

# ELECTRON MICROGRAPHIC STUDIES OF CLAYS

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## ABSTRACT

In order to provide a set of reference photographs to be used in identification studies, electron micrographs at relatively high magnification (40,000 to 132,000 diameters), together with some electron diffraction patterns, have been obtained of a group of (a) kaolinites, (b) halloysites, and (c) South Texas outcrop soil samples. Some of the kaolinites consist of well-formed hexagonal crystal plates with edges still sharp at a magnification of 132,000 diameters. Other kaolinites consist of irregular, relatively thin crystal sheets, which may be bent or folded. In one instance it has been possible to demonstrate that the average thickness of the sheets is only 10 Å. At high magnification the halloysite clay minerals exhibit a structure consisting of rolled sheets, rather than hollow rods. In some cases, it is evident that several separate crystal sheets are coaxially rolled to form multiple concentric hollow tubes. In the South Texas outcrop samples, the morphology is very complex, as the samples do not consist of one uniform type of particle. Matted sheets composed of interlaced bundles of lath-like particles have been observed. These oriented particles exhibit typical "fiber" type electron diffraction patterns. Kikuchi lines were observed in a thin quartz crystal plate, examined for comparative purposes.

## INTRODUCTION

Numerous excellent micrographic studies of the clay minerals have been reported in the literature (see References, p. 35). Especially noteworthy are the electron micrographs displayed in Report No. 6 from the Clay Mineral Standards Project 49 of the American Petroleum Institute, for a series of carefully selected "standard" clays.

In these laboratories a need arose for a set of reference electron micrographs, to be used in identification studies of unknown clay and soil samples. It is the purpose of this paper to present some of the results of a comprehensive study which has been carried out. High magnification electron micrographs, which may be of value to other workers in the field, have been selected from "standard" clay minerals and from certain South Texas outcrop soil samples. In some instances, the electron micrographs have been supplemented by electron diffraction patterns.

## EXPERIMENTAL

*Selection of Samples.* Most of the standard clays selected for this study are API specimens and are identified by the API reference number. Others are identified by the location of the clay mineral deposit. These clays were obtained from Dr. Richard C. Mielenz of the Bureau of Reclamation at

Denver, Colorado, and the authors are indebted to him for them. The soil samples examined were selected from a group of South Texas outcrop samples, which have been described in detail by Taggart and Simons (1953).

*Preparation of Samples.* The samples were ground in an agate mortar for a short time and were then either (a) dispersed in distilled water rendered slightly alkaline with a trace of freshly distilled ammonium hydroxide, or (b) dispersed in distilled water by means of an ultrasonic generator. The dilute suspensions were allowed to sediment for 4 hours, and a drop of the slightly turbid supernatant liquid was allowed to dry on a collodion membrane supported by an Athene metal grid.

*Electron Microscopy.* The electron micrographs were taken with a Philips Type EM-100 electron microscope. The accelerating potential was 100 KV, except in a few instances where 80 KV was employed. In all cases the exposure times were not more than 4 seconds. Care was taken to avoid excessive exposure of the samples to the electron beam or to the oil vapor in the residual vacuum.

*Shadowcasting.* Shadowcasting was employed in some instances, using a standard instrument. The samples were placed at an angle of  $14^\circ$  at a distance of 140 mm. from the tungsten filament, and 30 mg. of gold-manganin alloy was evaporated. Extreme precautions were taken to insure a good vacuum.

## DISCUSSION

Typical electron micrographs, and in some instances electron diffraction patterns, of the selected samples are displayed in Figures 1-29.

*Kaolinite Clay Minerals.* Electron micrographs of several kaolinite clays are given in Figures 1-9. The sample originating from Murfreesboro, Arkansas, consists of regular hexagonal crystals of reasonably uniform size, as shown at 33,000 diameters in Figure 1. Attention is directed towards the extremely sharp crystal edges displayed at 132,000 diameters in Figure 2. The kaolinite from Chudleigh-Knighton does not possess such a uniform distribution of crystal size (Fig. 3), but numerous sharp edges are visible at 132,000 diameters in Figure 4. The kaolinite from Bath, S.C. shown in Figures 5 and 6 likewise contains hexagonal crystals exhibiting a wide range of size, although some of them are quite regular even at high magnification. The sample originating from mountain cork, Hot Springs, Arkansas, is of especial interest. The low magnification photograph (16,500 diameters) in Figure 7 displays the relatively large irregular single crystal sheets, which may occur in layers and which may be readily folded without breakage. The marked rectangle in Figure 7 is likewise given at 132,000 diameters in Figure 8. Attention is called to the clear delineation of the several layers comprising some of the sheets. The shadow in the lower right-hand corner of Figure 8 is approximately 200 Å in length, corresponding to a height of 50 Å, inasmuch as the tangent of the shadowcasting angle

is one-fourth. Hence, the thickness of the entire stack of crystal sheets is about 50 Å. It will be noted that at least 5 layers are involved, and therefore, the average thickness of each single crystal sheet is approximately 10 Å. In Figure 9 there is given a view of another area for the mountain cork sample. This photograph is of especial interest because of the manner of folding of the extremely long and narrow single crystal sheet. The ribbon-like crystal is approximately 1.5 microns in width, and several microns in length. It is not known whether the folding occurred during the drying of the specimen or occurred during the formation of the clay deposit.

*Halloysite Clay Minerals.* Electron micrographs of several halloysite clay minerals are given in Figures 10-17. The halloysite from Bedford, Ind. (Fig. 10), consists of fairly uniform-sized rod-like particles which appear to be hollow, in confirmation of the work of Bates *et al.* (1953). The sample from Spruce Pine, N.C. (Figs. 11 and 12), consists of relatively longer rod-like particles, some being 10 to 15 microns in length. At the high magnification (132,000 diameters) shown in Figures 13 and 14, it is apparent that halloysite particles actually consist of rolled sheets, often irregular at the ends. The rolled sheets comprise a tube, and at low magnification appear to be hollow rods. A detailed examination of high magnification electron micrographs of halloysite clay minerals, such as the one shown in Figure 13, appears to rule out a structure based on hollow rods.

In Figures 14-17 (halloysite from Silver City, N.M.) there will be noted numerous examples of rolls within rolls. In Figure 17, at least 3 or 4 sheets are rolled together, the smallest resulting tube probably being broken.

It is not known whether the structure found here pre-exists in the natural wet clay, or results from the drying operation. It is conceivable that the clay particles may exist in a fully extended or "peptized" form in dispersions in an appropriate medium, and fold or roll as the sample dries, in "two-dimensional" analogy to the coiling of "one-dimensional" macromolecules, such as certain proteins, as the dispersion medium is removed, or as the solvation and electrostatic environment is changed. It would be of interest to examine some of these samples from dispersions at various pH values and concentrations of electrolytes, but such studies have not been made as yet.

In Figure 18, there is given an electron diffraction pattern arising from a single roll of the Silver City halloysite. It will be noted that a typical "fiber-like" pattern has resulted. The strong, elongated, horizontal diffraction lines, arise from reflections of the 001 type. This diffraction pattern is consistent with the view that the tubes actually consist of rolled sheets, but does not allow any deduction concerning the mechanism of formation of the hollow tube-like rolled particles. Quantitative interpretation of this electron diffraction pattern will not be given here.

*South Texas Outcrop Soil Samples.* The South Texas outcrop soil samples selected for presentation in this report, have been described in detail by Taggart and Simons (1953).

The electron micrograph shown in Figure 19 is of a soil sample collected at the surface from the Manning formation. The particles shown in the figure are irregular bent sheets of montmorillonite, exhibiting typical rolled edges. In contrast, are the smaller thin sheets or plates of montmorillonite found in the sample collected in the Austin chalk formation (Fig. 20). Attention is called to the lath-like plates in the lower center of Figure 20, where they are matted together, so as to form an aggregate similar in appearance to a woven mat. In other areas in Figure 20, arrays of lath-like particles are oriented in approximately parallel positions.

In Figure 21, a sample collected 20-25 feet below the surface in the Goliad, or Lagarto, formation, it is apparent that the sample is not homogeneous. Most of the clay plates are very irregular, but an occasional crystal with sharp edges is visible, one exceptionally large broken crystal being present at the upper left-hand corner of the photograph.

A sample collected at the surface in the Carrizo formation (Fig. 22) exhibits a very inhomogeneous structure. In the lower left-hand corner of the photograph, there is one plate-like particle containing several pores of an approximate diameter of 50-100 Å. These pores are much smaller than the holes seen in diatoms, and their significance is not known. It will be noted that the relatively large rod with irregular edges shown in Figure 22, may be partially hollow.

The folded sheets with rolled edges shown in Figure 23 were observed in a sample collected at the surface of a basalt plug. Similar sheets with rolled edges were observed (Fig. 24) in a sample collected at the surface from another basalt plug. This sample exhibits also some occasional needle- or lath-like particles, which may be fragments from broken sheets.

*Quartz.* Inasmuch as quartz is commonly a constituent of clay and soil samples, it was considered of interest to obtain some electron micrographs of quartz samples, for purposes of comparison. However, it turns out that the usual sedimentation methods of sample size selection employed in our treatment of the sample, very effectively removes possible silica particles, and only rarely have we observed such particles in electron micrographs. Nevertheless, we present here some results from our examination of quartz particles, because of their general interest. The quartz sample was prepared by grinding Ottawa sea sand in a ball-mill for several hours, followed by separation of the smallest size range by standard sedimentation methods. In Figure 25 there is given an electron diffraction pattern obtained from the quartz crystal fragment shown in Figure 26 at a magnification of 40,000 diameters. The small area contributing to the diffraction pattern was 2.5 x 3 microns as marked in Figure 26. The electron diffraction exhibits both light and dark Kikuchi lines which arise from the thin crystal plate shown in the micrograph, as well as some Debye-Scherrer rings arising from the small crystal fragments adhering to the crystal plate.

*Electron Diffraction.* In addition to the electron diffraction studies on quartz, certain South Texas outcrop samples have been examined by this technique. In Figure 27 there is included an electron micrograph (b) show-

ing the sample area from which arises the electron diffraction pattern shown in (a). This sample was collected at the surface of the Beaumont formation. Another area of the sample consists of some single crystal plates, as shown by the cross-grating pattern presented in Figure 28. The sample area contributing to diffraction pattern (b) was 4 x 6 microns, and diffraction pattern (c) arises from an area of 10 x 10 microns, as indicated in the figure. The superimposed cross-grating pattern and the Debye-Scherrer rings indicate that both large and small crystals are present. The diffracting crystals are identical in structure since the spots fall upon the rings.

A sample collected 20-25 feet below the surface of the Lissie formation has been described in detail by Taggart and Simons (1953). In Figure 29 there is given a low magnification electron micrograph (18,000 diameters) of a sample area exhibiting an oriented bundle of the needles. The oriented needles exhibit a typical "fiber" diffraction pattern, the results suggesting that the matted bundle of needles comprises a sheet, tilted at an angle with respect to the collodion membrane. Larger aggregates visible in the sample give a typical cross-grating design as shown in (c) of Figure 29.

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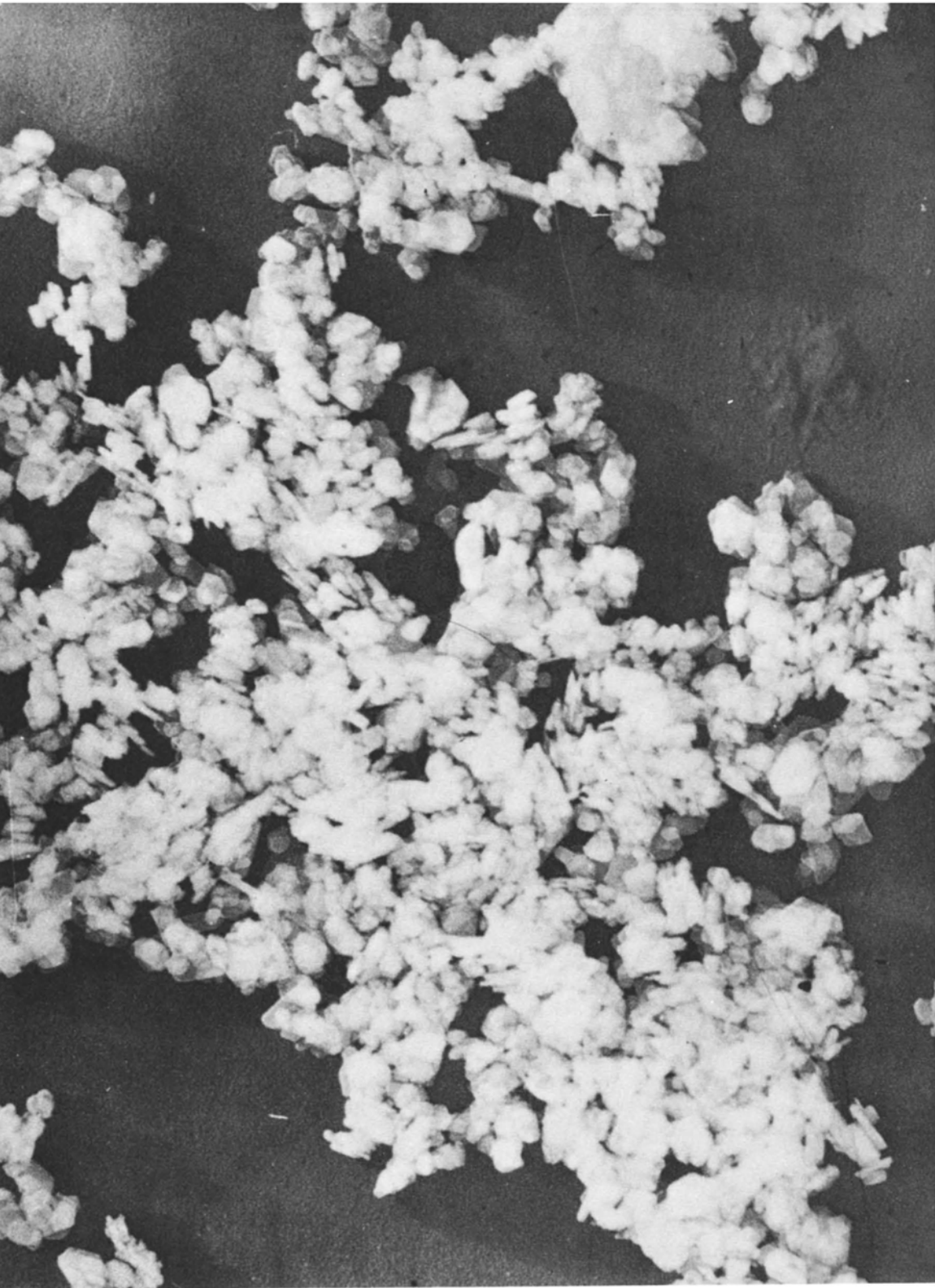


FIGURE 1. — Kaolinite. A.P.I. No. 1a, Murfreesboro, Arkansas. Magnification: 33,000  
(1 mm. = 300 Å.)

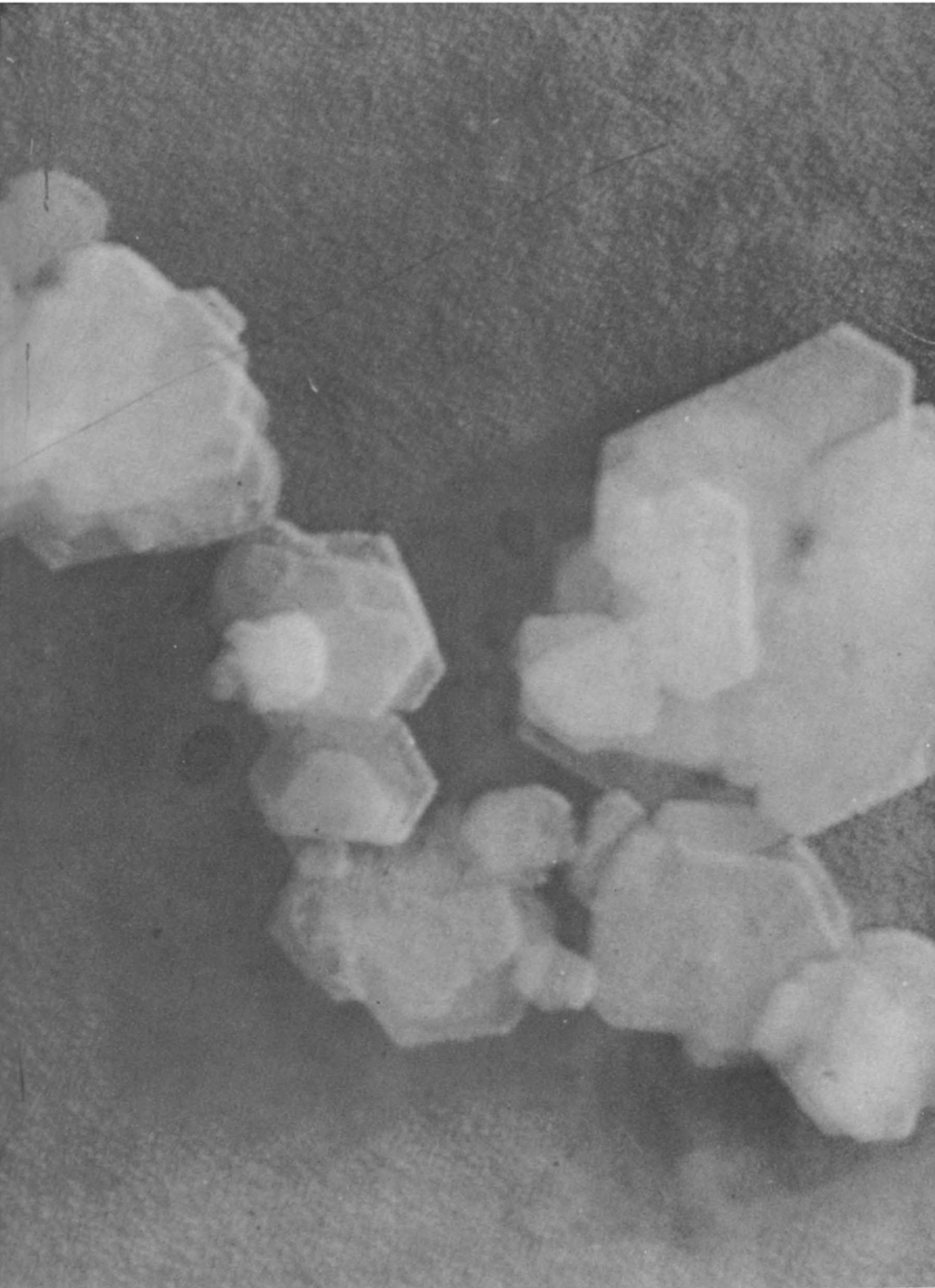


FIGURE 2.—Kaolinite. A.P.I. No. 1a, Murfreesboro, Arkansas. Magnification: 132,000.  
(1 mm. = 75 Å.)

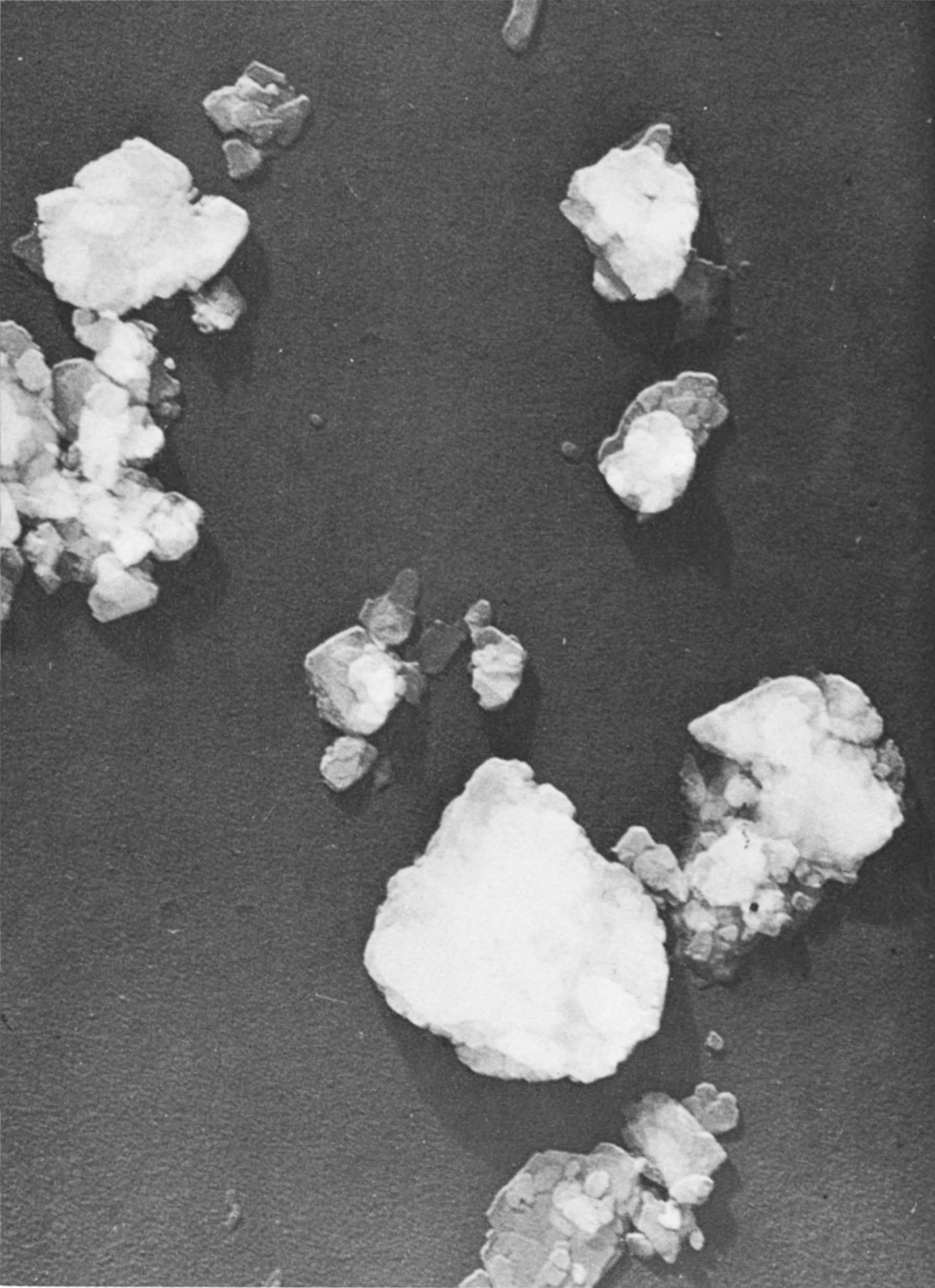


FIGURE 3.—Kaolinite. A.P.I. No. 112a, Chudleigh-Knighton, England. Magnification: 33,000.  
(1 mm. = 300 Å.)



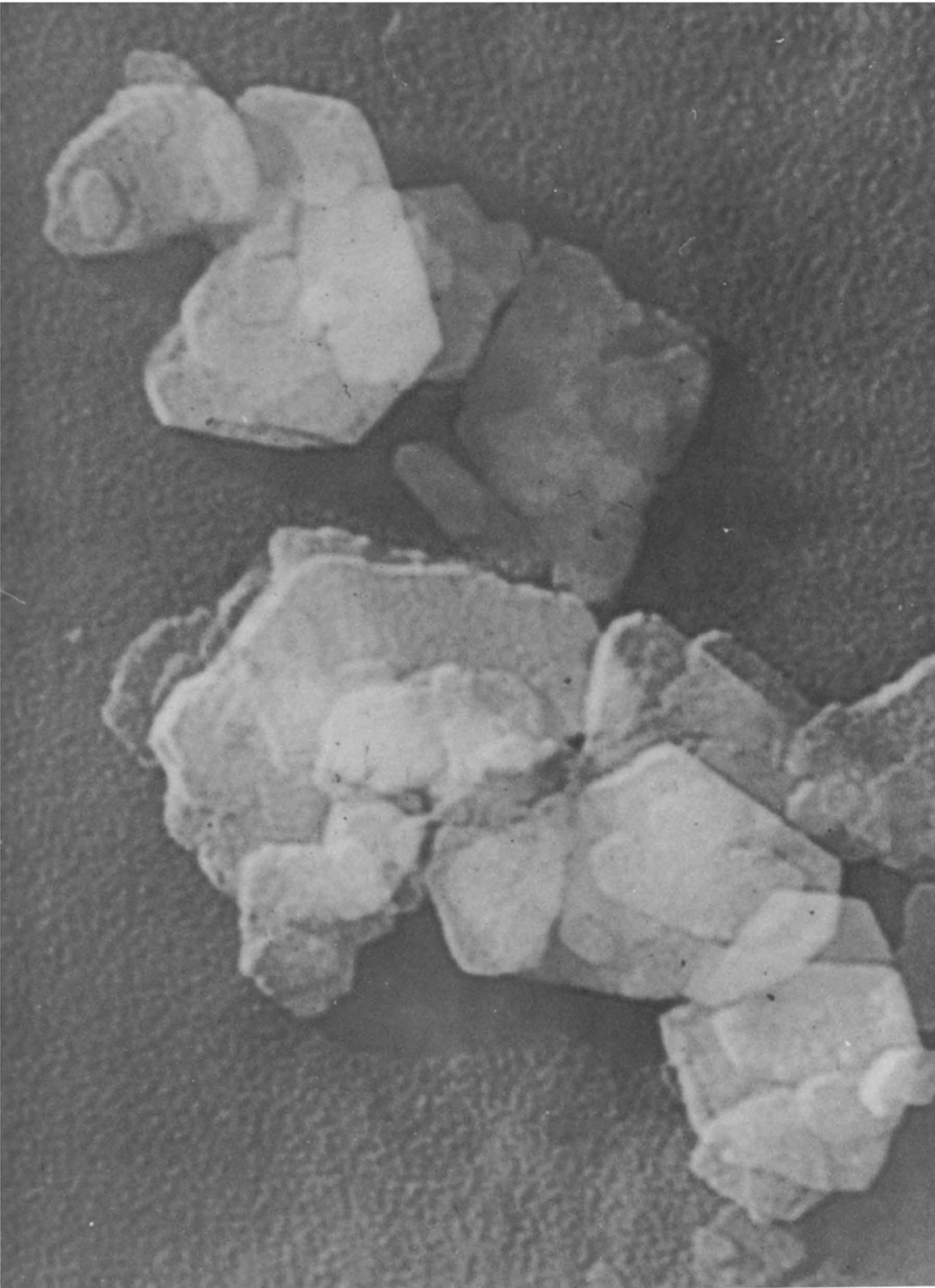


FIGURE 4. — Kaolinite. A.P.I. No. 112a, Chudleigh-Knighton, England. Magnification: 132,000.  
(1 mm. = 75 Å.)

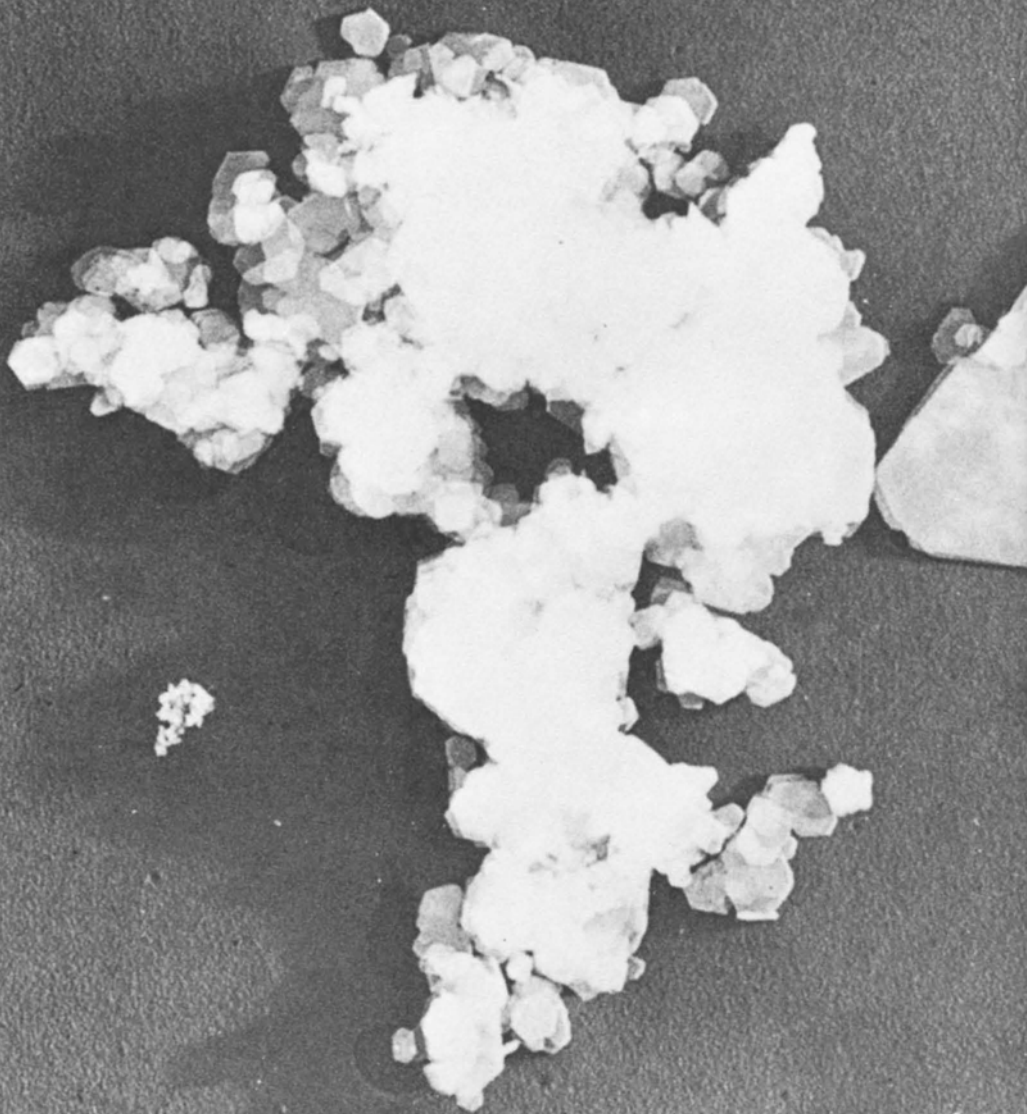


FIGURE 5. — Kaolinite. A.P.I. No. 6, Bath, South Carolina. Magnification: 33,000.  
(1 mm. = 300 Å.)

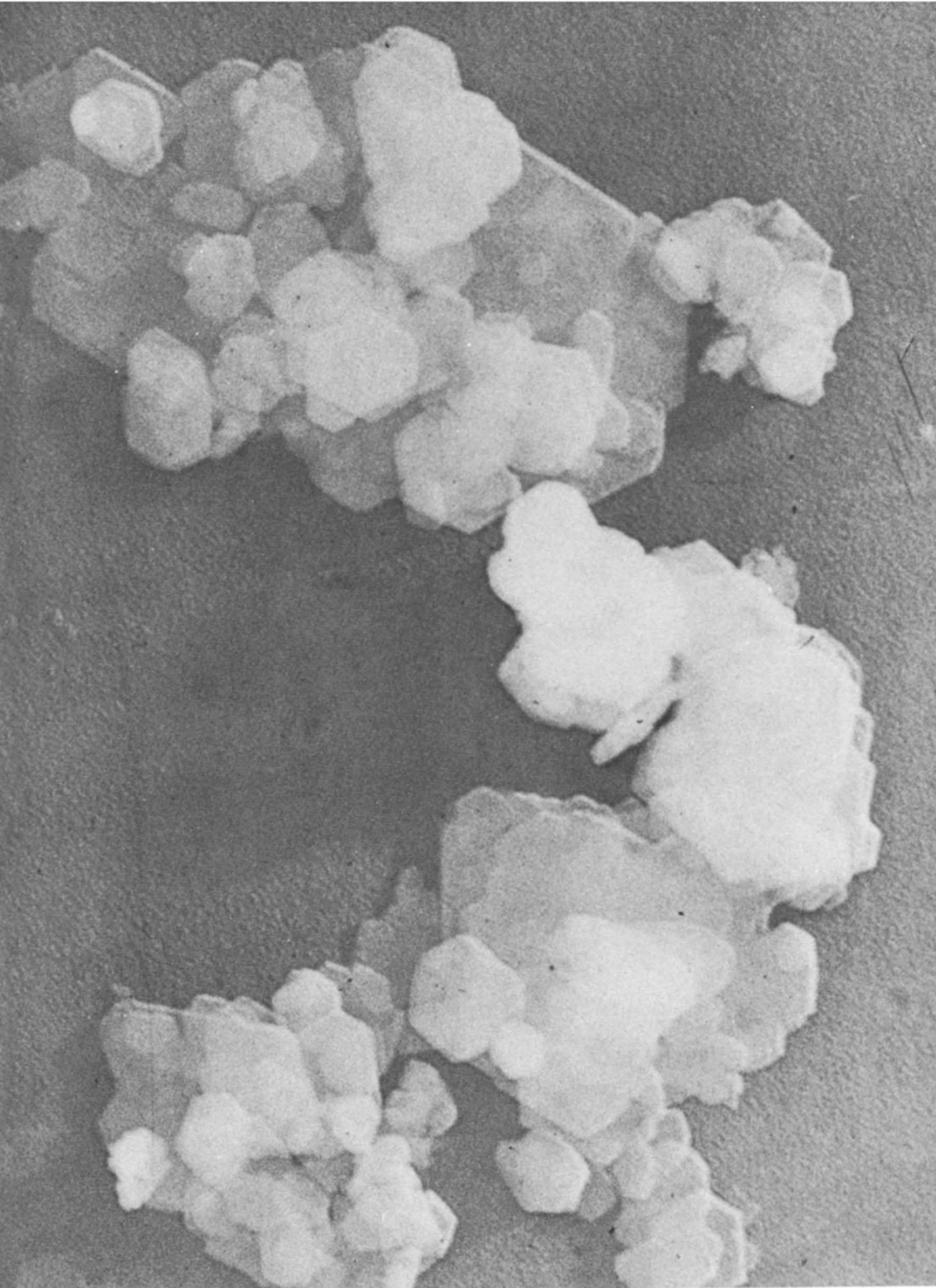


FIGURE 6. — Kaolinite. A.P.I. No. 6, Bath, South Carolina. Magnification: 66,000.  
(1 mm. = 150 Å.)



FIGURE 7.— Mountain Cork, Hot Springs, Arkansas. Magnification: 16,500. (1 mm. = 600 Å.)  
The marked rectangle is shown at 132,000 diameters in Figure 8.

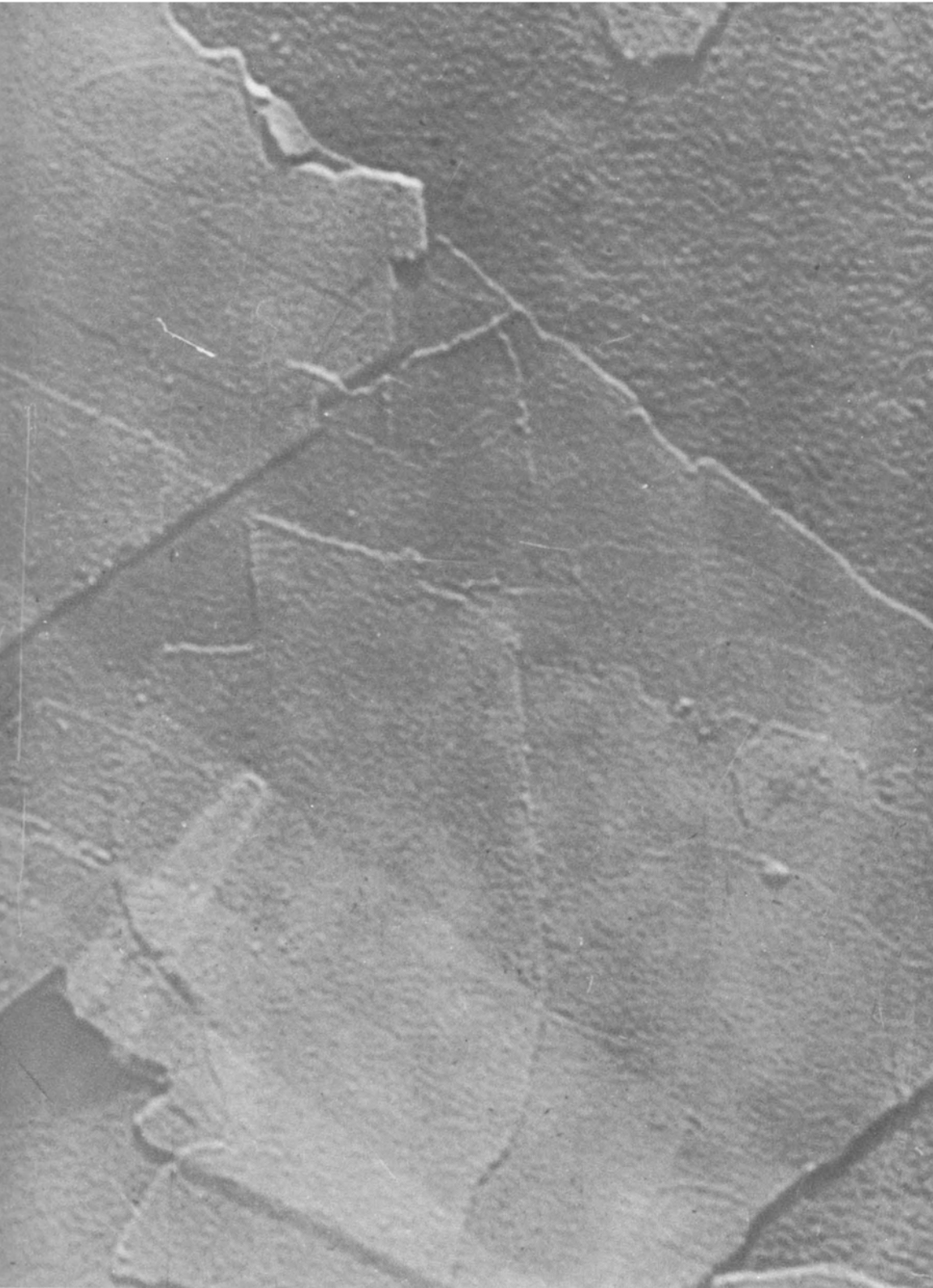


FIGURE 8. — Mountain Cork, Hot Springs, Arkansas. Magnification: 132,000. (1 mm. = 75 Å.)

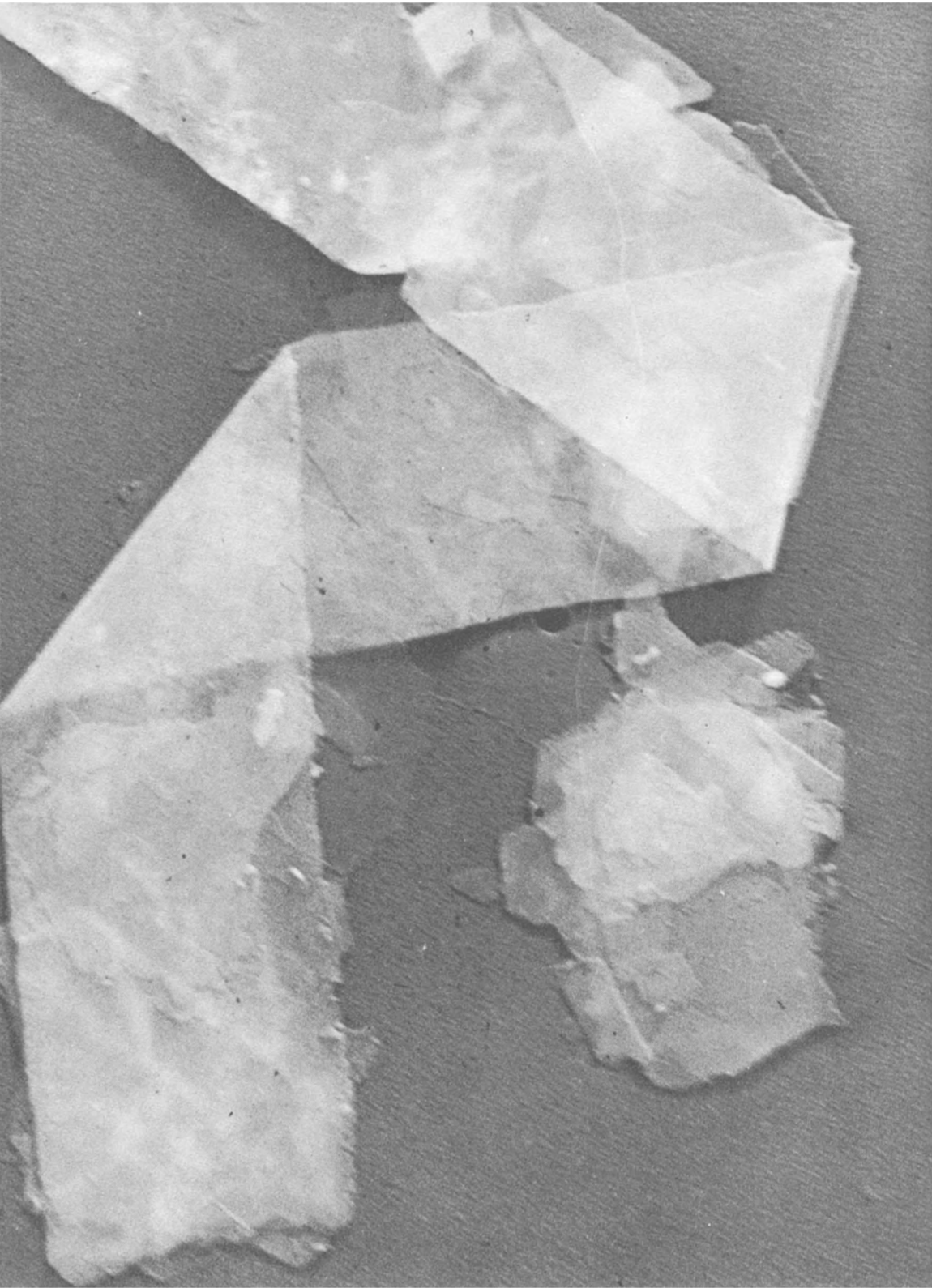


FIGURE 9.— Mountain Cork, Hot Springs, Arkansas. Magnification: 33,000 (1 mm. = 300 Å.)



FIGURE 10. — Halloysite. A.P.I. No. 12a. Bedford, Indiana. Magnification: 33,000.  
(1 mm. = 300 Å.)



FIGURE 11. — Halloysite. A.P.I. No. 51. Spruce Pine, North Carolina. Magnification: 33,000.  
(1 mm. = 300 Å.)



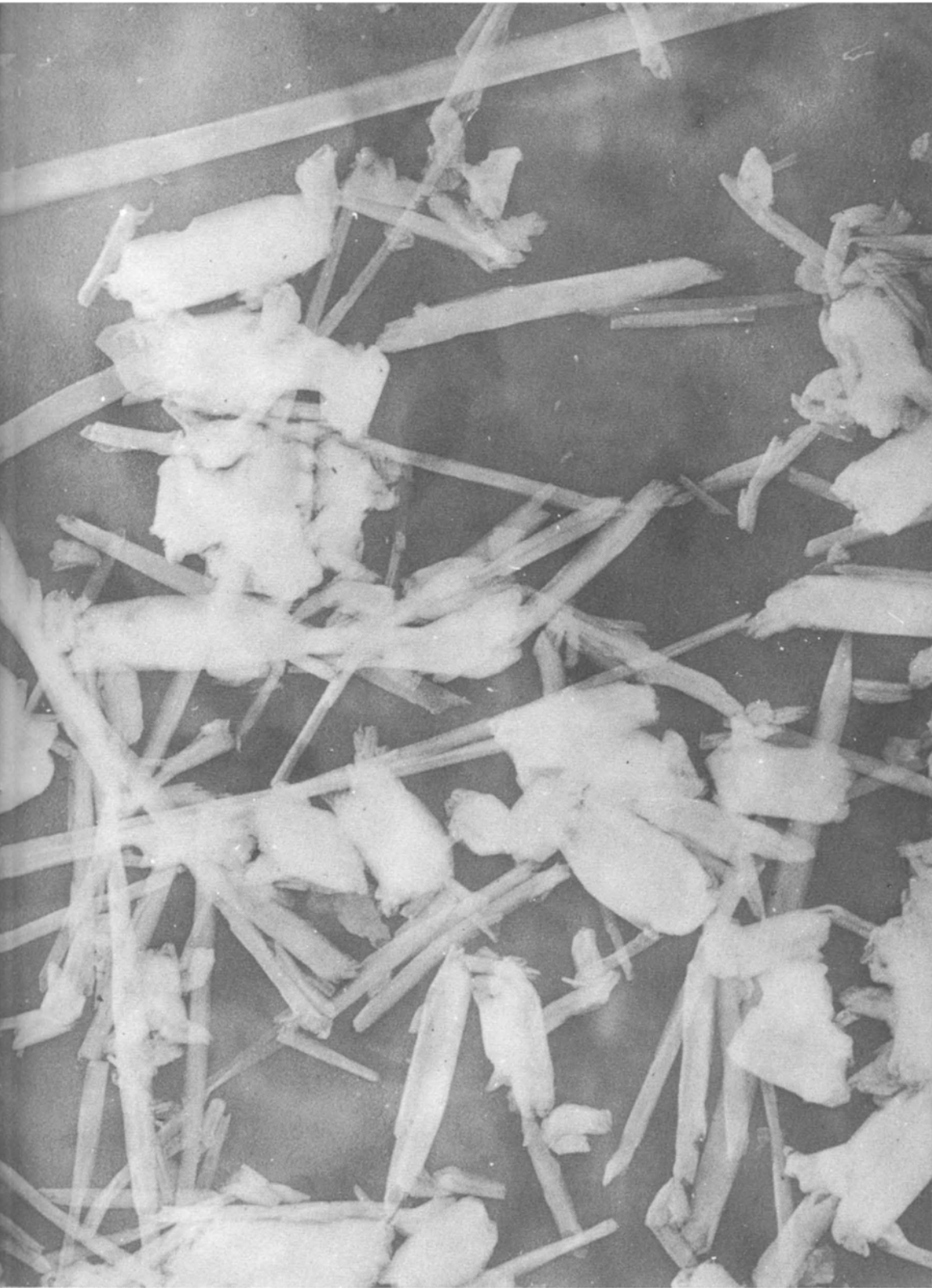


FIGURE 12. — Halloysite. A.P.I. No. 51. Spruce Pine, North Carolina. Magnification: 33,000.  
(1 mm. = 300 Å.)



FIGURE 13. — Halloysite. A.P.I. No. 51. Spruce Pine, North Carolina. Magnification: 132,000.  
(1 mm. = 75 Å.)



FIGURE 14. — Halloysite. Silver City, New Mexico. Magnification: 33,000. (1 mm. = 300 Å.)

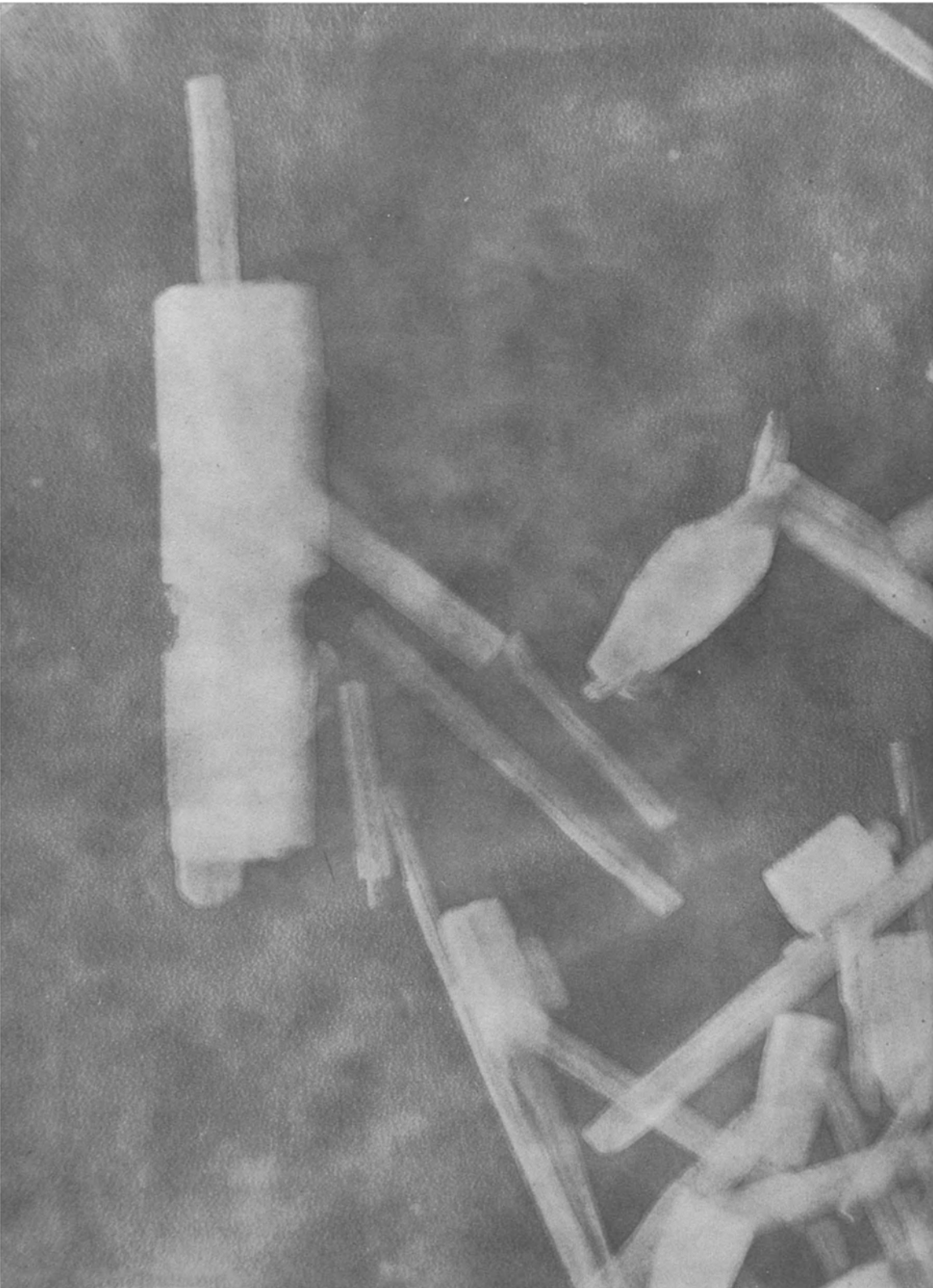


FIGURE 15. — Halloysite. Silver City, New Mexico. Magnification: 80,000. (1 mm. = 125 Å.)

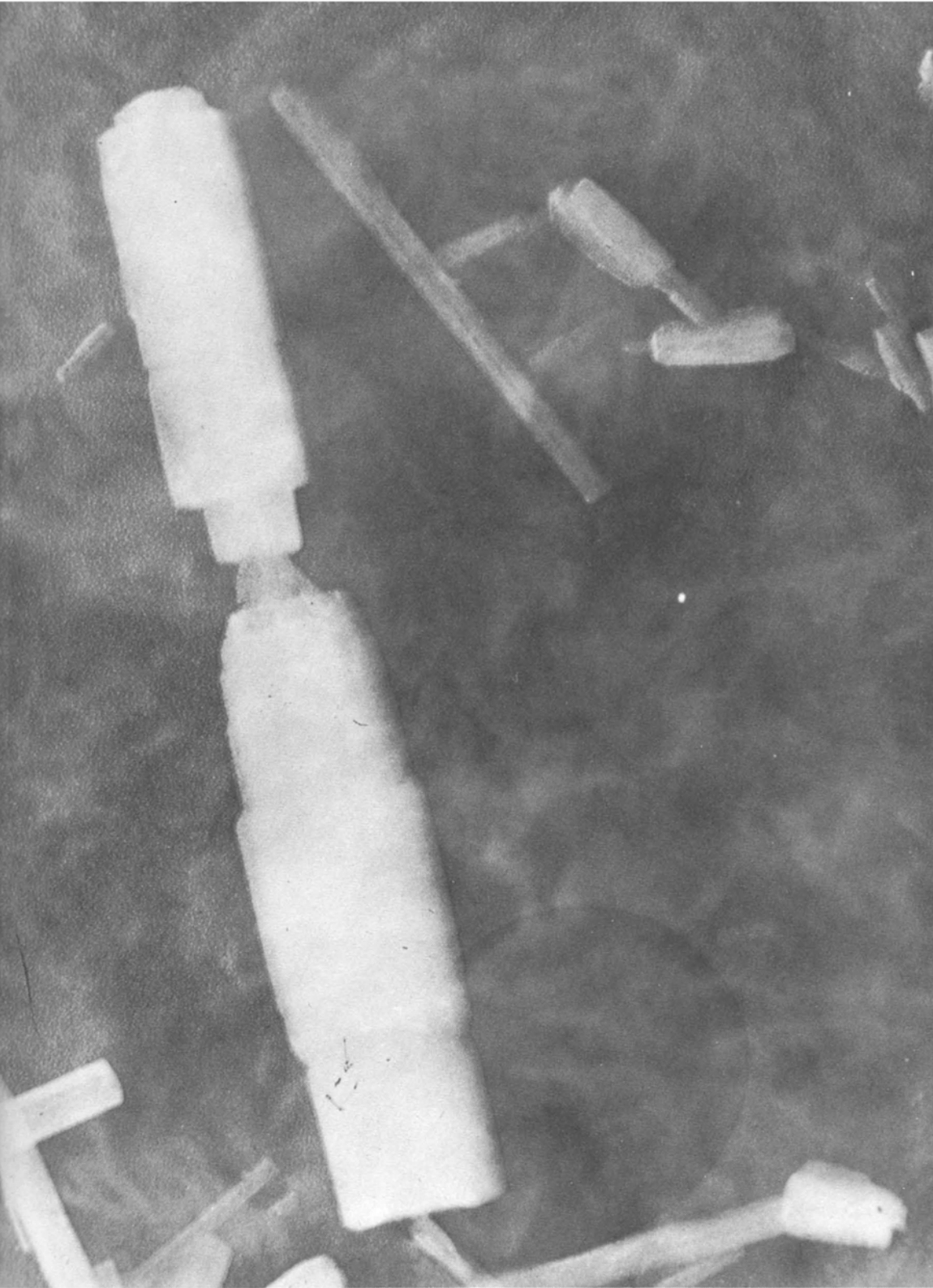


FIGURE 16.—Halloysite. Silver City, New Mexico. Magnification: 80,000. (1 mm. = 125 Å.)

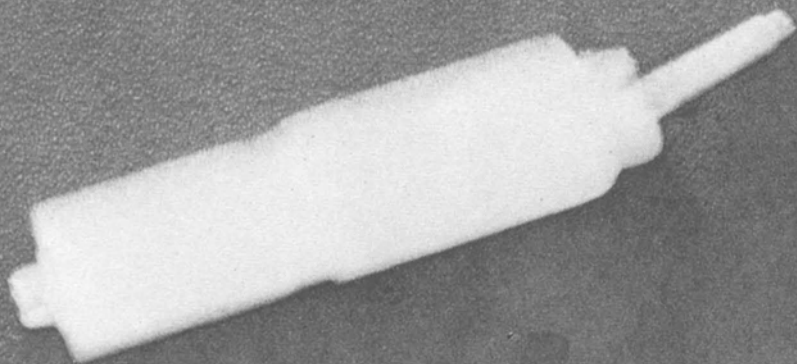


FIGURE 17. — Halloysite. Silver City, New Mexico. Magnification: 80,000. (1 mm. = 125 Å.)

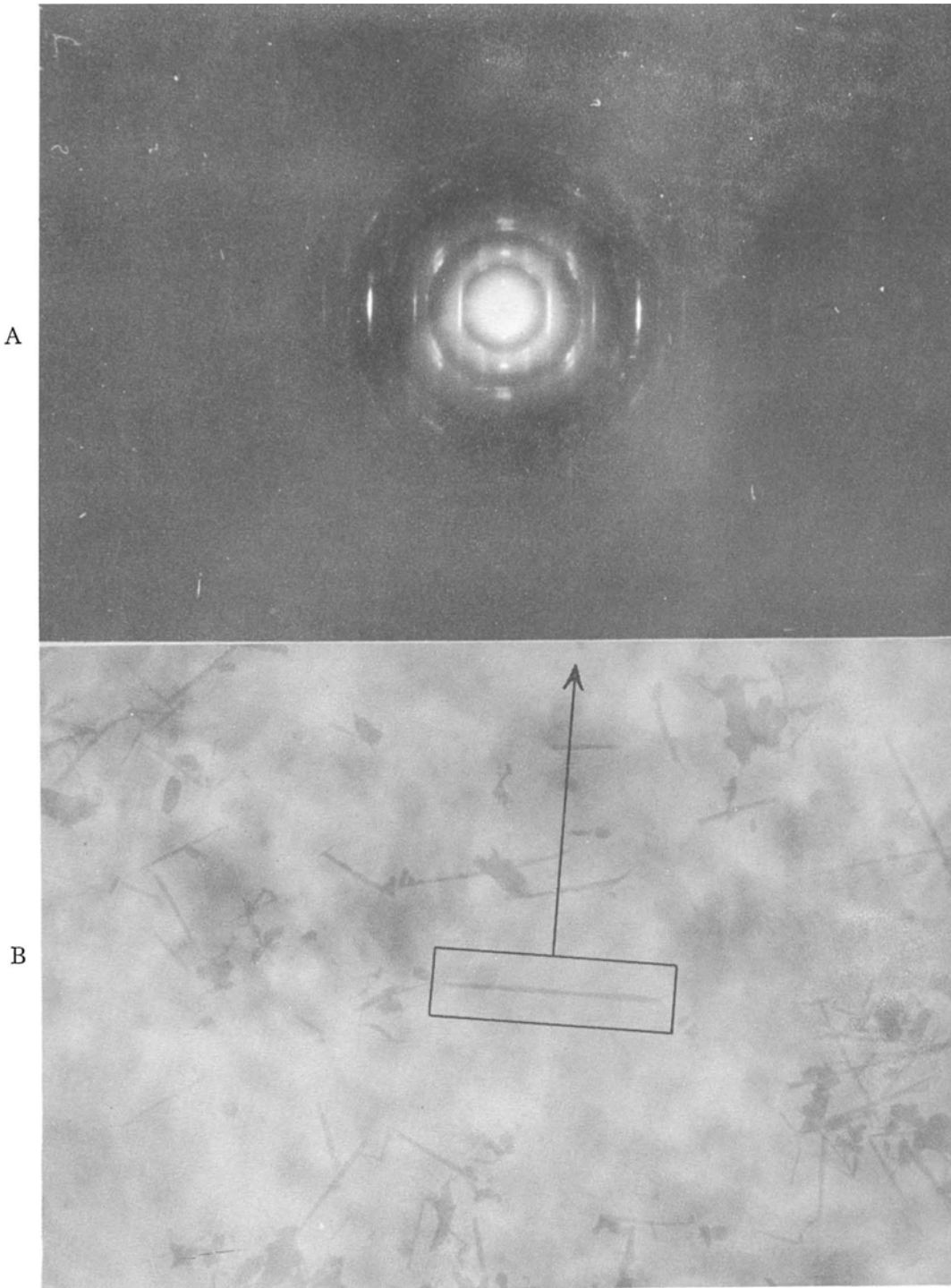


FIGURE 18. — Halloysite. Silver City, New Mexico. (A) Electron diffraction pattern from single crystal. (B) Electron micrograph of single crystal.



FIGURE 19.— South Texas Outcrop. Manning formation (surface). Magnification: 80,000.  
(1 mm. = 125 Å.)



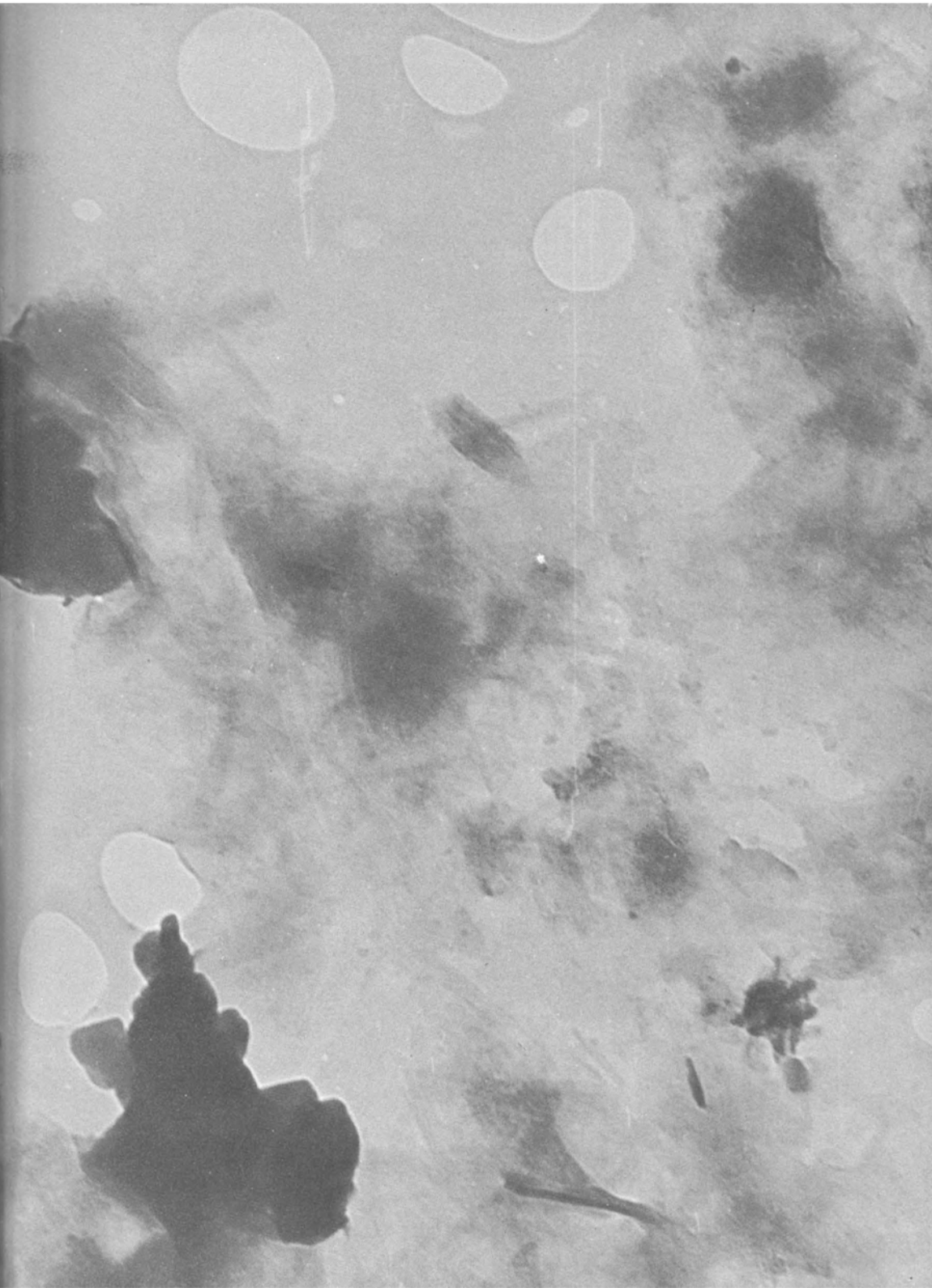


FIGURE 20. — South Texas Outcrop. Austin (subsurface). Magnification: 80,000.  
(1 mm. = 125 Å.)

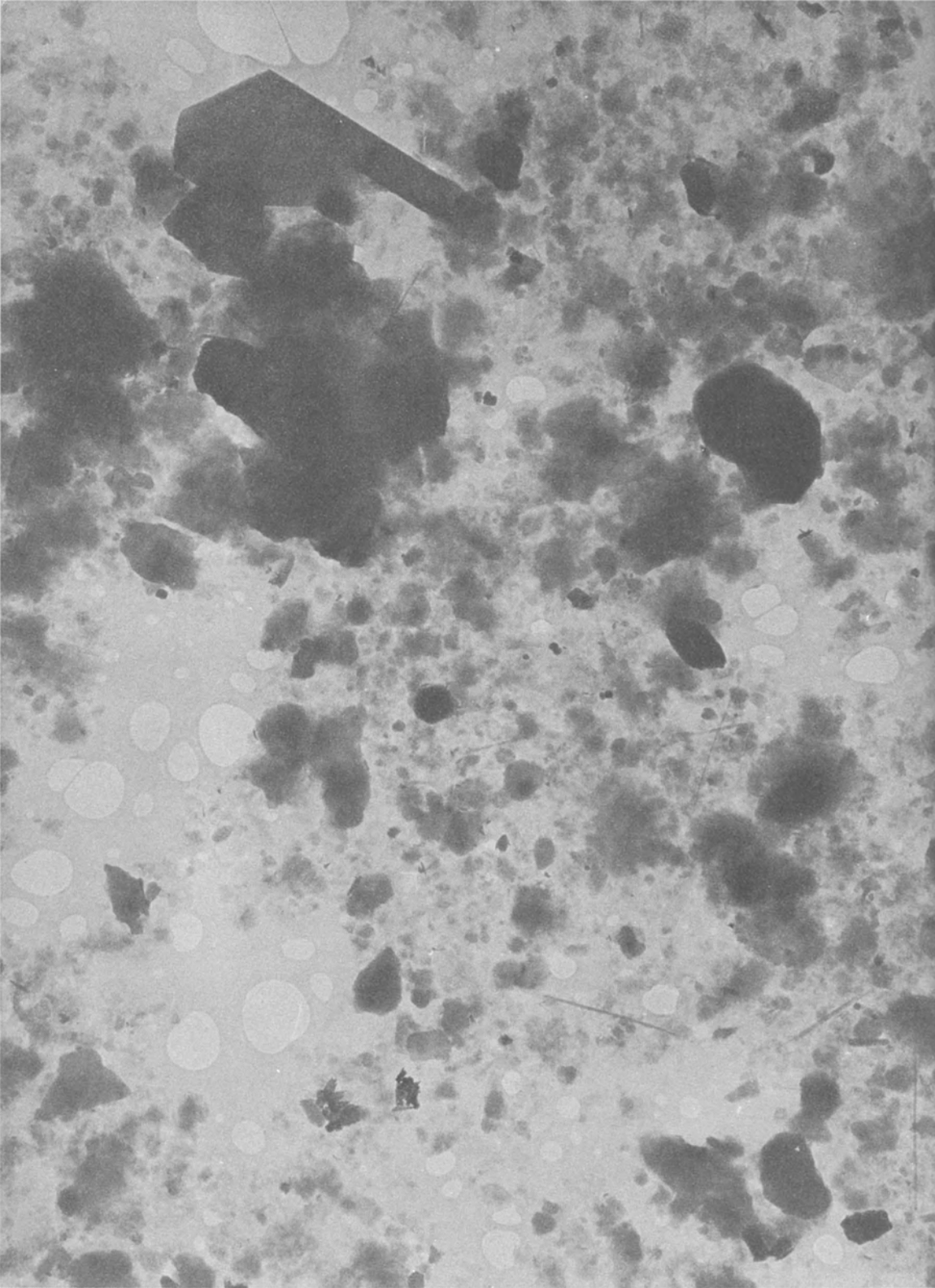


FIGURE 21. — South Texas Outcrop. Goliad or Lagarto formation (20-25 ft. below surface).  
Magnification: 16,000. (1 mm. = 625 Å.)

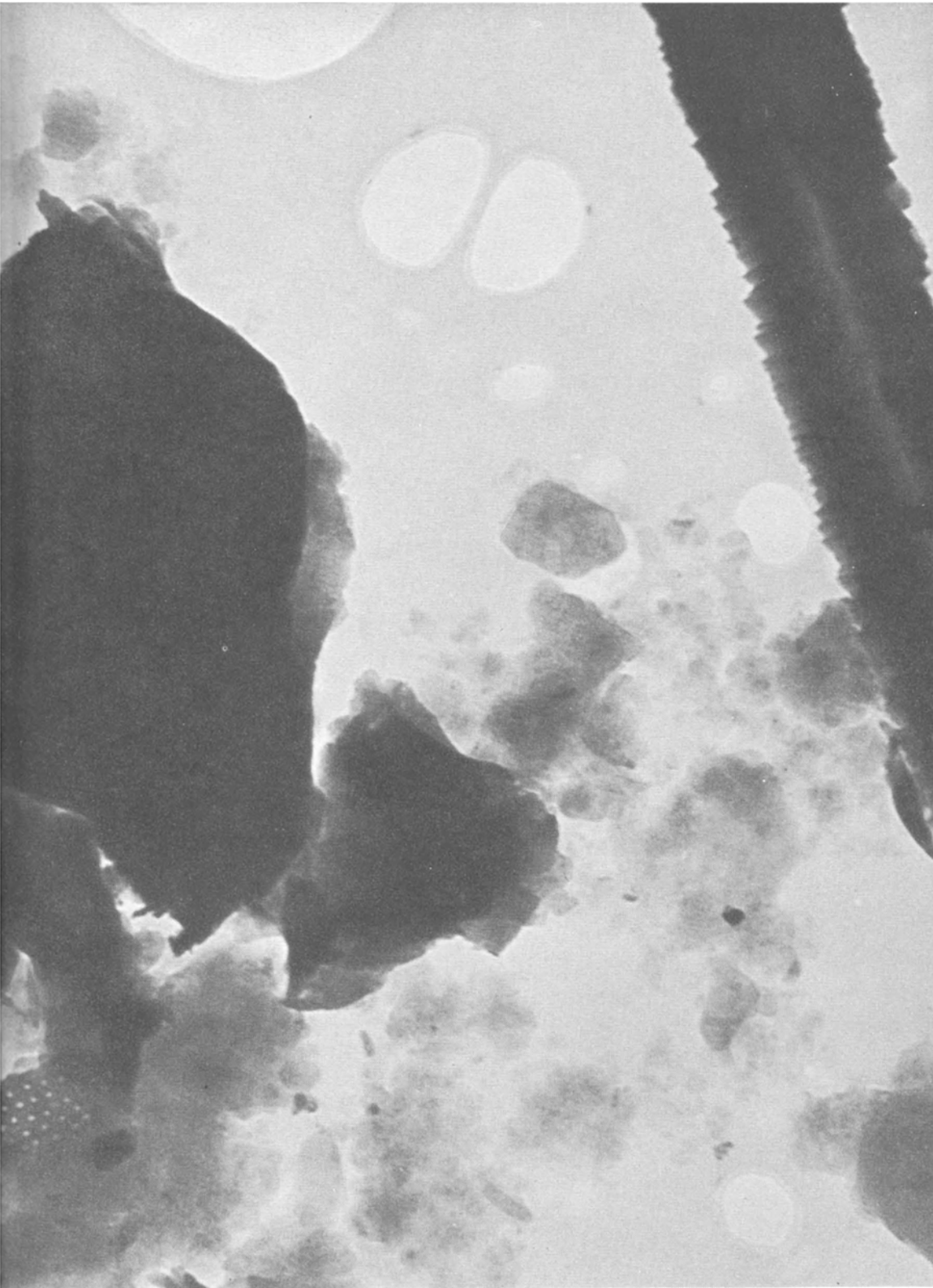


FIGURE 22.— South Texas Outcrop. Carrizo formation (surface). Magnification: 80,000.  
(1 mm. = 125 Å.)



FIGURE 23. — South Texas Outcrop. Basalt plug (surface). Magnification: 16,000.  
(1 mm. = 625 Å.)

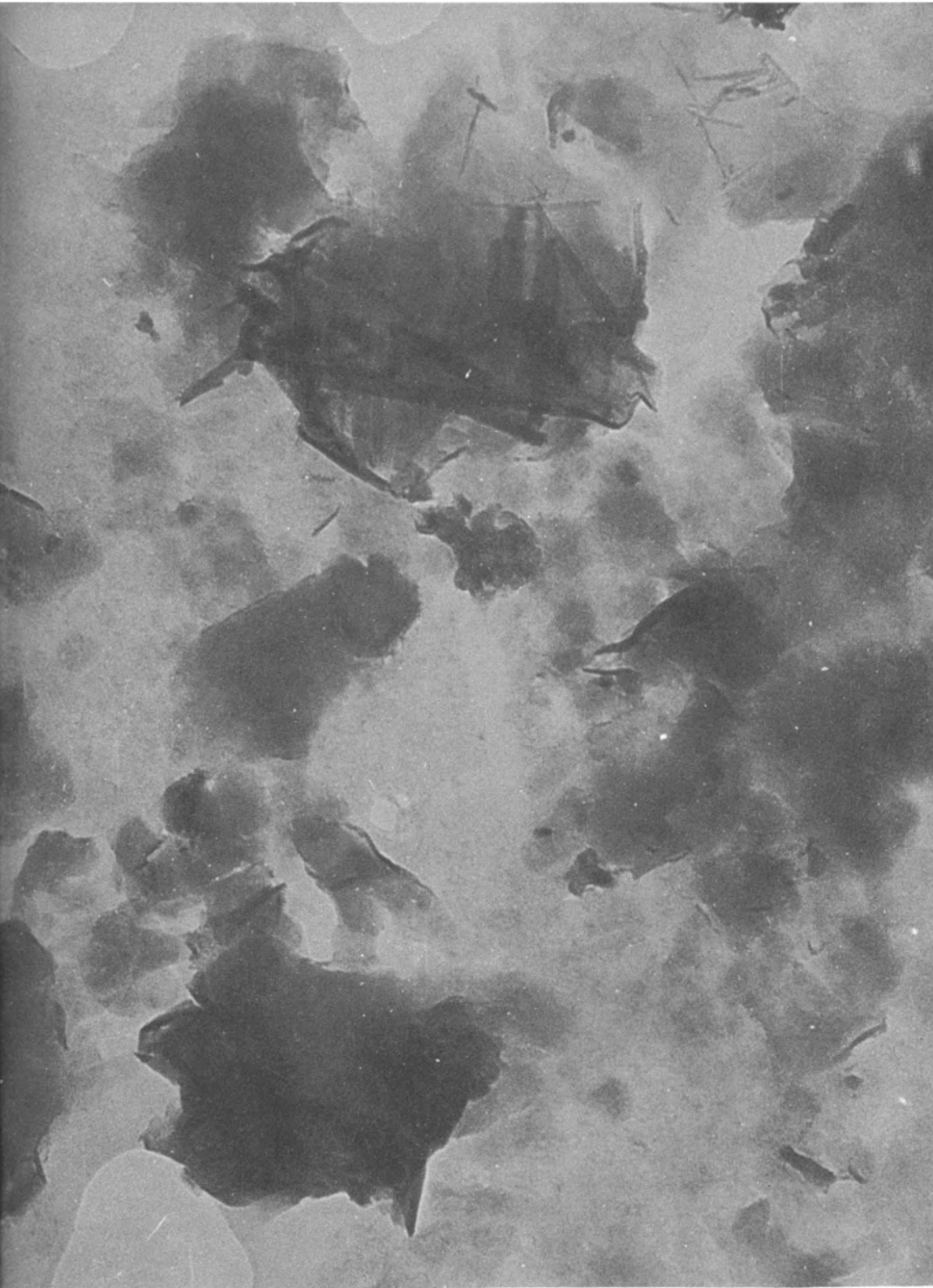


FIGURE 24. — South Texas Outcrop. Basalt plug (a different location) (surface).  
Magnification: 80,000. (1 mm. = 125 Å.)

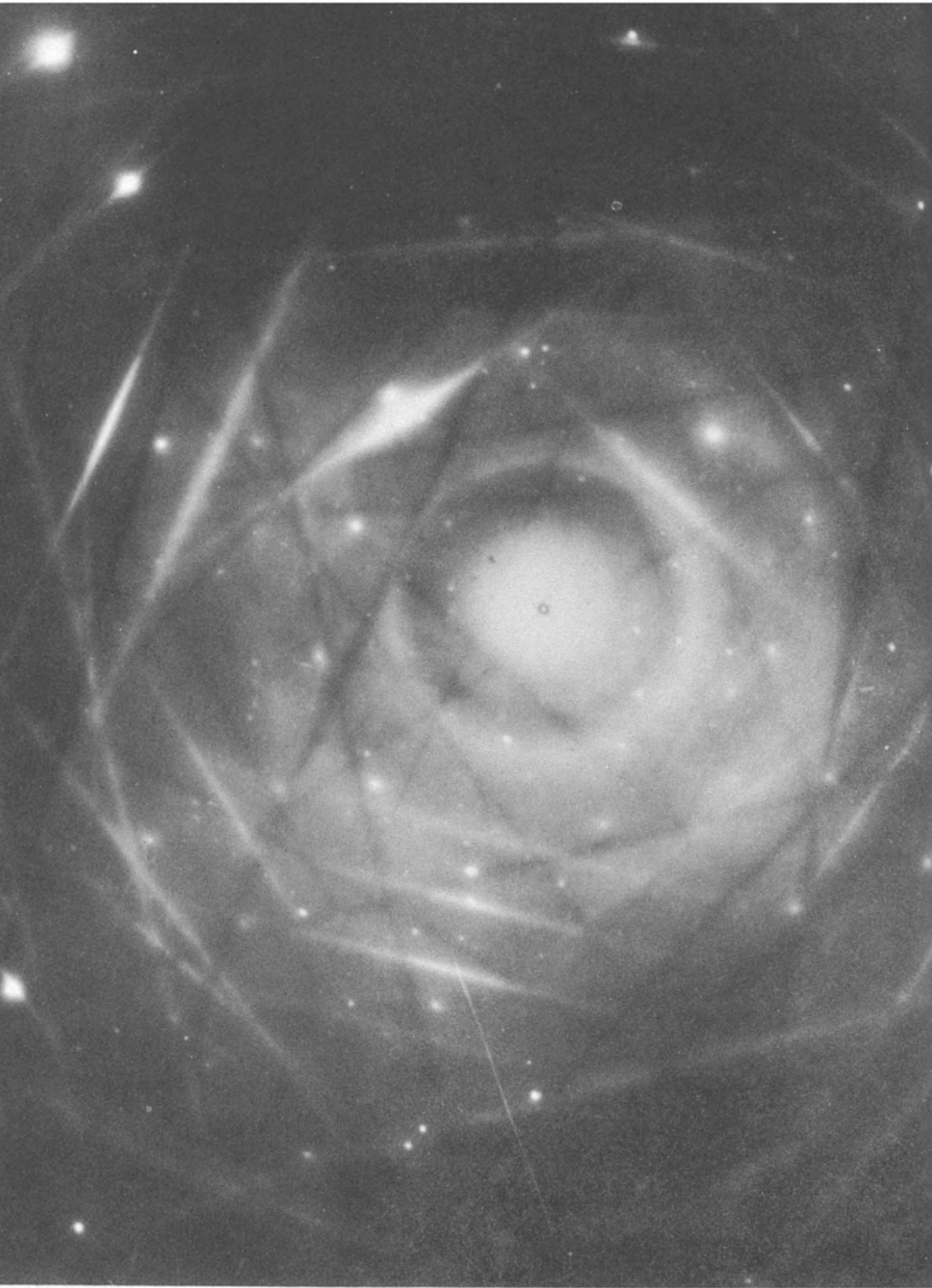


FIGURE 25.—Ground Ottawa Sea Sand. Electron diffraction pattern showing Kikuchi lines. The sample area contributing to the pattern is  $2.5 \times 3$  microns, as indicated in Figure 26.

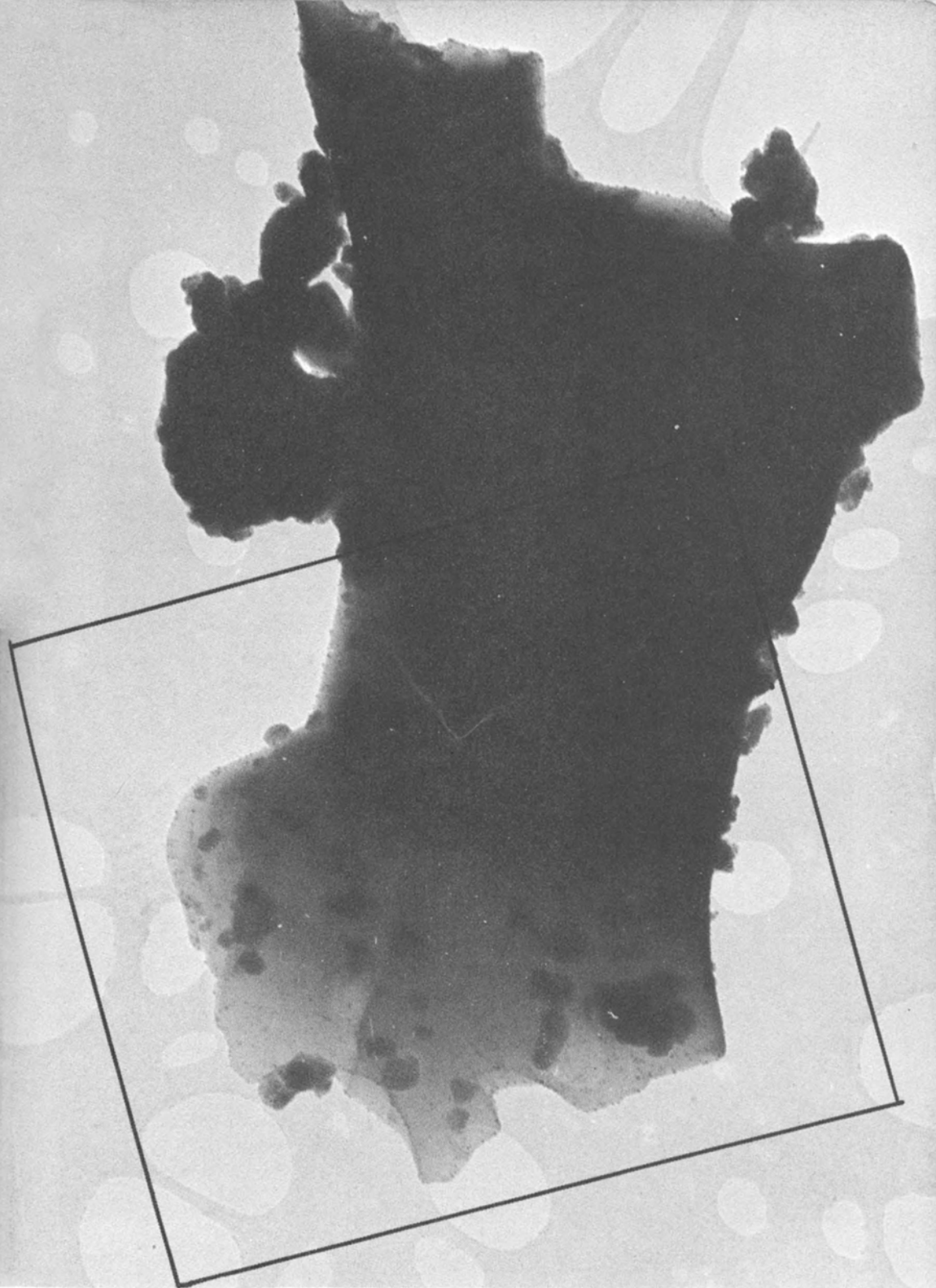


FIGURE 26. — Ground Ottawa Sea Sand. Magnification: 40,000. (1 mm. = 250 Å.) The marked area (2.5 x 3 microns) gave the electron diffraction pattern in Figure 25.

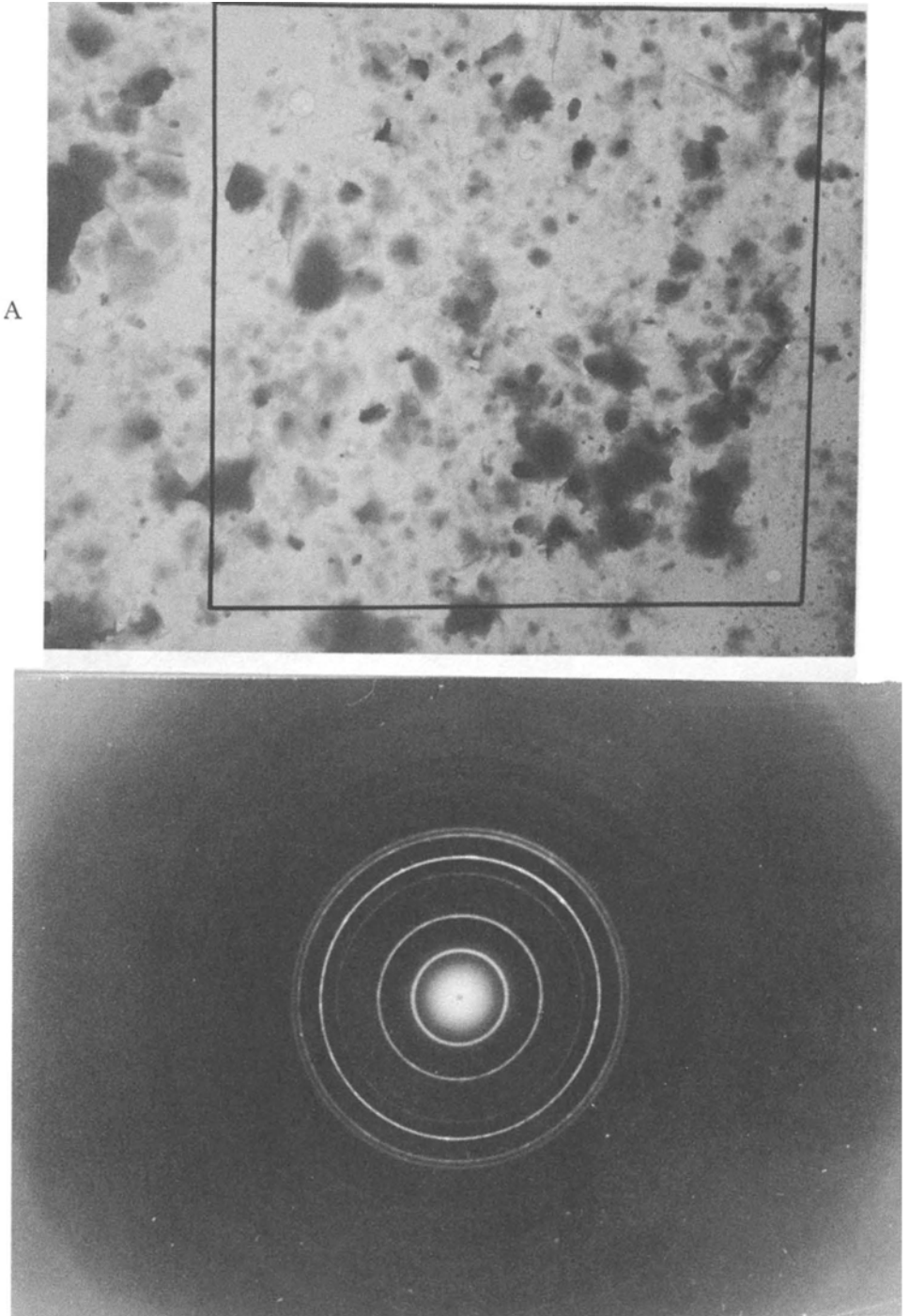


FIGURE 27. — South Texas Outcrop. Beaumont formation (surface). (A) Electron diffraction pattern. (B) Electron micrograph of sample area ( $10 \times 10$  microns) yielding the diffraction pattern. Magnification: 8,000.



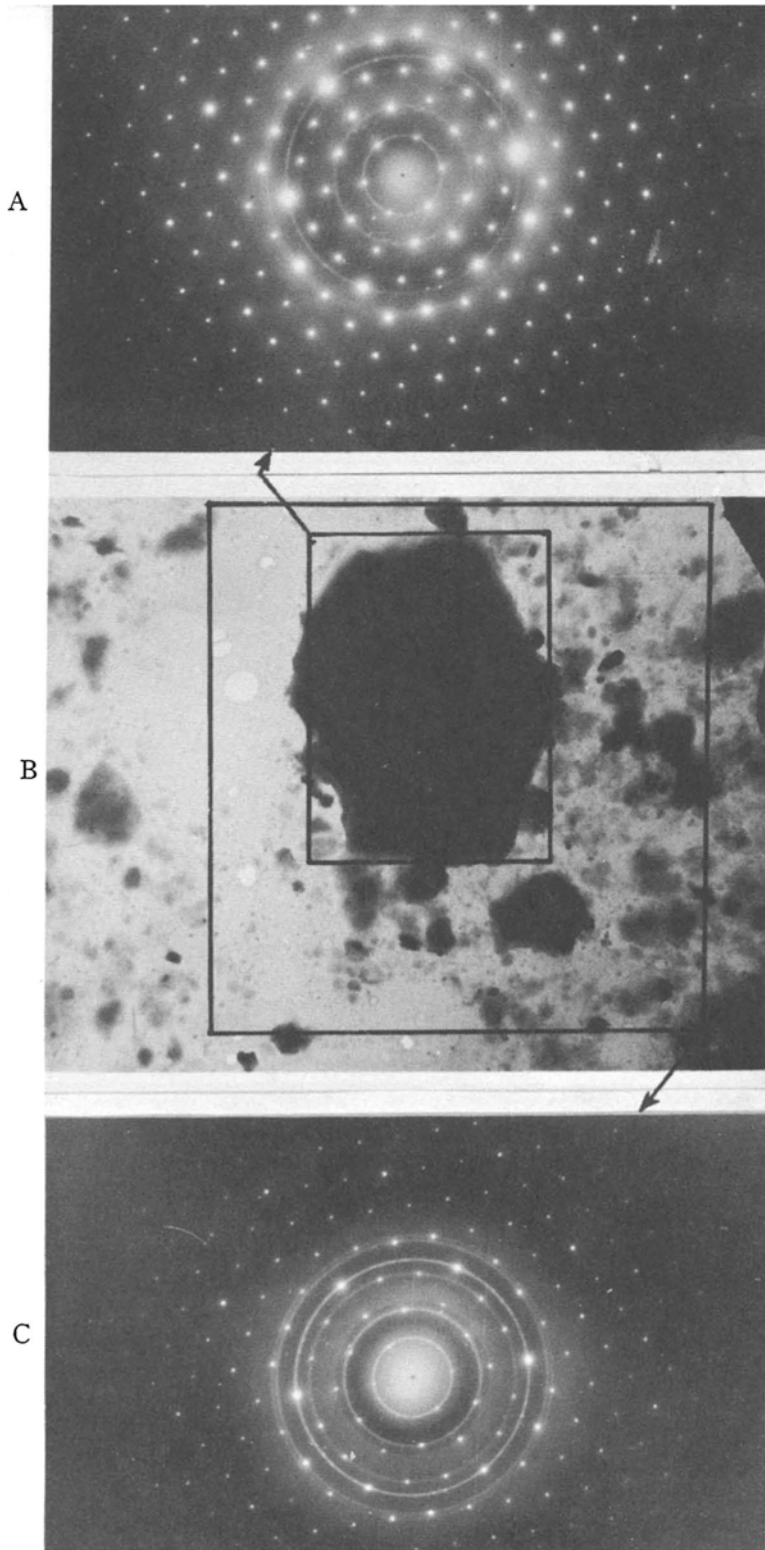


FIGURE 28.— South Texas Outcrop. Another Sample Area. Beaumont formation (surface). (A) Electron micrograph. Magnification: 8,000. The smaller marked area (4 x 6 microns) gave electron diffraction pattern (B), and the larger marked area (10 x 10 microns) gave diffraction pattern (C).

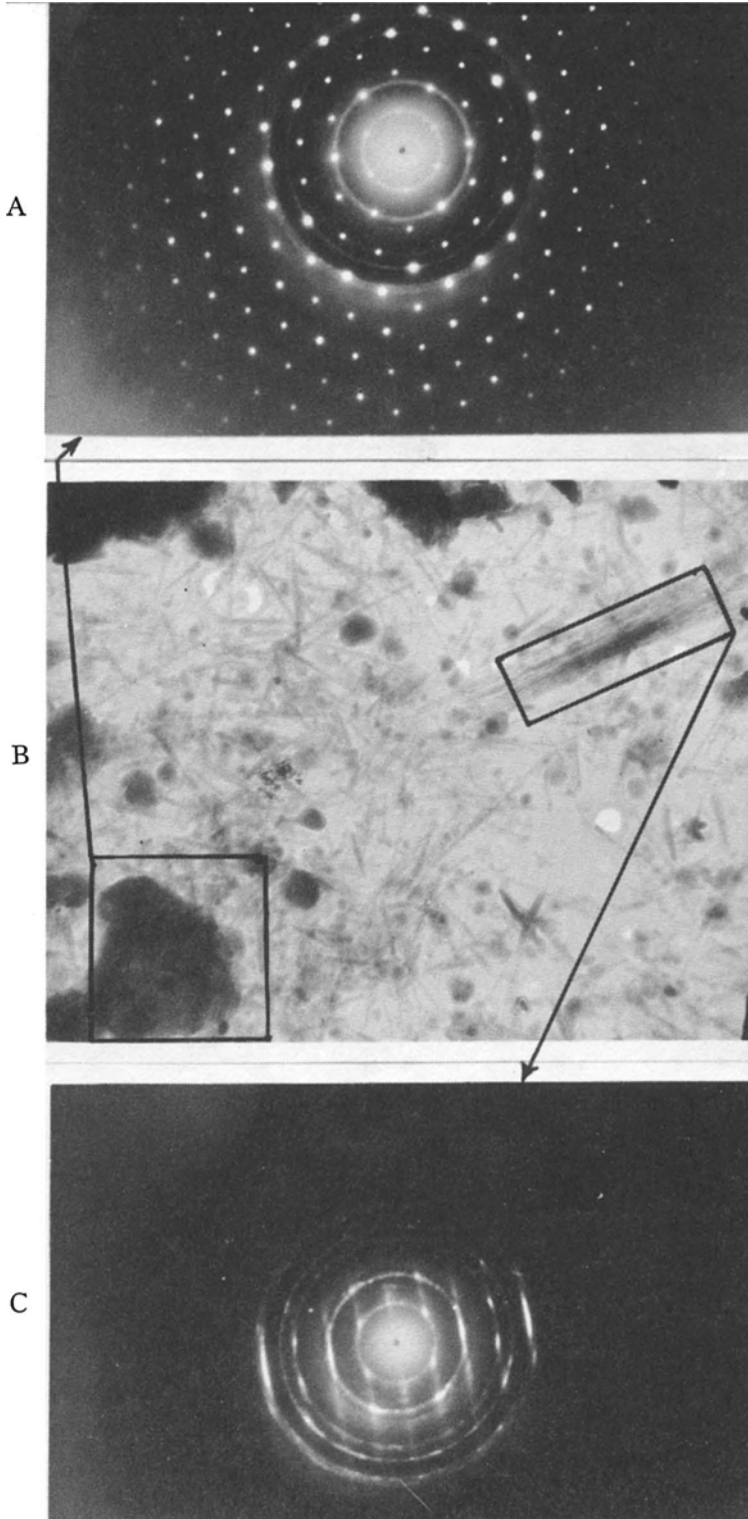


FIGURE 29. — South Texas Outcrop. Lissie formation (20-25 ft. below surface). (A) Electron micrograph. Magnification: 18,000. The smaller marked area (1 x 2 microns) gave electron diffraction pattern (B), and the larger marked area (2 x 2 microns) gave diffraction pattern (C).