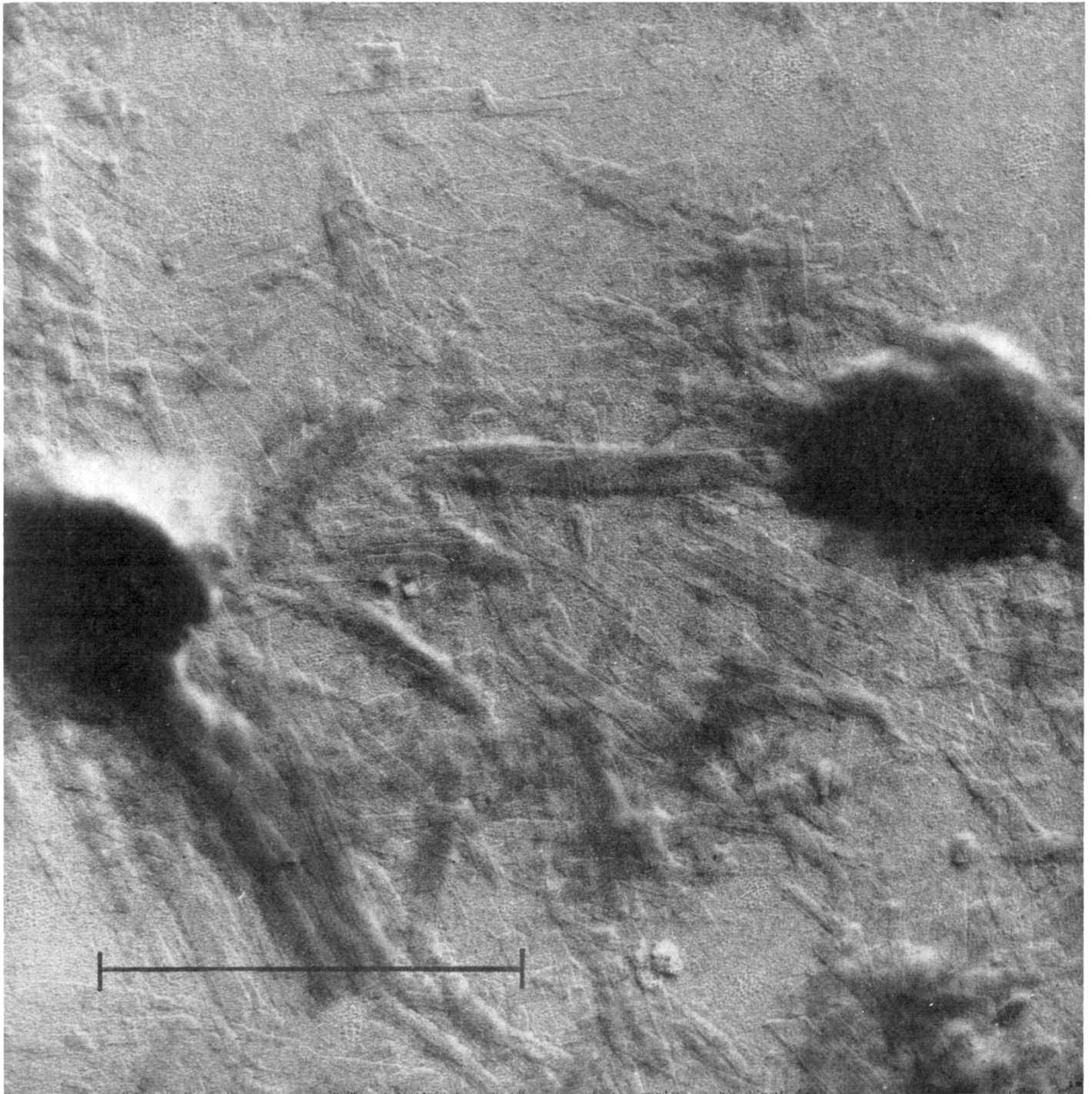


FIGURE 16. Hectorite from Hector, California. Pt-Pd shadowed. Graphic scale represents one micron.



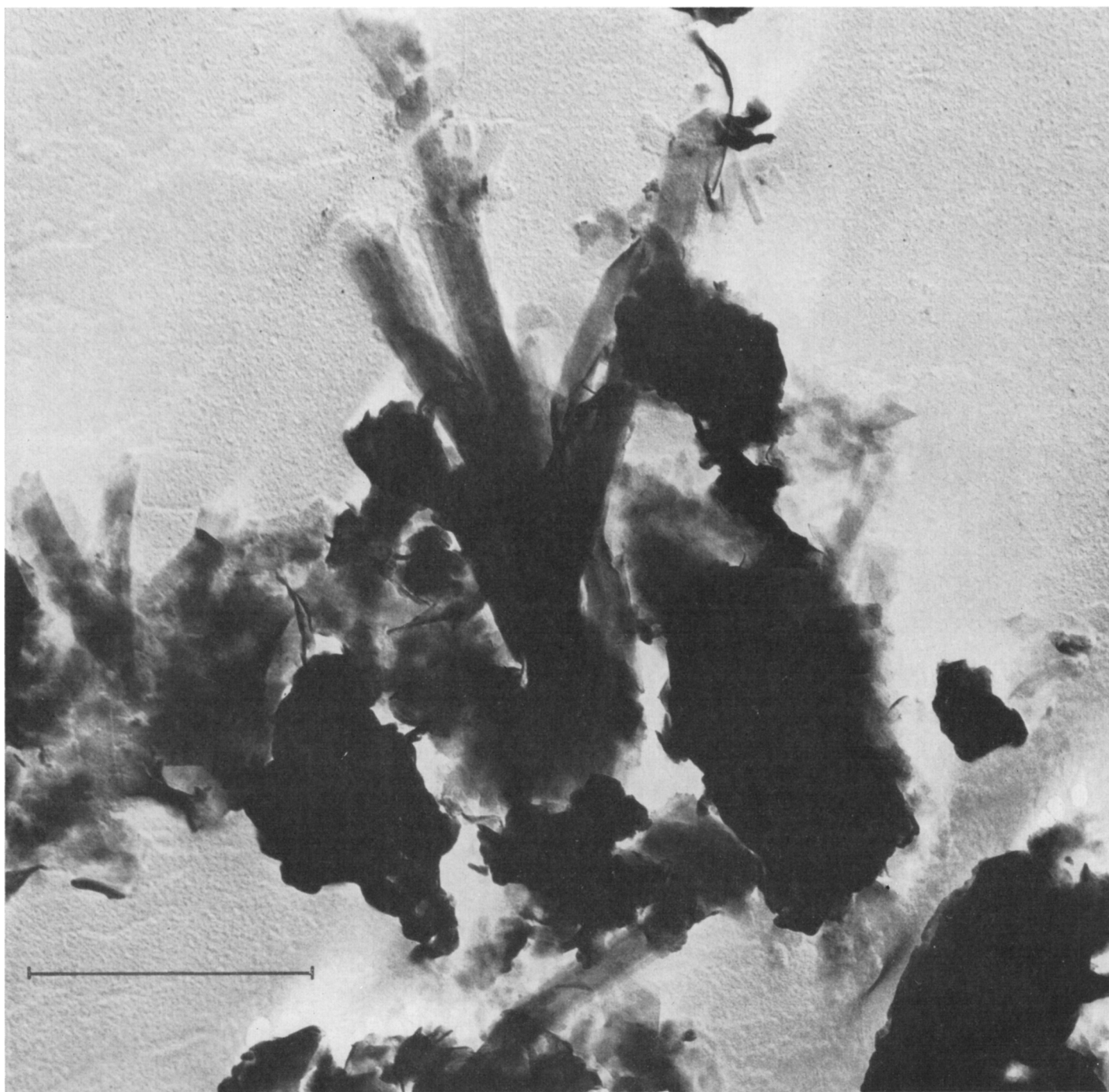


FIGURE 17. Nontronite from Sandy Ridge, North Carolina. Pt-Pd shadowed. Graphic scale represents one micron.

graph point out edge intersections of  $120^\circ$  noted by the authors.

Some of the other minerals in the montmorillonite group have more diagnostic morphology. The Zn-montmorillonite, sauconite, from Friedensville, Pennsylvania (figure 14), shows some discrete laths somewhat similar to but coarser than those of beidellite (figure 15), nontronite, and hectorite. Hectorite (figure 16) is particularly interesting because of the extreme thinness of the laths. Precision shadowing in which spheres of polystyrene latex are used for calibration shows that particles with a measurable shadow are only  $30 \text{ \AA}$  thick, indicating that those barely visible against the background are only one unit cell in height.

This is also true of nontronite (figure 17) although there is more of a tendency for the laths to agglomerate into rods and bundles as well as into irregular, more equidimensional particles.

**Replica Studies.** The problem of studying the clay minerals in their natural state, i.e. without having effected dispersion, ion exchange, etc., can be solved by the perfection of replica techniques. Figure 18 shows the simplest manner in which a replica can be made of the surface of a specimen for study in the electron microscope. Figure 19 illustrates the application of this technique to a freshly broken surface of a specimen of nontronite from Sandy Ridge, North Carolina. The particle near the center indicated by an arrow has been pulled off with the plastic substrate material but around it are visible the results of replication of laths and aggregates making up the surface of the clay. The slide shows something of the complexity of texture produced during the emplacement of the individual clay particles. Figure 20 of another replica of this same material shows interesting rolls or folds commonly oriented perpendicular to the length of the laths. Similar features are believed by Mathieu-Sicaud, et al. (1951) to result from the thinness and flexibility of the ribbons. Their appearance in replicas casts some doubt on such an origin. Because of difficulties encountered in the preparation of suitable replicas, this method has not been applied extensively to the clay minerals. However, with improvement of technique such studies will greatly aid in the investigation of all types of fine-grained aggregates and will yield textural information obtainable only by this method or by ultra-thin sectioning.

**Conclusion.** In conclusion I should like to point out that the science of applied electron microscopy is less than 15 years old and we can still look for vast improvement in instrumentation and technique. At the same time, the micrographs shown here illustrate the cream of the clay-mineral crop. There is still ahead of us the tremendous research task of investigating the great bulk of the clay minerals, not those that occur in more or less homogeneous clay deposits which are sometimes almost monomineralic to start with, but those which make up a large percentage of our sedimentary rocks and soils and are intimately mixed with other fine-grained minerals and organic matter. The soil scientists have made considerable progress in this direction and it is my belief that the electron microscope will play a leading role in future studies of these and other clay-mineral problems.

## DISCUSSION

### H. F. Coffey:

In regard to the illite sample which you shadow-cast twice, did you consider the possibility that some water of swelling might have been removed during the evaporation of the metal on the clay and that the observed swelling represents only a minor part of the actual swelling of the particle in its wet state?

### T. F. Bates:

The work with double shadow casting is very preliminary, and we are encountering many difficulties. We have no idea as to the orientation of the individual plates in the aggregate and therefore no real calibration of the length of the double shadow in terms of expansion. By working with some of the platy montmorillonites (hectorite, nontronite, etc.) which presumably are oriented with the C-axis parallel to the beam, the production of two shadows would permit a measurement of the expansion. This, however, demands some very precise work.

### Padraic Partridge:

Have you seen any dendritic patterns in your electron micrographs which could have been formed from evaporation of solubles in the water, or that came from the clay or its alteration products? I have seen such patterns and wondered about the cause.

### T. F. Bates:

We sometimes run into them but so far have been able to eliminate their occurrence by using freshly distilled water in the preparation of our suspensions.

### H. F. Coffey:

What would you estimate to be the thinnest sheet of a montmorillonite that you have photographed?

### T. F. Bates:

We have not as yet seen any montmorillonite in well defined sheets that can be measured. Thus far we have found montmorillonite to consist of fluffy aggregates without crystalline pattern.

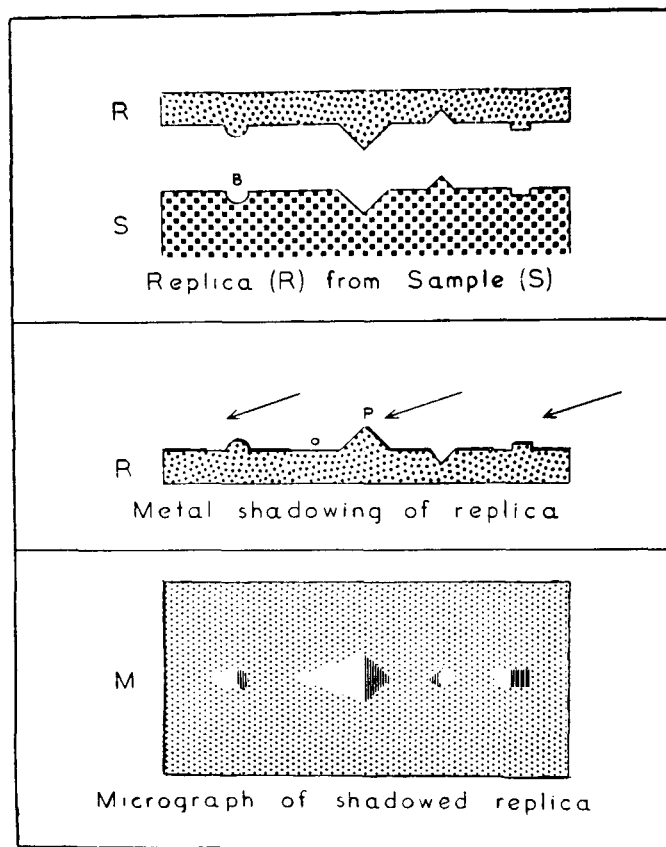


FIGURE 18. Negative replica technique.

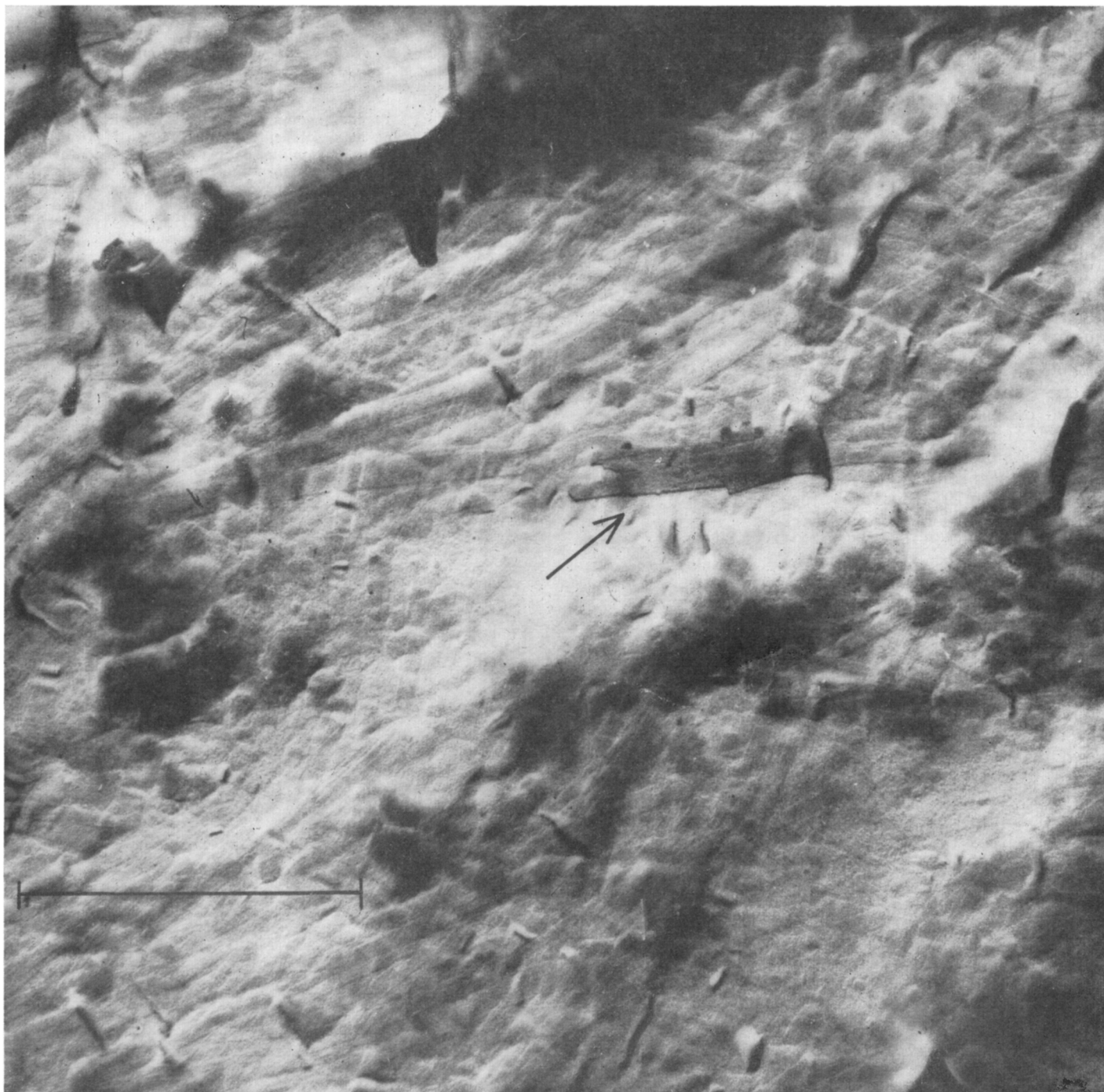


FIGURE 19. Replica of nontronite from Sandy Ridge, North Carolina. Pt-Pd shadowed. Graphic scale represents one micron.

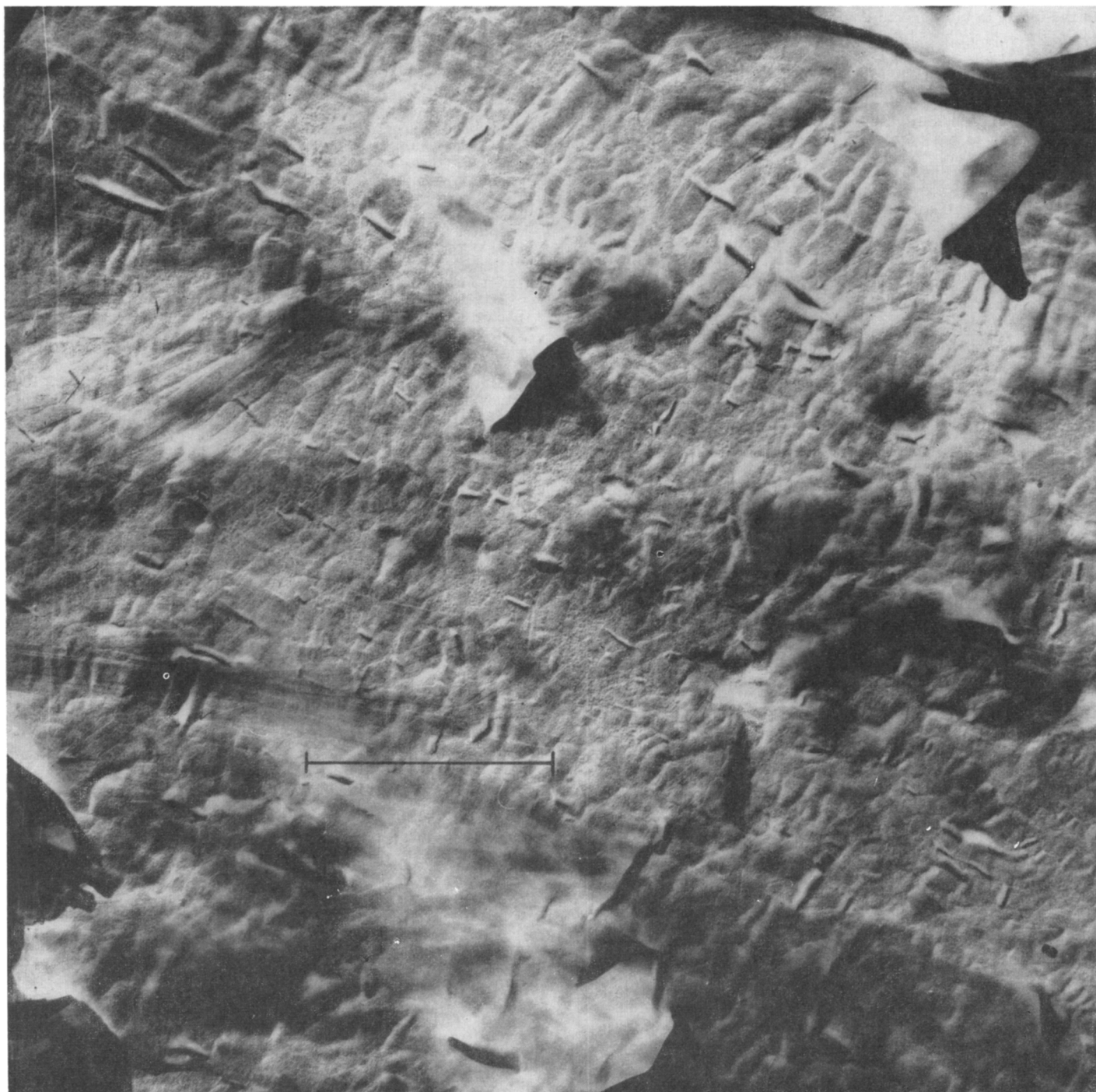


FIGURE 20. Replica of nontronite specimen showing interesting rolls. Pt-Pd shadowed. Graphic scale represents one micron.

**R. L. Stone:**

In the pictures you showed, with few exceptions, there is a considerable amount of aggregation of the particles. Will it be possible in the future to take a picture of a clay in its most dispersed form?

**T. F. Bates:**

This has already been achieved for minerals of the kaolinite group. With proper control of the sample, such as regard to pH and exchangeable cation, it should be possible to take photographs of any clay in a highly dispersed condition. In the case of montmorillonite there has been more success in this respect in France than anywhere else.

**H. F. Coffey:**

I believe that this can be done by use of the freeze-dry technique. A 2 or 3 percent highly dispersed suspension is prepared and frozen rapidly at about minus 80° C. The water is then driven off while the suspension is in the solid state. I have not applied this to montmorillonite but believe it would be successful.

**M. D. Foster:**

Recently Ed Dwornik made an electron micrograph of Mg-saturated montmorillonite from Santa Rosa, Mexico. It gave a beautiful crystalline pattern, much better than any other electron micrograph that I have seen of montmorillonite.

**T. F. Bates:**

I have recently received a manuscript by Mr. H. P. Cahoun of the University of Utah which describes a Utah saponite with very well-formed, large, thin, and almost equi-dimensional square plates.

They are crystalline, and have well-defined angles, but these angles do not seem to be related to the usual crystallographic directions.

**Padraic Partridge:**

What is Murray's technique of dry-sampling for the electron microscope?

**H. H. Murray:**

A toothpick wrapped with lens paper is dipped into the powdered sample and rolled on a glass slide coated with collodion. The collodion film is removed from the slide by floating it on distilled water and then mounting it on a  $\frac{1}{8}$ -inch disk of 200-mesh screen. The sample is then shadow-cast and electron micrographs taken.

**SELECTED REFERENCES**

- Bates, T. F., 1947, Investigation of the micaceous minerals in slate: *Am. Mineralogist*, v. 32, pp. 625-636.
- Bates, T. F., 1951, Morphology of layer lattice silicates: *Denison Univ. Bull.*, v. 42, pp. 83-91.
- Bates, T. F., Hildebrand, F. A., and Swineford, A., 1950, Morphology and structure of endellite and halloysite: *Am. Mineralogist*, v. 35, pp. 463-484.
- Grim, R. E., Bray, R. H., and Bradley, W. F., 1937, The mica in argillaceous sediments: *Am. Mineralogist*, v. 22, pp. 813-829.
- Mathieu-Sicaud, A., Méring, J., and Perrin-Bonnet, I., 1951, Étude au microscope électronique de la montmorillonite et de l'hectorite saturées par différents cations: *Soc. franç. minéralogie Bull.*, v. 74, pp. 439-456.
- Weaver, C. E., 1953, A lath shaped non-expanded dioctahedral 2:1 clay mineral: *Am. Mineralogist*, v. 38, pp. 279-289.