ELECTRON MICROSCOPY OF CLAY SURFACES

Thomas F. Bates and J. J. Comer

The Pennsylvania State University

ABSTRACT

Improvements in replica techniques have made possible the high magnification study of textural characteristics and surface features of clay aggregrates found either in nature or in the laboratory. The most successful method of sample preparation involves pre-shadowing the specimen with platinum and backing this with a layer of carbon prior to removal of the clay with a suitable solvent.

Data on orientation and packing of clay particles are readily obtained. The method is useful to investigate clays in which the characteristic morphology is easily affected by environmental conditions or by sample preparation for other methods of study.

Replicas of kaolinite indicate that many of the pseudohexagonal plates seen in electron micrographs are cleavage fragments. Investigations of halloysite (4 H_2O) using this technique prove that the tubes exist as such in the bulk clay. Striations on montmorillonite flakes that intersect at an angle of sixty degrees suggest a degree of morphological crystallinity that is apparently destroyed when the material is dispersed prior to study in the electron microscope. Replicas of dickite, attapulgite and weathered feldspar also show features that have not heretofore been seen in electron micrographs.

INTRODUCTION

The scientist engaged in the study of clay minerals is concerned not only with the clay particle *per se* but with the clay as it relates to a specific environment. The environment of interest may be the rock or soil in which the clay particles are found, the fluid systems in which they are suspended, or the manufactured product of which they are a part. Since many clay minerals have properties which are sensitive to slight changes in surrounding conditions, the best methods for the investigation of the "clay-environment" system are those which involve a minimum of disturbance to the sample in the preparation for the analysis.

From this standpoint most of the standard procedures used in the electron microscope study of clays are subject to the same limitations that apply to other methods of investigation. The sample may be ground, fractionated, suspended in liquid, centrifuged, resuspended and allowed to settle or evaporated to dryness before the analytical instrument even enters the picture. It is little wonder that the resulting micrograph may yield little direct evidence as to the state of the clay before it found its way to the preparation bench.

THE REPLICA METHOD

The replica technique was first used by electron microscopists to study metals and other materials too dense for electron transmission studies. The

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method, in its simplest form, involves the formation of a thin plastic film on the surface to be studied, its subsequent removal and investigation in the microscope.

The important requirements of a replica are lack of self structure, which impairs resolution, high contrast and strength. These are particularly stringent on clay surfaces where lateral dimensions in the range of 50 Å or less must be detectable on an overall rough surface with differences in height between depressions and elevations as low as 10-15 Å or as great as 2-3 microns.

Probably the most frequently used replica technique has been that of the one-step plastic replica (Schaefer and Harker, 1942) which gives a negative image of the surface. This type of replica may be made by applying solutions of collodion, Formvar or other suitable plastics directly to the surface to be studied. When dry the film formed on the surface may be stripped and metal-shadowed (Williams and Wyckoff, 1946) to increase the contrast. Hast (1947) used this technique to strip thin layers of clay particles from the bulk material for examination in the electron microscope. However, the use of this or any other method which involves making a plastic impression of the surface is not suitable for examination of most clays because of their porosity. A thorough study of plastic replicas of bulk clays (Comer and Turley, 1953) indicated that reliable replicas of these surfaces could not be obtained largely because of flow of the plastic into the pores of the clay. In addition it was difficult to remove the clay adhering to the replicas.

By preshadowing (Williams and Wyckoff, 1945) the clays with platinum prior to the application of the plastic film, details of the surface were more accurately reproduced and the porosity to the plastic somewhat decreased. The technique and the results obtained have been described by Comer and Turley (1955). However, because the plastic tended to envelop the particles and protect them from the acid, a thin film of clay was often found adhering to the replica surface. It was obvious that the plastic should be replaced by a supporting film of material which would not penetrate the surface to as great a depth and would not be affected by the hydrofluoric acid used to dissolve the clay.

Evaporated films of silica have been used on many materials (*e.g.* Hamm and Comer, 1948) and meet the first of these requirements but not the second. The method of making carbon films by an evaporation technique was first described by D. E. Bradley (1954) and appeared to the authors to be a possible solution to the problem at hand. The adequacy of the platinum-carbon combination is illustrated by the accompanying micrographs. The result is a positive replica showing elevations and depressions as they are on the surface. The preparation of the replica involves the following 5 steps, three of which are illustrated in Figure 1 :

   1. Shadow casting the clay surface with platinum
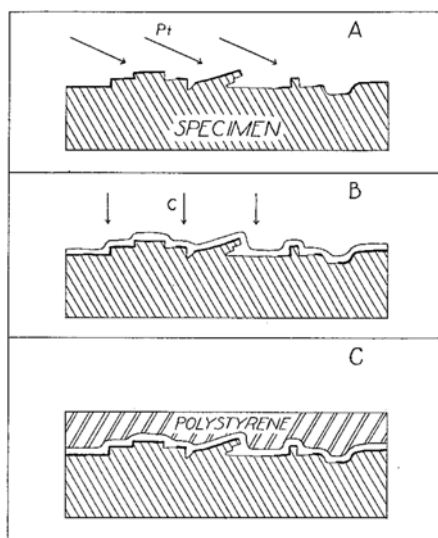   2. Evaporation of carbon

FIGURE 1. — Steps in the replica method.

3. Embedding in polystyrene
4. Removal of clay from the replica
5. Removal of the replica from the polystyrene.

Shadow Casting

Sections of the bulk material are broken to yield fresh surfaces. In extreme cases excess moisture is removed in a vacuum desiccator. No other treatment is applied except to blow gently any loose material from the fracture surface. Due to the uneven surfaces of many of the clays it is necessary to shadow with the platinum at two angles in directions mutually perpendicular to each other. In some areas both shadows may be seen while in others only one of the evaporated films may have deposited on the specimen. The first layer is applied at an angle of incidence of 20 degrees using enough platinum to give a film approximately 6-8 Å in thickness. A second evaporation is made at 45 degrees in a direction normal to the first to deposit a film of approximately the same thickness as the first one.

Evaporation of Carbon

The shadowed clay specimen is next coated at normal incidence with an evaporated film of carbon following the method described by Bradley (1954). The thickness of the evaporated film was not determined but is estimated to be between 100-150 Å. It has been found that the required thickness is determined by the surface roughness of the clay. If breakage of the replicas is to be avoided, thicker films of carbon must be applied to a

rough surface than to a smooth one. Care must be exercised, however, to avoid unnecessarily thick films since contrast and resolving power decrease as the thickness is increased.

Embedding in Polystyrene

In order to avoid breakage of the combined platinum and carbon films during the removal of the clay it is necessary to support these films in a plastic base. Polystyrene granules are heated and compressed between glass microscope slides to form discs approximately 2-3 mm. in thickness. These discs resting on a slide or other suitable surface are heated on a hot plate and softened to the point where cavities made in the surface of the plastic by a pointed object disappear as soon as the object is withdrawn. The clay is then placed with the replica side in contact with the plastic and is gently but firmly pushed into intimate contact with it. The slide is removed from the hot plate and the plastic allowed to harden without disturbing the clay. Inspection through the plastic will determine if good contact has been achieved between the plastic and the evaporated films.

Removal of Specimen from the Replica

The plastic disc containing the replica and the clay is placed with the replica side down in 48 percent hydrofluoric acid for as long as necessary to remove the specimen. Some specimens fall free from the replica within a period of only 30 minutes or 1 hour. More frequently it requires several hours for this to occur. When it appears that the surface of the replica is free of all clay the disc containing the embedded replica is placed in fresh acid for at least another hour. It is then washed in several changes of distilled water and allowed to dry.

In the event that a given clay is too fragile to embed successfully in polystyrene it may be possible to float it directly on the surface of the acid with the clay surface down. Upon removal of the clay the replica can be transferred to other acid or water on large sections of 200-mesh stainless steel screening. There is usually considerable breakage when the replica is transferred to the surface of water. It may be found necessary to pick up the fragments on specimen screens containing thin films of collodion to avoid further breakage upon drying. It was necessary to use this technique on some samples of halloysite.

Removal of Replica from the Polystyrene

The replica was removed from the plastic in the same manner that silica replicas are separated from polystyrene in the polystyrene-silica replica technique (Gerould, 1947). The surface was scored with a sharp blade to divide it into $\frac{1}{8}$ in. squares. The polystyrene disc was pushed to the bottom of a dish of ethylene dichloride. With the replica side up the plastic adheres to the bottom of the dish and the sections of replica float free within

a few minutes. As soon as the squares separated from the plastic they were removed to a fresh dish of solvent by means of a medicine dropper or sections of stainless steel screening. An additional wash in a third dish of fresh solvent is recommended before picking up the replicas on the $\frac{1}{8}$ in. diameter specimen screens.

CLAY MINERAL STUDIES

General

The purpose of this paper is to illustrate the application of the replica method just described to the study of clay particles as they appear on a freshly broken surface of the lump of clay. It is important to bear in mind, therefore, that the micrographs illustrate the manner in which the material fractures. No attempt was made to include a large number of clay minerals. Rather, the emphasis is placed upon a limited number of specimens which vary appreciably in morphological characteristics.

Kaolinite

Figure 2 is an electron micrograph of a replica of kaolinite from Langley, South Carolina. Before discussing the clay, several aspects of the picture pertinent to the technique may be pointed out. The effect of the platinum used in pre-shadowing is brought out by the light "shadows" cast to the right of each projecting particle. The double-shadow was used to bring out as much detail as possible. Particles such as that at "A" show both shadows, that on the lower right being weaker than that on the upper right. The carbon also tends to accentuate the outlines of the particles.

The scale shown on all electron micrographs represents one micron.

From the standpoint of the clay itself, several features are of interest. Particularly outstanding is the large amount of smooth background which appears to be at the same level in the photograph. Rising like "mesas" above this "plain" are pseudohexagonal units of the size and shape that appear in electron micrographs taken of the dispersed clay. It is evident in this picture that units like that at "B" are partially cleaved from the larger area around it presumably as a result of strains produced in fracturing the material. Another feature characteristic of the photograph is the parallelism of many of the crystal edges throughout the picture. This feature is more marked in the background area than in the projecting hexagonal particles probably because the position of some of the latter may have been shifted on fracturing.

These features suggest that the area covered by the picture is a large crystalline unit of the clay out of which smaller cleavages have broken.

Figure 3 shows similar features except that here the smooth plain is broken not only by sharp edged "mesas" but by low undulations of more nebulous outline. The "crystal" defined by parallel edges is over four microns across whereas the smaller pseudohexagonal units range from

0.08 to 1.5 μ. Edges such as that at A suggest that the smaller units result from breaking of the larger. The significance of the "undulations" is not at present understood.

The feature seen at A in Figure 3 is also illustrated in Figure 4 taken at another place on the same surface pictured in the preceding micrographs. Here the roughly parallel lines and planes are believed to represent the edges of the sheets in a book of kaolinite. These edges are over 14 μ long and are noticeably serrated, whereas the small hexagonal crystals range from 0.1 to 1.0 μ in diameter. The latter cluster along the edges and appear to be derived from them. It seems likely that grinding or perhaps simply placing these sheets in water would cause them to break down completely into the smaller units.

Figures 2, 3 and 4 indicate that at least in kaolins similar to that from Langley, South Carolina, the crystals photographed after grinding or dispersal of the specimen in water are largely cleavage fragments from larger units and not primary crystals in their own right.

Figure 5 shows another view of the Langley material. In this case a book is viewed on edge showing interesting relationships in the grouping of the "sheets" and the incipient cleavage between them.

The texture illustrated in Figure 6 is quite different from that observed in the Langley koalin. This replica was made from the conchoidal fracture obtained on breaking a sample of a flint clay from Murfreesboro, Arkansas. Here, in addition to the larger crystals and books, there are abundant small hexagons ranging from 0.05 to 0.3 μ in size which are apparently unrelated to larger units. The bending effects seen in some of the large crystals are also of interest.

Figure 7 is another picture of this flint clay. Although the surface appears relatively smooth there is little evidence of parallel orientation of crystal edges. Individual hexagons which range from 0.02 to 0.75 μ in size often appear to blend together but not in a crystalline array. The smoothness appears to result in part from breakage across rather than around the crystalline particles, presumably as a result of stronger interparticle bonds.

Dickite

In contrast to the platy character of the kaolinite books, the edge of the dickite crystal from the anthracite area in Schuylkill Co., Pa. seen in Figure 8 has a wall-like appearance when viewed at high magnification. Incipient cleavage is evident but the massive character and smooth surfaces bespeak the stronger interlayer bonding that differentiates this mineral from kaolinite.

The same characteristics are illustrated in Figure 9, taken of the same dickite specimen. The small specks seen on both cleavage planes and edges are unexplained. They range in size from 25 to 100 Å and are sufficiently dense to have a high scattering power for electrons.

Halloysite

The tubular characteristics of the mineral were first described and explained by Bates, Hildebrand and Swineford (1950). The theory put forth by these authors that hydrous halloysite crystals assume the tubular form during growth has not been seriously questioned. However, proof of this point has only recently been forthcoming (Comer and Turley, 1955; Sand and Comer, 1955). Figure 10 is a typical micrograph of the hydrous halloysite from Wendover, Utah. Although some of the tubes may be complete, many show a longitudinal parting which the authors cited attributed to dehydration of the 4 H_2O form. The replica of this clay shown in Figure 11 shows conclusively that the tubes exist as such in the bulk sample of the clay. Numerous circular to elliptical cross-sections can be seen where the tubes intersect the surface of the specimen at angles approaching 90°. The cylinders vary in diameter from 250 to 750 Å in this photograph and the wall thickness in measurable cross sections is between 25 to 50 Å.

Figure 12 illustrates the wide range in tube size found within a few square microns of clay surface. Such relationships indicate that the wide range of particle size exhibited in micrographs of the dispersed material is not necessarily the result of particle breakage during preparation. In considering the morphology of the tubes seen in replica, it is important to keep in mind that particle shape may have been affected either by fracturing of the clay lump to obtain the surface to be replicated or by partial dehydration of this surface in the vacuum of the evaporating unit prior to and during metal shadowing. Such effects are believed negligible except perhaps for particles which lie largely in or on the surface. The tubes in this micrograph vary from 270 to 1700 Å in width, are up to 1.83 μ in length, and have walls 41 to 75 Å thick.

Montmorillonite

Just as montmorillonite is typically the least photogenic of the clay minerals when the sample is dispersed on the electron microscope screen, it is similarly ill-defined when viewed in replica. However, because the morphology of this type of clay is so sensitive to slight changes in environment, the application of this new technique may well be more important here than in the study of the clays that are more amenable to and less affected by treatment. This is well illustrated in Figure 13 of montmorillonite from Montmorillon, France where striations are present on areas marked A, B, and C. The faint lines intersect at angles of 60 and 120 degrees and represent a higher degree of morphological crystallinity than can normally be found in dispersed particles. The faintness of the lines is indicative of cleavage and separation of the very thin sheets typical of this material.

The fullers earth from Surrey, England pictured in replica in Figure 14 shows a jumble of flakes and edges which is perhaps to be expected of montmorillonite-type clay. No order is apparent and it is obvious that the breakage has occurred across as well as parallel to the shreddy flakes.

Attapulgite

A typical replica of the surface of the material from Attapulgus, Georgia is shown in Figure 15. Individual fibers shown here range from 90 to 360 Å in diameter. The grouping into bundles is characteristic of the mineral. Figure 16 shows an area where many of the rods lie at an angle to the surface rather than parallel to it. End sections are difficult to measure because rods that project appreciably from the surface become surrounded with a "halo" of carbon. Many of those that are visible appear elliptical in shape and range from 150 to 400 Å in diameter.

Weathering of Feldspar

There has been much speculation as to the detailed mechanism of clay formation at the expense of other minerals. In studies now in progress on the weathering of feldspars, preliminary experiments with the replica technique have yielded encouraging results. Figure 17 shows a portion of a cleavage surface of microcline on which there are occasional hexagons, such as at A and B, presumably of kaolinite.

ACKNOWLEDGMENTS

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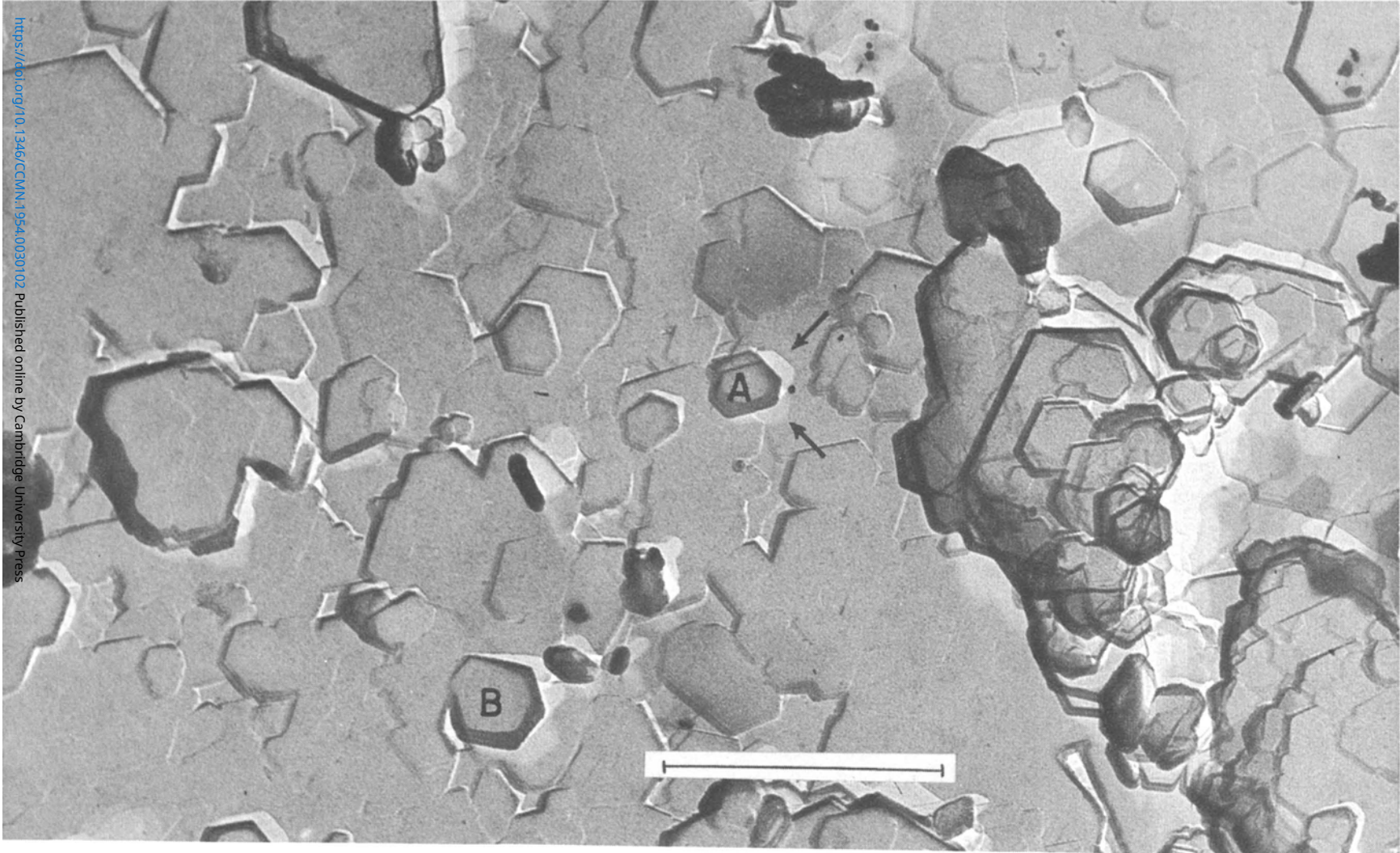
FIGURE 2. — Kaolinite, Langley, South Carolina. (A) Arrows indicate double shadow from particle. (B) Cleavage fragment partly broken away from underlying crystal.
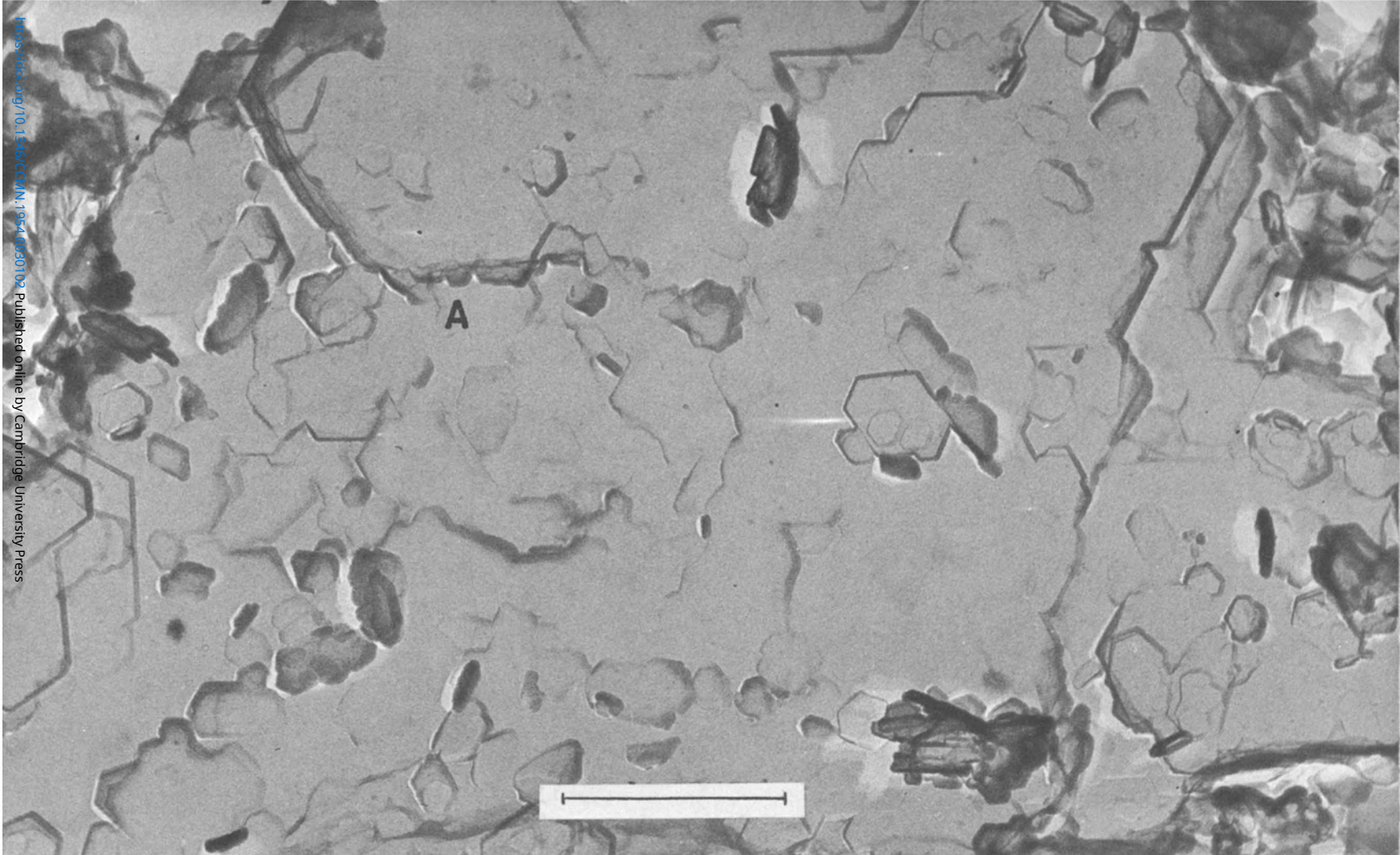
FIGURE 3. — Kaolinite, Langley, South Carolina. (A) Edge showing incipient cleavage of small hexagonal units.
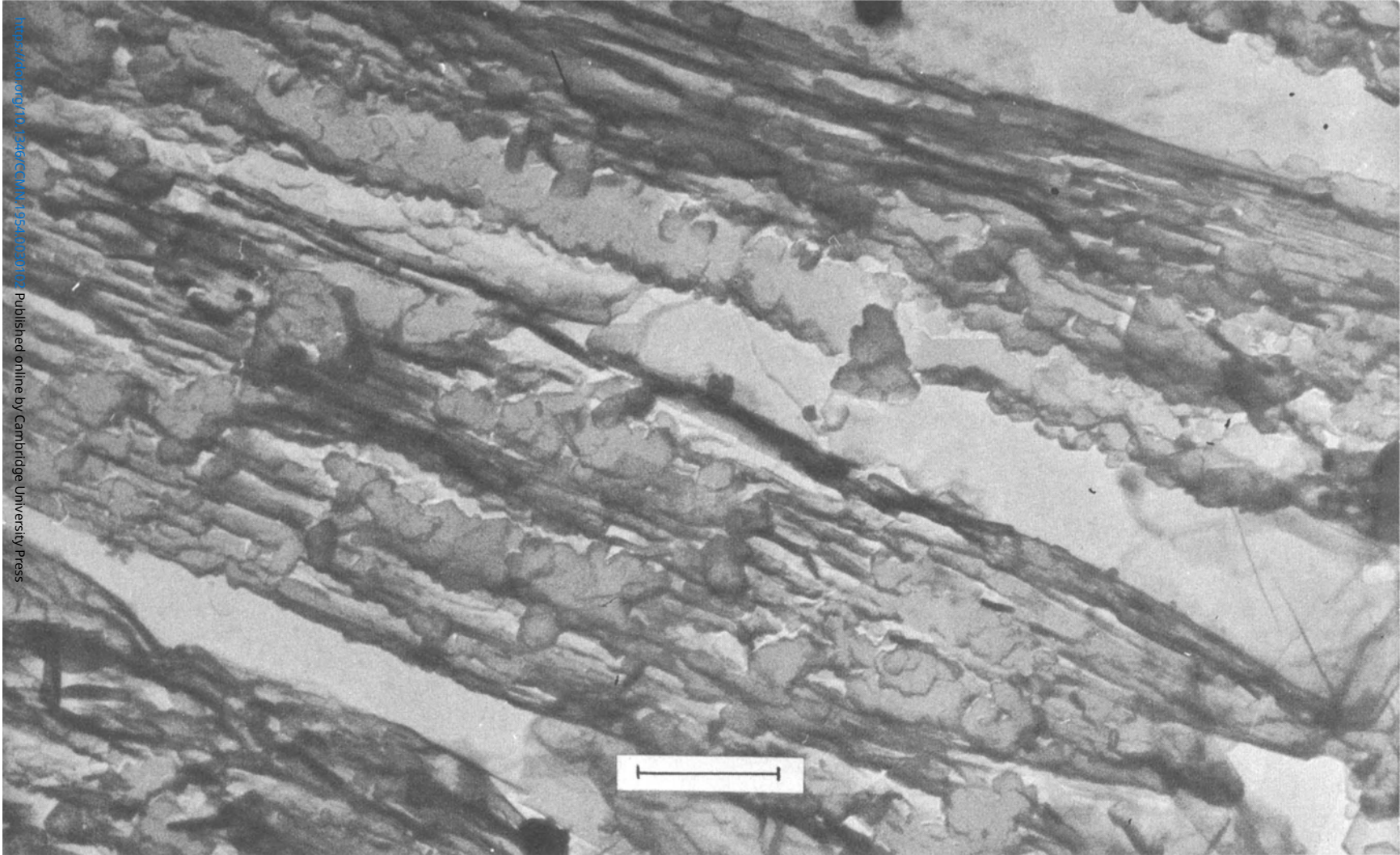
FIGURE 4. — Kaolinite, Langley, South Carolina. Edges of book showing tendency to form small, hexagonal cleavage flakes.
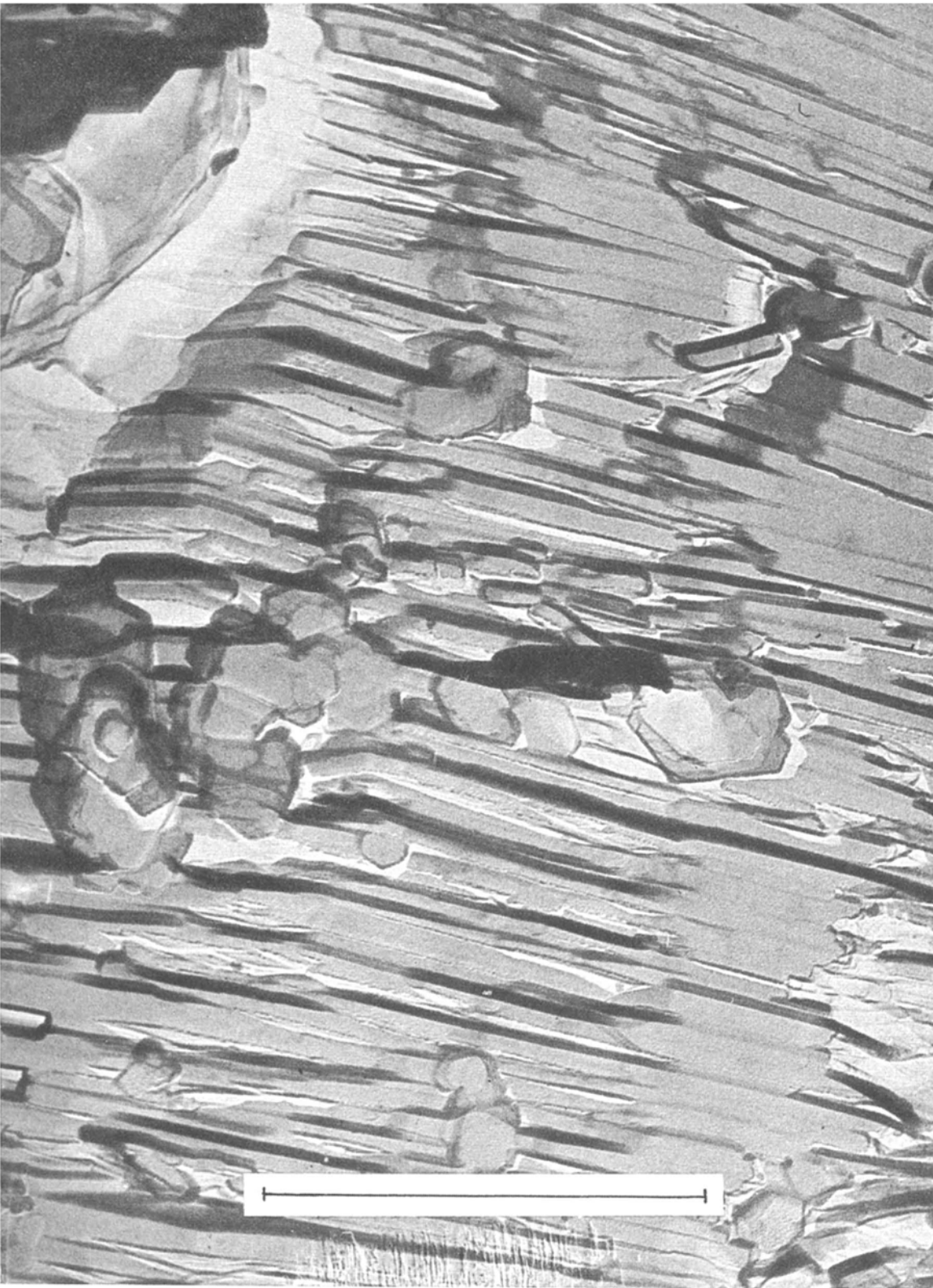
FIGURE 5. — Kaolinite, Langley, South Carolina. Edge view of kaolinite book.
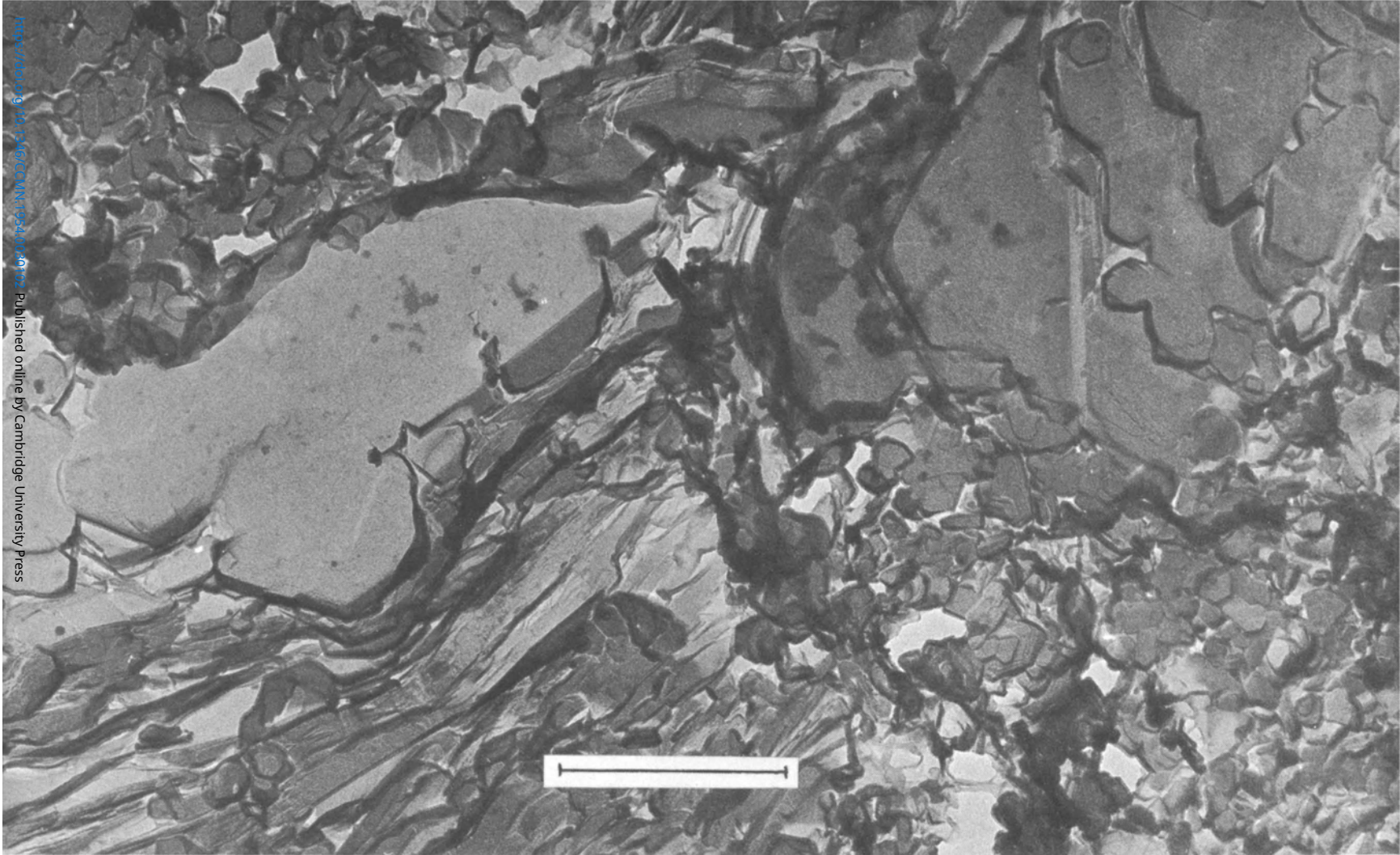
FIGURE 6. — Flint clay, Murfreesboro, Arkansas.
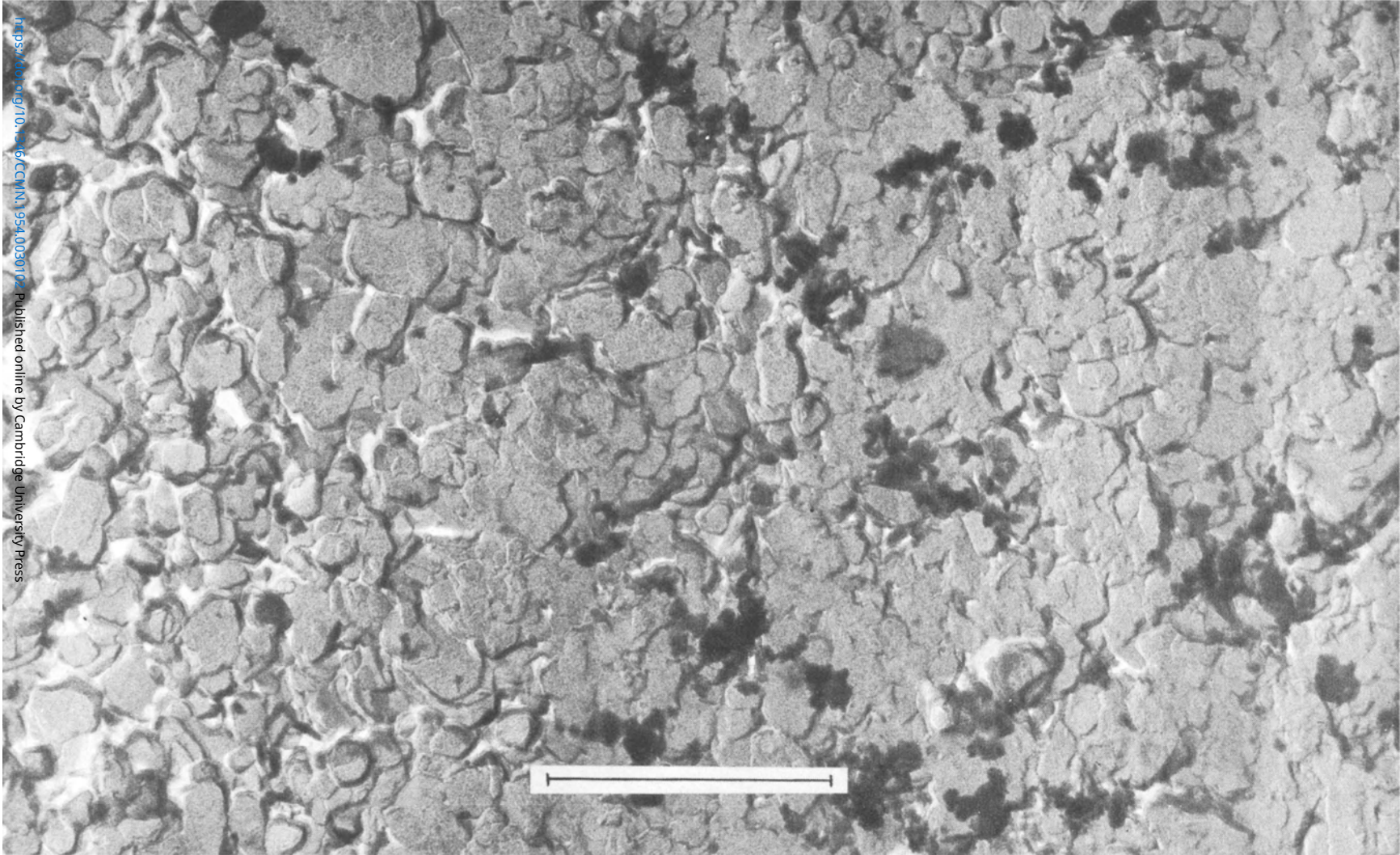
FIGURE 7. — Flint clay, Murfreesboro, Arkansas.
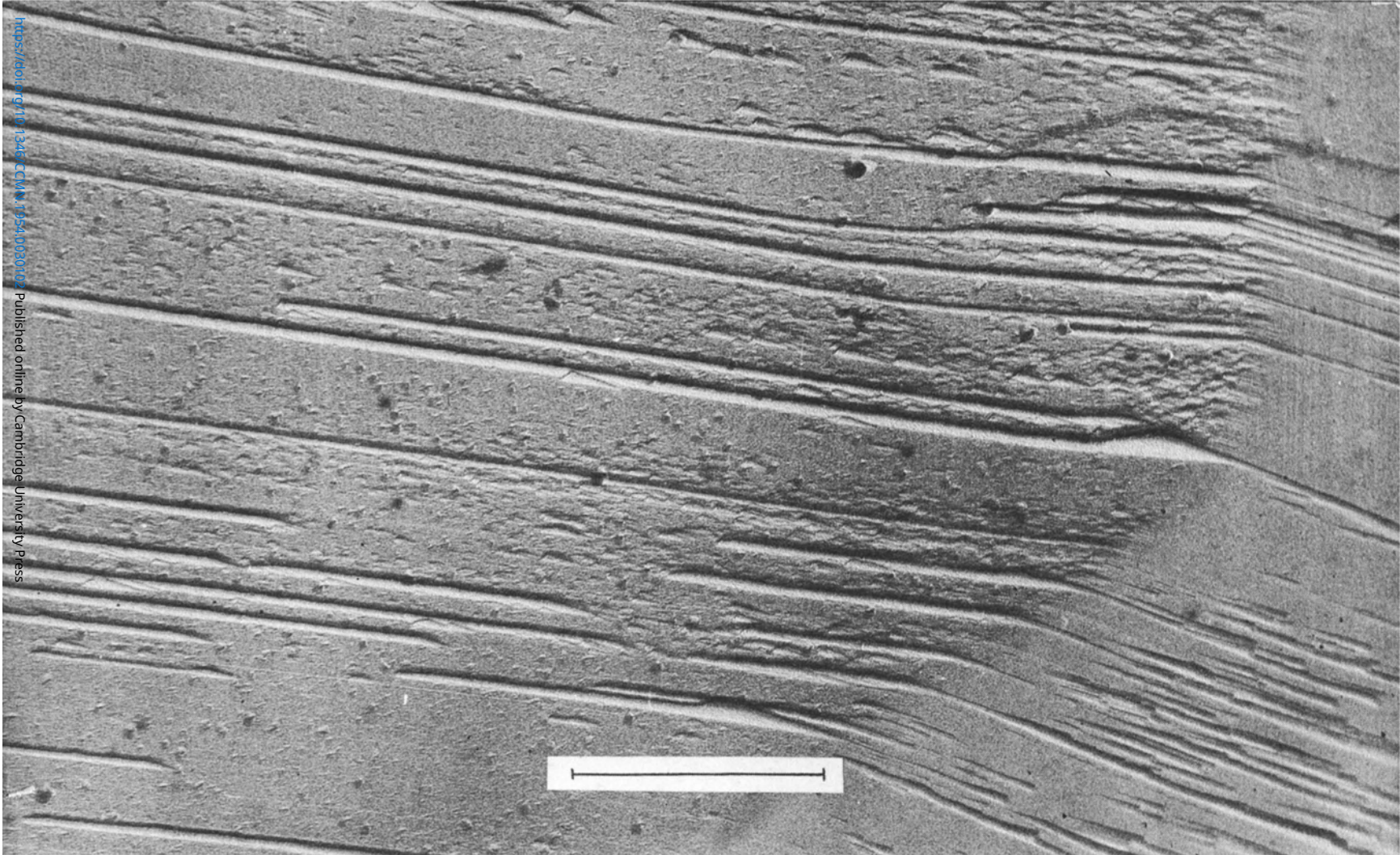
FIGURE 8. — Dickite, Schuylkill County, Pennsylvania. Edge of book showing incipient cleavage.
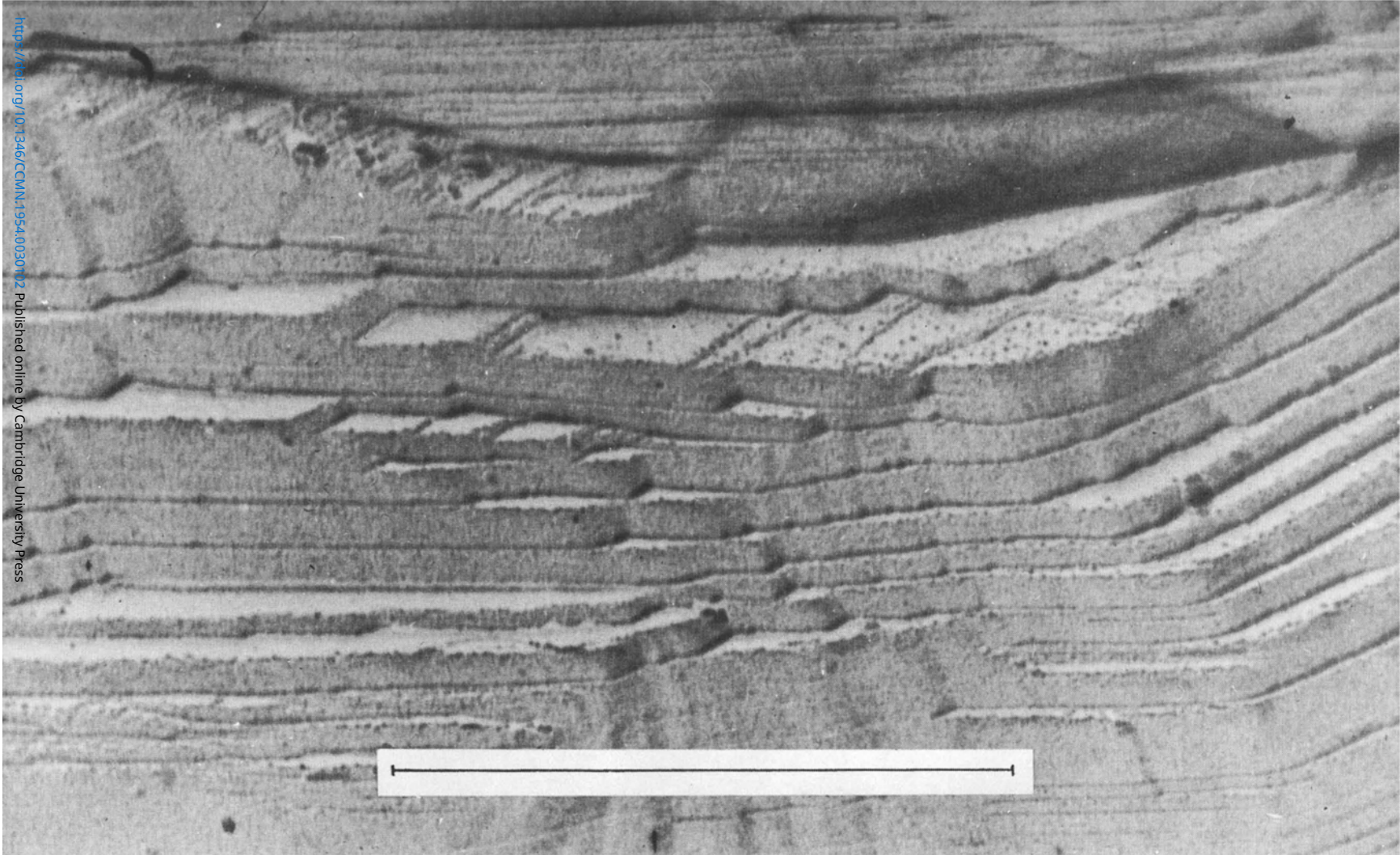
FIGURE 9. — Dickite, Schuylkill County, Pennsylvania.
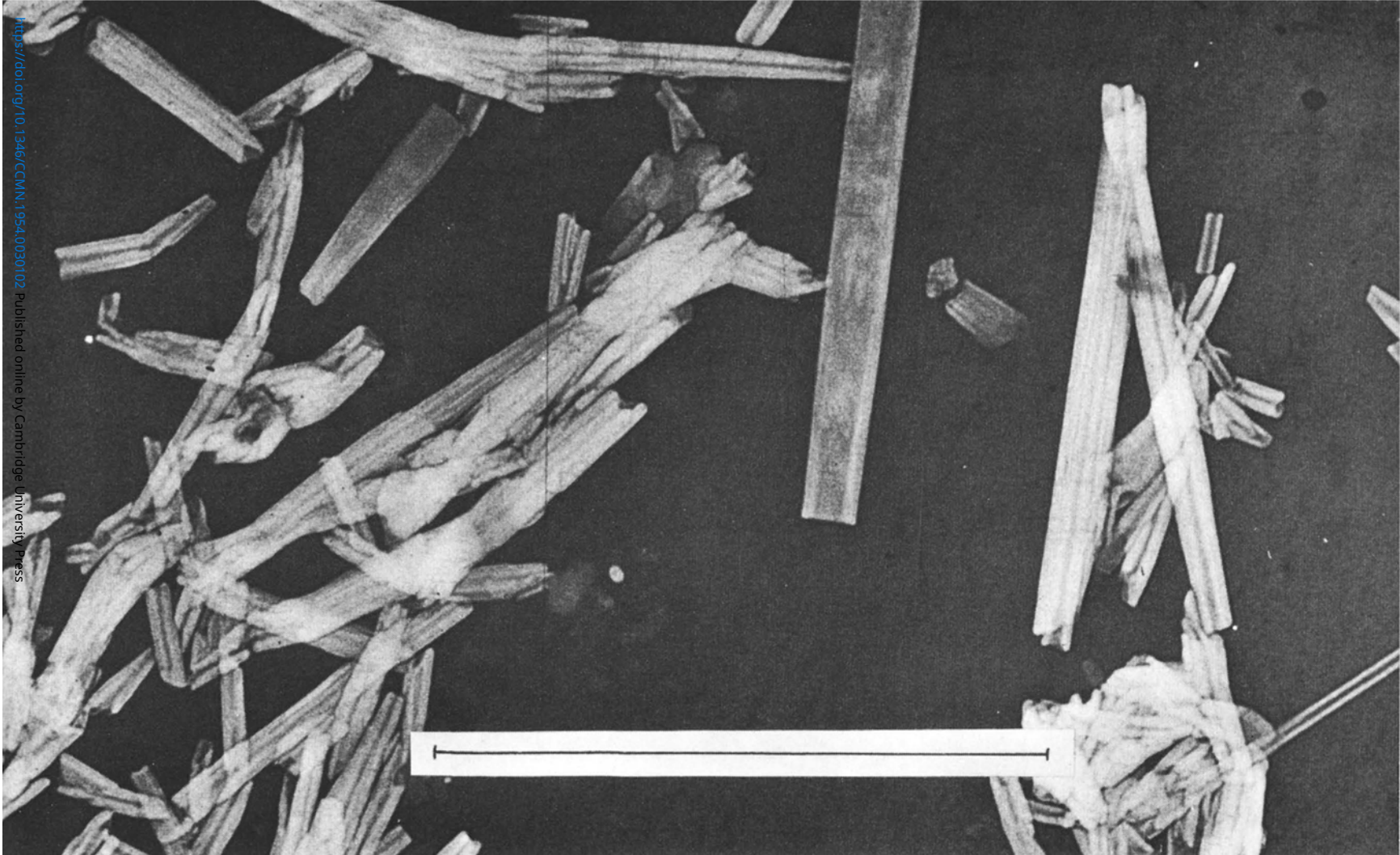
FIGURE 10. — Dispersed sample of Wendover, Utah, halloysite.
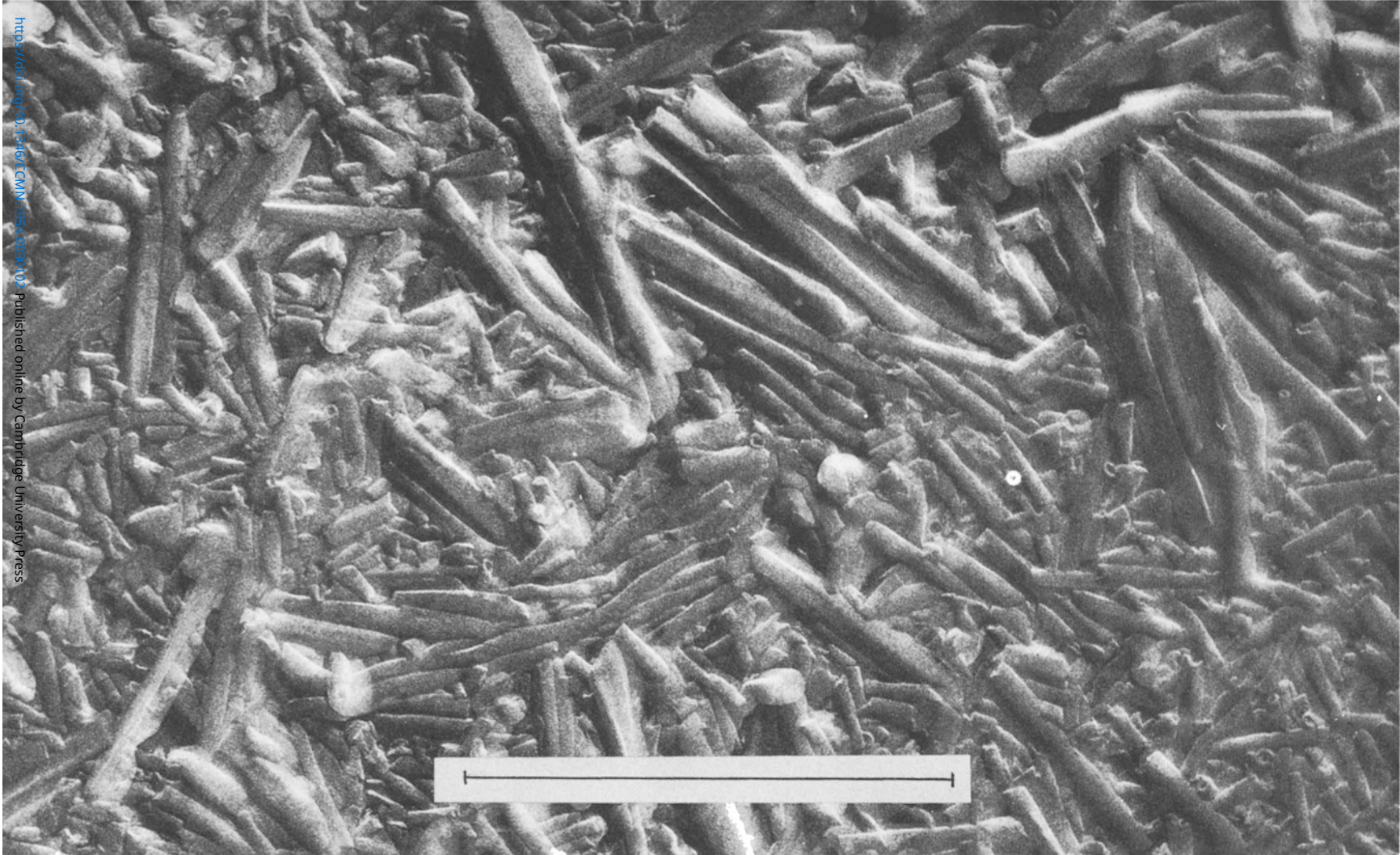
FIGURE 11. — Surface replica of halloysite from Wendover, Utah, showing tubular morphology of crystals.
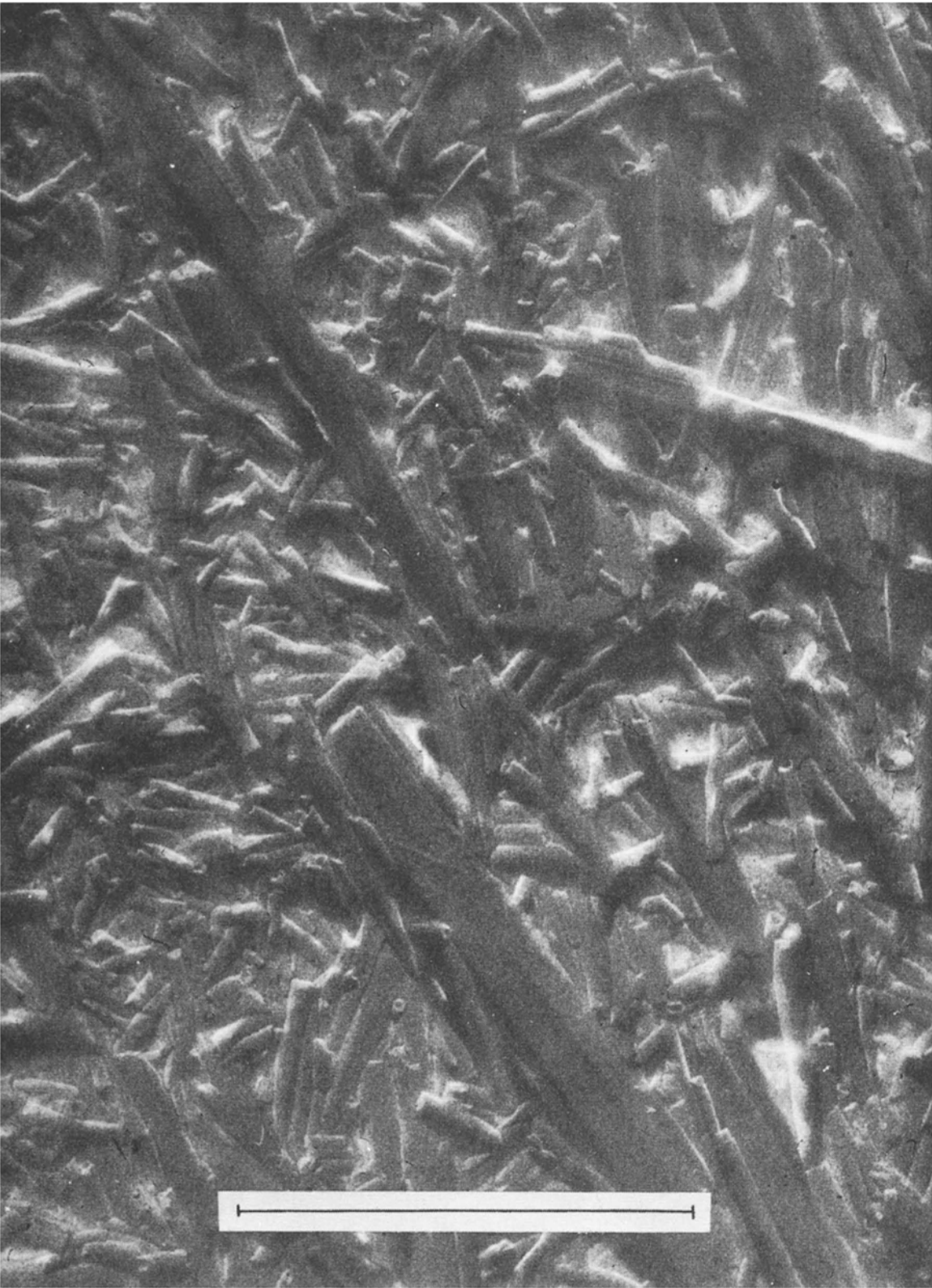
FIGURE 12. — Halloysite, Wendover, Utah showing large variation in particle size.
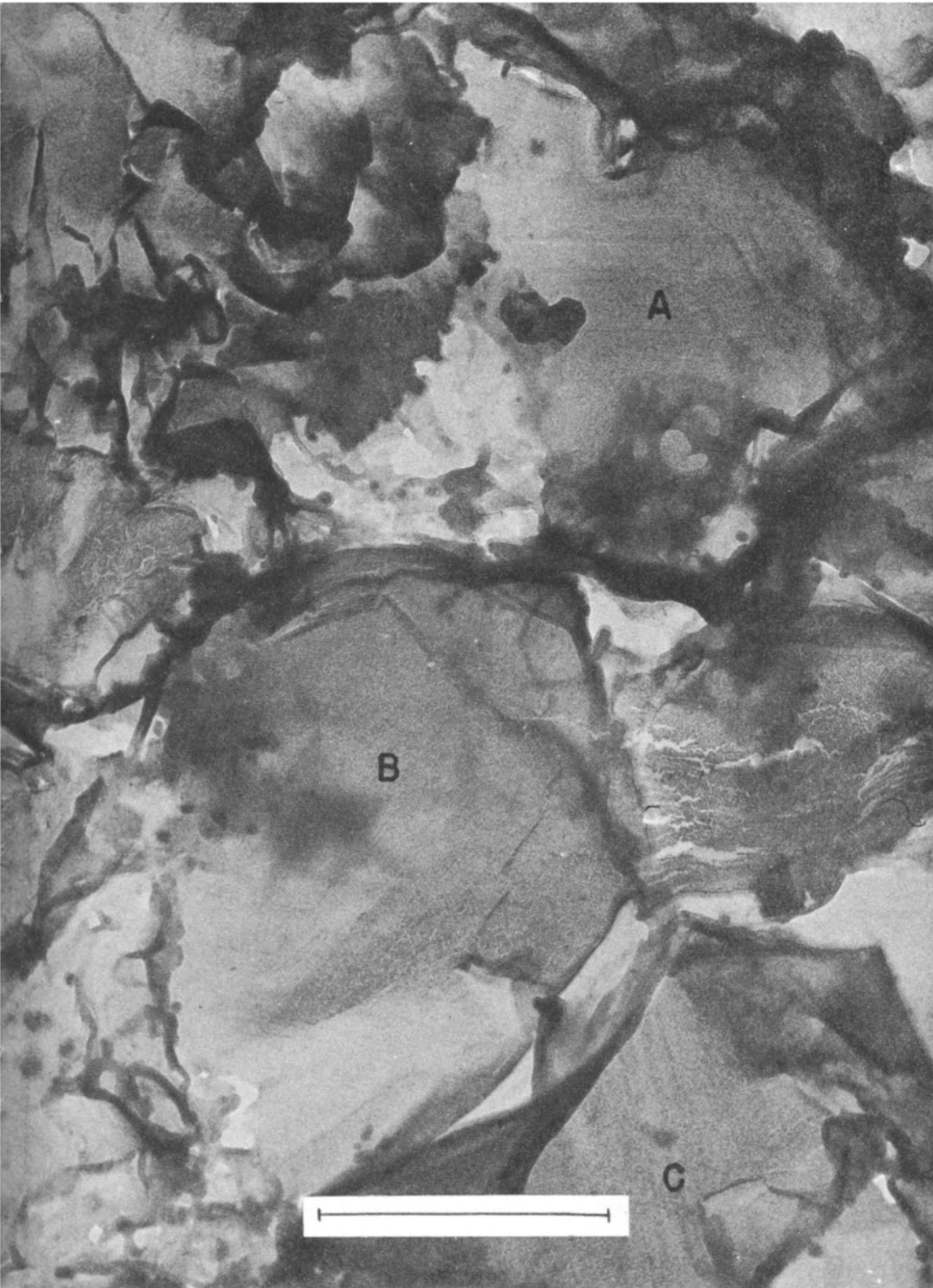
FIGURE 13. — Montmorillonite, Montmorillon, France. Striations intersecting at 60 and 120 degree angles are present in crystals A, B, and C.
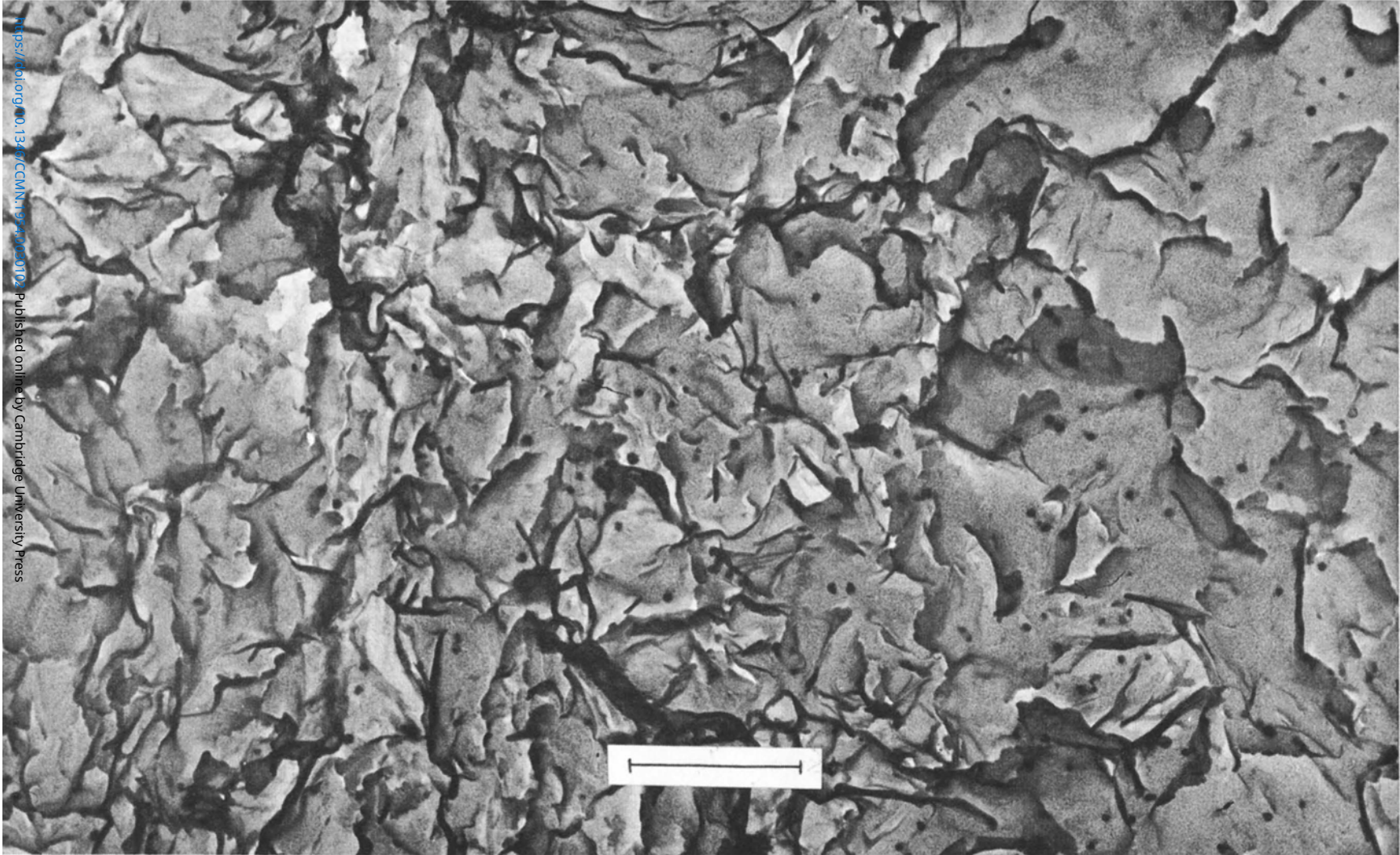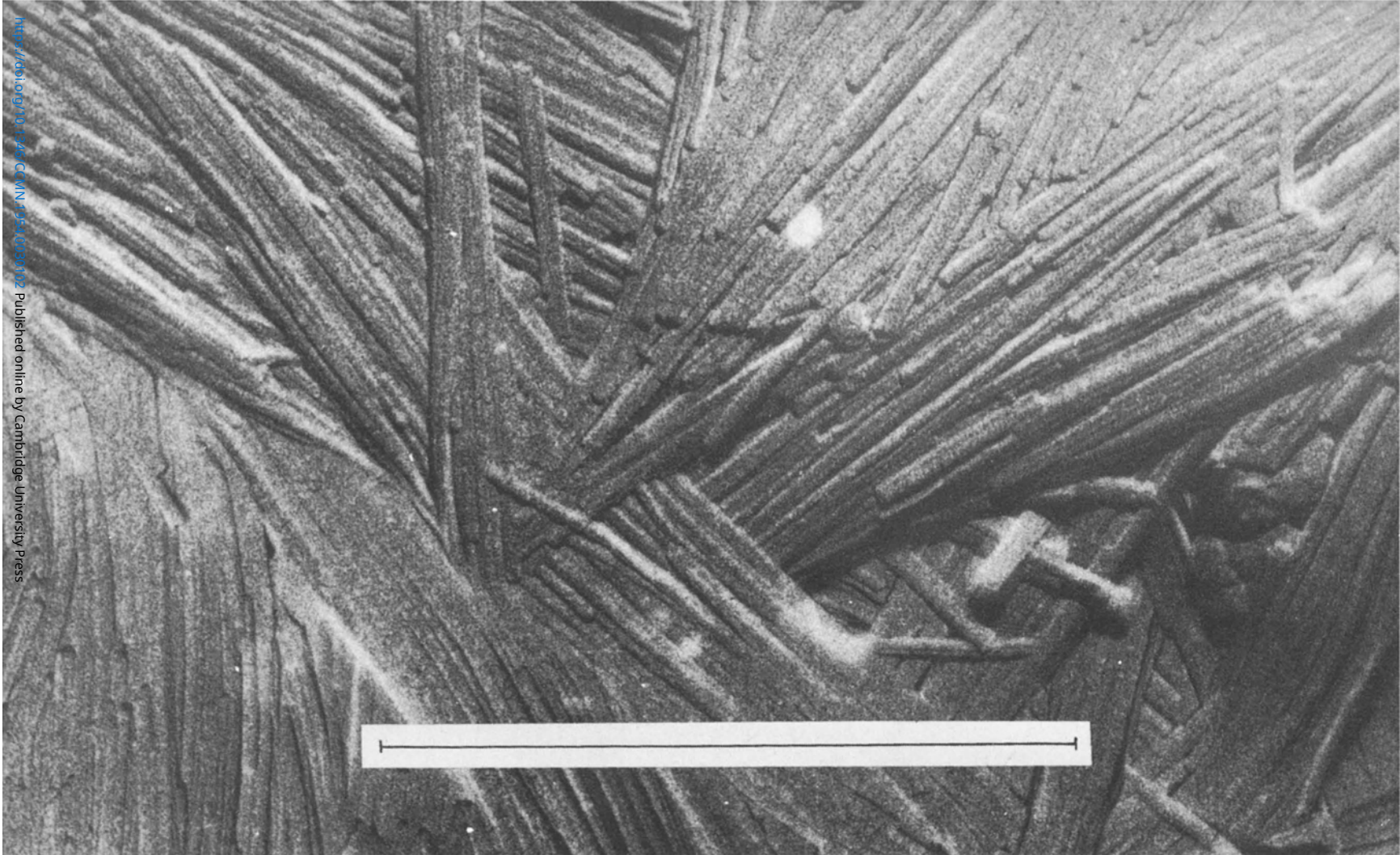
FIGURE 14. — Fullers Earth, Surrey, England.

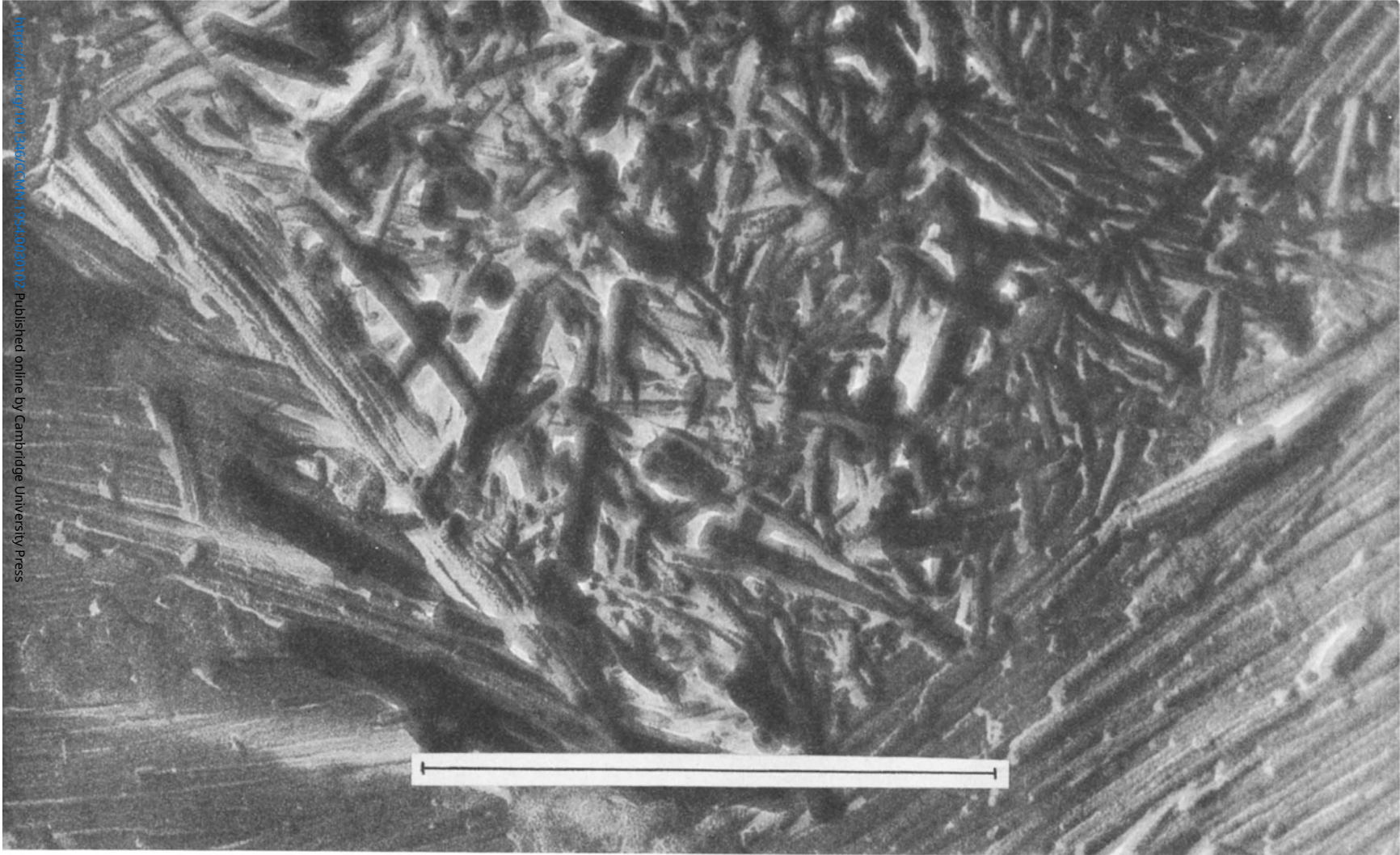FIGURE 15. — Attapulgite, Attapulgus, Georgia.

FIGURE 16. — Attapulgite, Attapulgus, Georgia, showing some end sections.

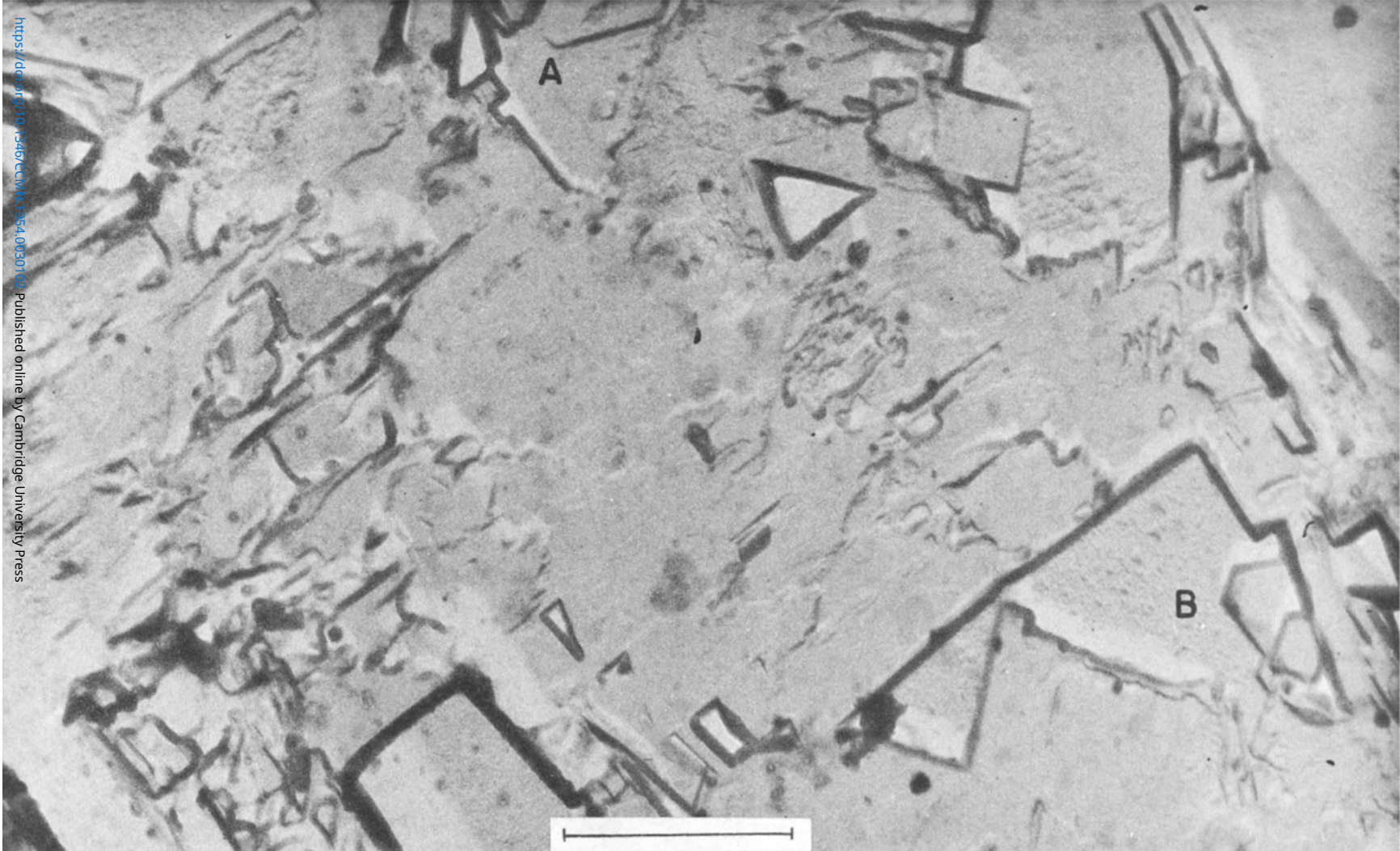FIGURE 17. — Cleavage surface of microcline showing hexagonal crystals at A and B presumed to be kaolinite.