

FURTHER OBSERVATIONS ON THE MORPHOLOGY OF CHRYSOTILE AND HALLOYSITE¹

by

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ABSTRACT

Electron microscope studies of chrysotile show that tubes are present in bulk specimens and that these tubes commonly have fuzzy, amorphous-looking material on both the inside and outside. Similar material is associated with synthetic chrysotile and has been noted previously in halloysite specimens. The existence of such material between and within the tubes, together with apparent irregularities in size, shape and packing of tubes, explains the apparent discrepancy between the measured density of bulk samples and the calculated density of a hypothetical sample consisting of close-packed, regular, hollow capillaries.

Replicas of fractured surfaces of halloysite ($2\text{H}_2\text{O}$) from various localities reveal that the particles occur as curved to flat laths commonly possessing "hexagonal" terminations and surface features indicative of a higher degree of crystallinity than tubes of halloysite ($4\text{H}_2\text{O}$).

It is suggested that a complete morphological series from plates through laths to tubes exists both in platy to fibrous serpentine and in kaolinite to halloysite ($4\text{H}_2\text{O}$). In each series a number of structural varieties are to be expected between the morphologically distinct "end members."

INTRODUCTION

In the period that has elapsed since the discovery that halloysite and chrysotile crystals appear as tubes in the electron microscope, numerous questions have been raised as to the relationships that exist between morphology on the one hand and natural occurrence, structure, chemical composition and bulk density on the other. These specific aspects bear on the broader questions as to the exact nature of the relationship of halloysite to kaolinite and of chrysotile fibers to platy varieties of serpentine. Numerous workers have made important contributions to our understanding of these problems. It is the purpose of this paper to present information recently obtained in our laboratory, pertinent to two specific parts of the general problem: (1) the detailed morphology of chrysotile serpentine and the bearing certain morphological features may have on reported density measurements of chrysotile and halloysite; and (2) the relationship of kaolinite to halloysite and the existence of lath-shaped material intermediate between kaolinite "hexagons" and halloysite ($4\text{H}_2\text{O}$) tubes. The more general problem of the relationship of morphology to the crystal chemistry of 1:1 layer lattice silicates is dealt with in another paper by the senior author.

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NOMENCLATURE

For reasons made evident in the following pages, the members of the serpentine group will be described simply as fibrous or platy, depending on their appearance in the electron microscope. Recent discussions of nomenclature are given by Nagy and Faust (1956), Zussman, Brindley and Comer (1957) and Fleischer (1957).

Fibrous serpentine consists of tubes, or of laths having a sufficiently high ratio of length to width to suggest a genetic relationship to tubes. All chrysotiles that have been studied in sufficient detail appear to belong in this category and therefore, on the basis of present knowledge, "fibrous serpentine" and chrysotile can be considered synonymous and the terms will be used interchangeably herein.

Platy serpentine consists of sheets which vary from equidimensional to elongate. The material known as antigorite falls in this category, but on the basis of recent work (Whittaker and Zussman, 1956; Zussman, Brindley and Comer, 1957) all platy serpentine does not have the crystal structure of the type material from Val Antigorite, Piedmont.

Material described in hand specimen as massive serpentine—including such varieties as williamsite, baltimoreite, antillite, picrolite, etc.—consists of an intimate mixture of fibrous and platy serpentine as demonstrated by earlier work of Nagy with the present authors and reported on by Nagy (1953) and by Nagy and Faust (1956).

The lath-shaped material belonging in the kaolinite group will be referred to as halloysite pending the results of single crystal electron diffraction work now in progress.

MORPHOLOGY OF CHRYSOTILE

The general morphological characteristics of chrysotile tubes have been pointed out by many workers following the original suggestion of Turkevich and Hillier (1949, p. 480) that the fibers they observed in electron micrographs appeared to be hollow. Subsequently the cylindrical character of material seen in dispersions has been evidenced best by pictures of synthetic

fibers showing a concentric arrangement of one tube within another (Bates, Sand and Mink, 1950), occasional circular cross sections (Noll and Kircher, 1950), and appropriate variation in density across the tubes (Noll and Kircher, 1951, pp. 223–224: and most of the more recent studies). In the case of the much longer and commonly thinner natural fibers, the variation in density and presence of “multiple” or concentric tubes provides the bulk of the evidence since the end views have in the past been difficult to obtain. Electron diffraction patterns of single fibers of halloysite and chrysotile taken by Honjo and Mihama (1954) are consistent with a tubular structure; as are the measurements and calculations of x-ray diffraction effects from a cylindrical lattice as studied by Jagodzinski and Kunze (1954) and by Whittaker (1953, 1954, 1955). In the most recent work involving morphological studies, Zussman, Brindley and Comer (1957, p. 150) observe that “chrysotile occurs in either silky or splintery fibers which in the dispersed state appear in electron micrographs as tubes and laths respectively.”

The problem as to whether chrysotile tubes exist in nature or are produced in preparation of the fibers for electron microscope observation has been brought to a head by the studies of Pundsack (1956, 1958) on the density of bulk samples, and by a thorough investigation by Kalousek and Muttart (1957) on the specific volume, x-ray diffraction effects, electron microscopy, and several other aspects of the fiber and matrix portions of selected serpentine samples. As the latter authors point out (p. 19):

The measurements in this study and by Pundsack on the specific volume of massive chrysotile fiber revealed generally a porosity far too low compared to that required for a massive specimen consisting of tubular crystals. It would follow that chrysotile could occur largely in the form of lath or sheet crystals in native form. If such laths or sheets contain internal strains due to misfit between layers, curling of the sheets into laths or tubes should occur. The present studies suggest that such a mechanism may apply to the formation of chrysotile in tubular crystals, but the evidence does not preclude the occurrence of tubular crystals in massive chrysotile (Globe, Ariz., in present studies).

The fact that tubular crystals of chrysotile do exist in nature is, in the opinion of the authors, demonstrated by electron micrographs such as that in Fig. 1a, which pictures a replica of a fracture surface obtained by the “pre-shadowed platinum-carbon replica” technique previously described by Comer and Turley (1955). Attempts to get clear-cut pictures of chrysotile tubes in cross section are hampered by the difficulty of fracturing bundles of asbestos fibers along a smooth plane perpendicular to their length. The fracture surface pictured here was obtained at the contact between the fibrous and massive portions of a serpentine specimen and shows the ends of a number of tubes that are inclined to the fracture surface. Measurable tubes have inner diameters ranging from 100 to 175 Å and outside diameters varying from 365 to 440 Å. These figures are somewhat larger than those obtained from measurements on 27 tubes in pictures of Globe, Arizona and Thetford, Quebec, material where the inner diameters range from 20 to 190 Å with a mean of 68 Å, and the outer diameters vary from 114 to 850 Å with a mean of

250 Å. When the tubes lie in the plane of the fracture surface, as in Figs. 1b and 2a, cross sections are more difficult to obtain but are in evidence at terminations of certain tubes. The apparent degree of curvature leaves little room for doubt that many of these fibers are cylindrical rather than lath-shaped.

The troughs appearing in the upper left corner of Fig. 1b were presumably left by tubes that adhered to the opposing fracture surface. The presence of these grooves with sharp cusps between them provides important evidence that, in this specimen at least, there is little if any void space between the tubes. The fact that breakage is around rather than across the tubes indicates that the material between the tubes may be less well crystallized than the material forming the tube walls. Similar features are evident in Fig. 2a.

The inset at upper right of this figure is an enlargement of the outlined area, and shows another feature characteristic of many chrysotile tubes. At the points indicated by the arrows a sharp increase in wall thickness can be observed. In dispersions of both synthetic and natural fibers this has been noted in so-called multiple or concentric tubes (Bates, Sand and Mink, 1950; Bates, 1951). In replicas such as that shown here it is not possible to determine in specific instances whether or not the outer layer completely surrounds the inner cylinder or simply forms a shell on part of the tube. In tubes like that at "A" in Fig. 1b the latter appears definitely the case. It seems apparent that, on dispersion and separation of fibrous material, "shells" of varying length and degree of curvature provide some of the "curled" plates and laths which have heretofore been interpreted by some workers as being in the process of rolling up or unrolling owing to the heat of the electron beam.

Figure 2b illustrates fibers of Arizona chrysotile that have fuzzy-appearing material both on the outside and inside of the tubes. The barely discernible "amorphous" material on the outside provides further evidence that void space between the tubes in the lump material is unlikely. Similar fuzzy and shreddy material is very evident on halloysite (Bates, Hildebrand and Swineford, 1950). The material intermittently spaced within the tubes was first noted in synthetic chrysotile by O'Daniel and Kedesdy (1947) prior to the discovery that the fibers were tubular. Noll and Kircher (1951, p. 223) described the feature in more detail and in a later note (Noll and Kircher, 1952) showed that it is produced as a result of the effect of the electron beam on the fibers. Similar observations have been made on halloysite by Behne and Müller (1954). Careful evaluation of many photographs leads the present authors to believe that "amorphous" material giving lower scattering of electrons is dispersed throughout the tubes in their natural state and becomes agglomerated into patches of greater density to the beam as exposure time is increased.

Similar structure is evident in Figs. 3a and 3b of synthetic chrysotile made by Dr. Rustum Roy. A paper by Gillery (1958) on an x-ray study of these and other synthetic Mg-Al serpentines and chlorites is in press.

These pictures show many features of morphological interest. Cross sections (A), cone-in-cone arrangements (B) and telescope-like sections of concentric

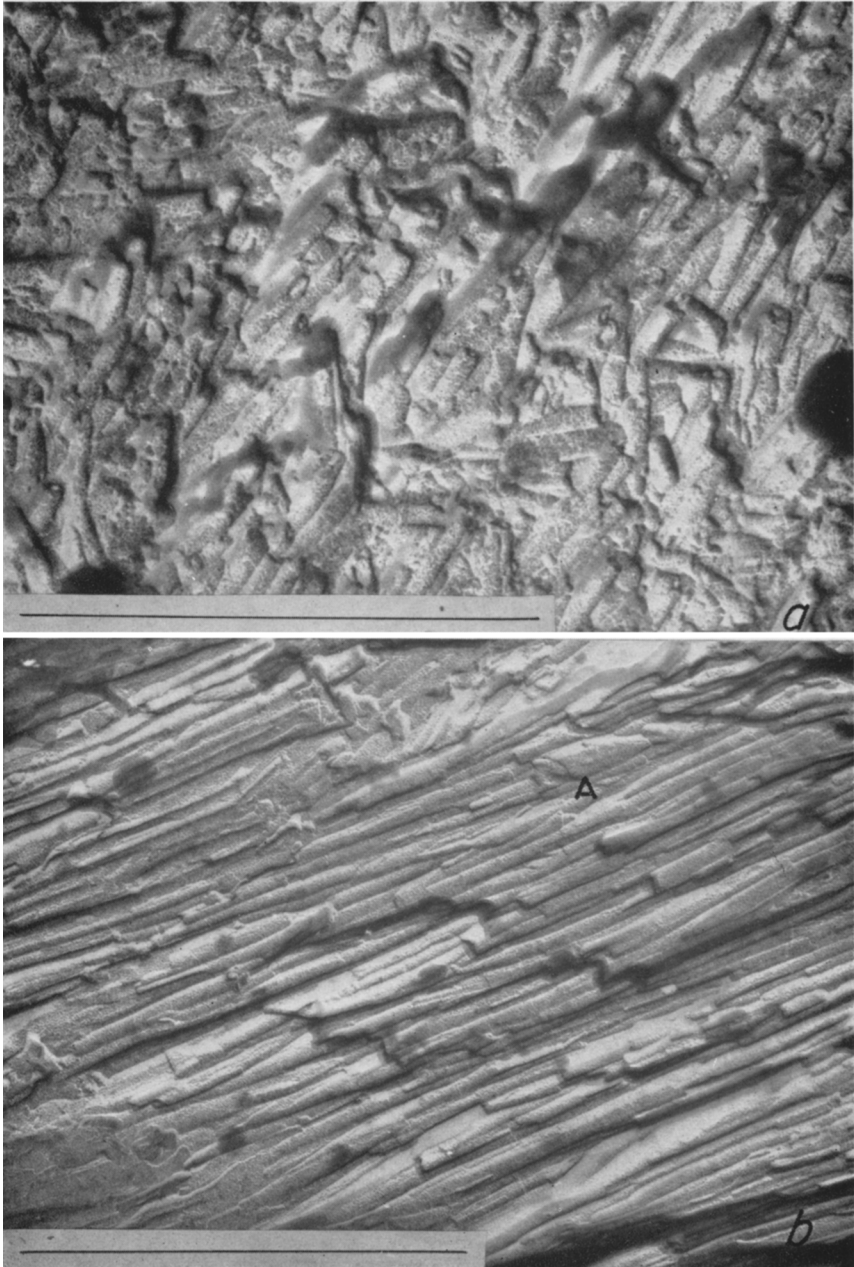


FIGURE 1.—Chrysotile, Madison County, Montana: *a*, Replica of fracture surface showing projecting tubes. Unless otherwise noted the scale on all figures represents 1 μ . *b*, Troughs at upper left show where fibers have been pulled away from fracture surface. A, Broad “shell” overlapping several tubes.

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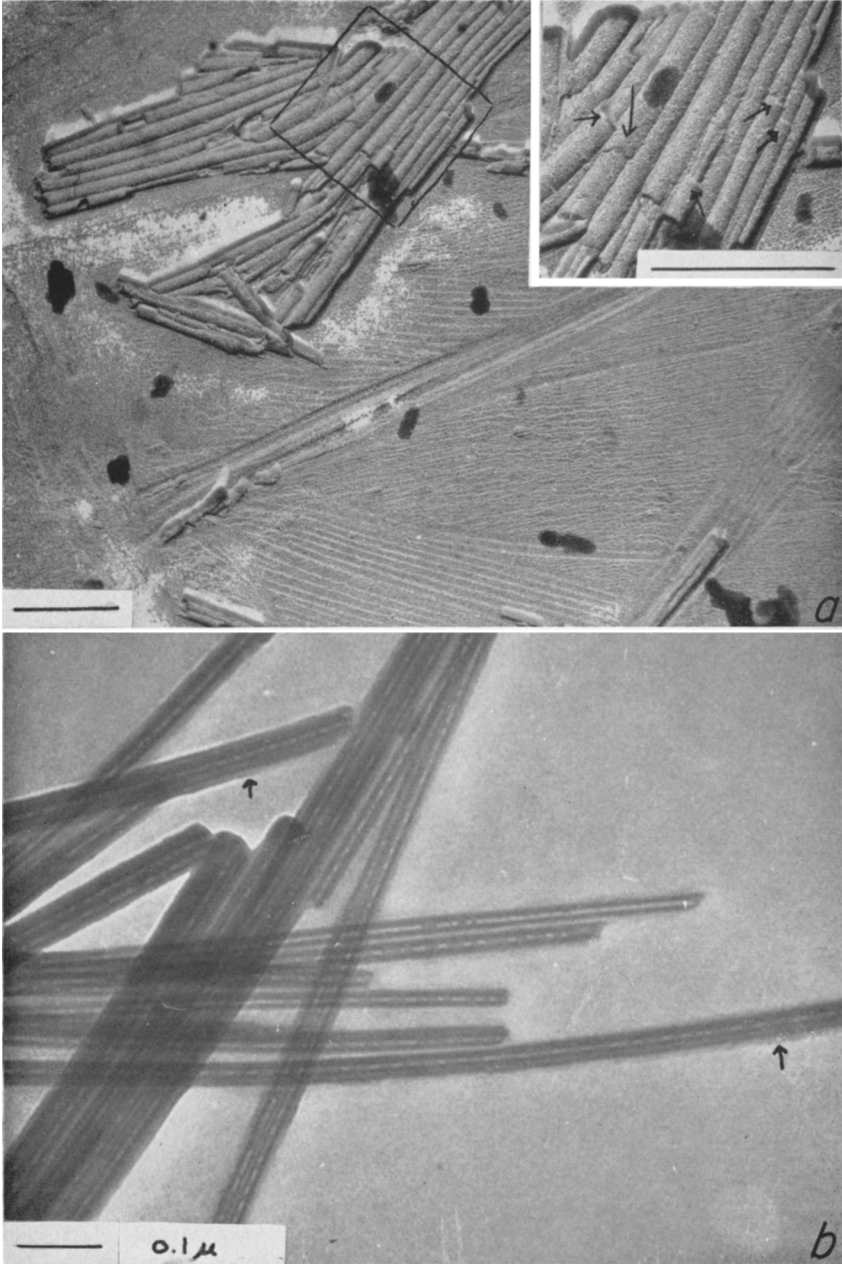


FIGURE 2.—*a*, Chrysotile—platy antigorite interface shown on fracture surface of specimen from Glen Urquhart, Scotland. Inset shows points where wall thickness increases. *b*, Chrysotile, Globe, Arizona: Tips of arrows indicate fuzzy material along outer edges of tubes.

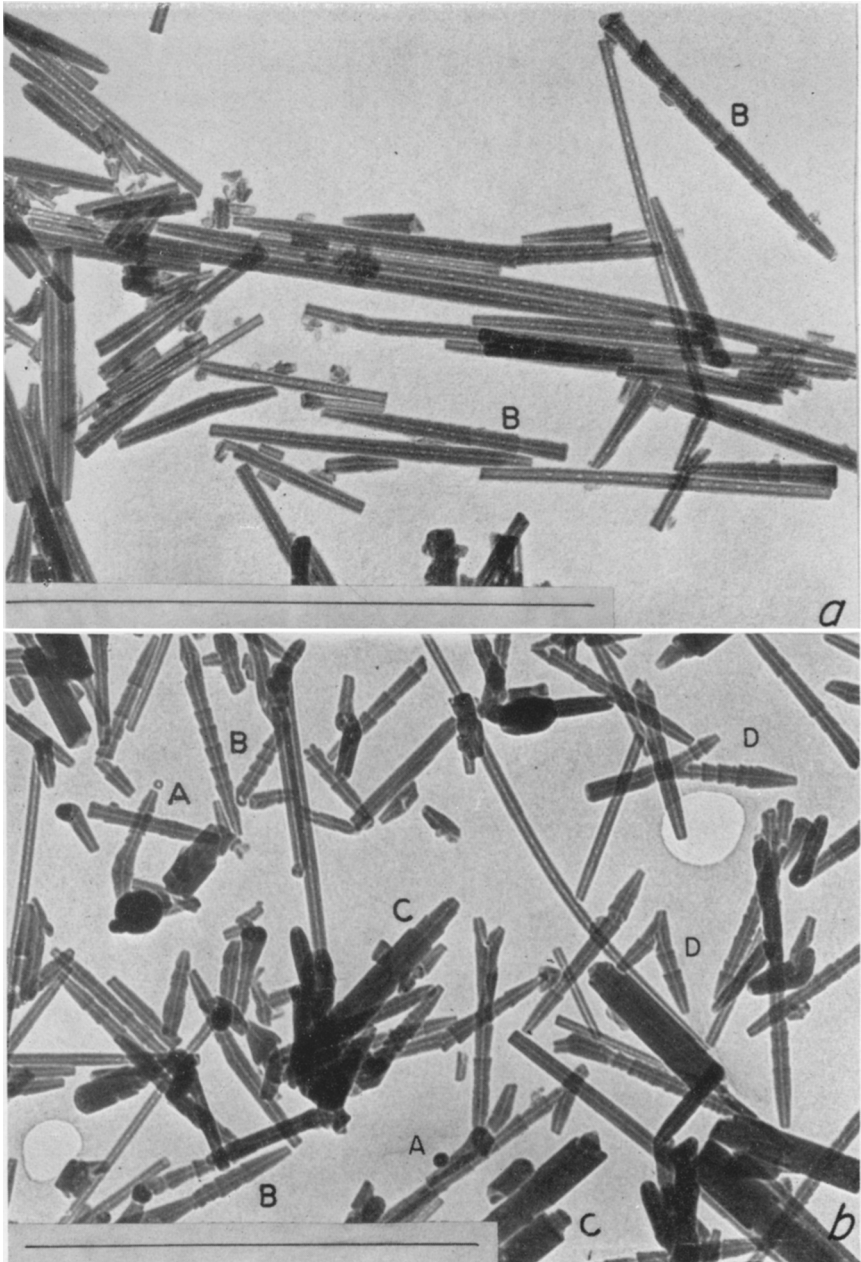


FIGURE 3.—*a*, Synthetic chrysotile, courtesy of Dr. R. Roy. A. Cross section, B. “Cone-in-cone” feature, C. Concentric tubes, D. “Y”-shaped intergrowths.

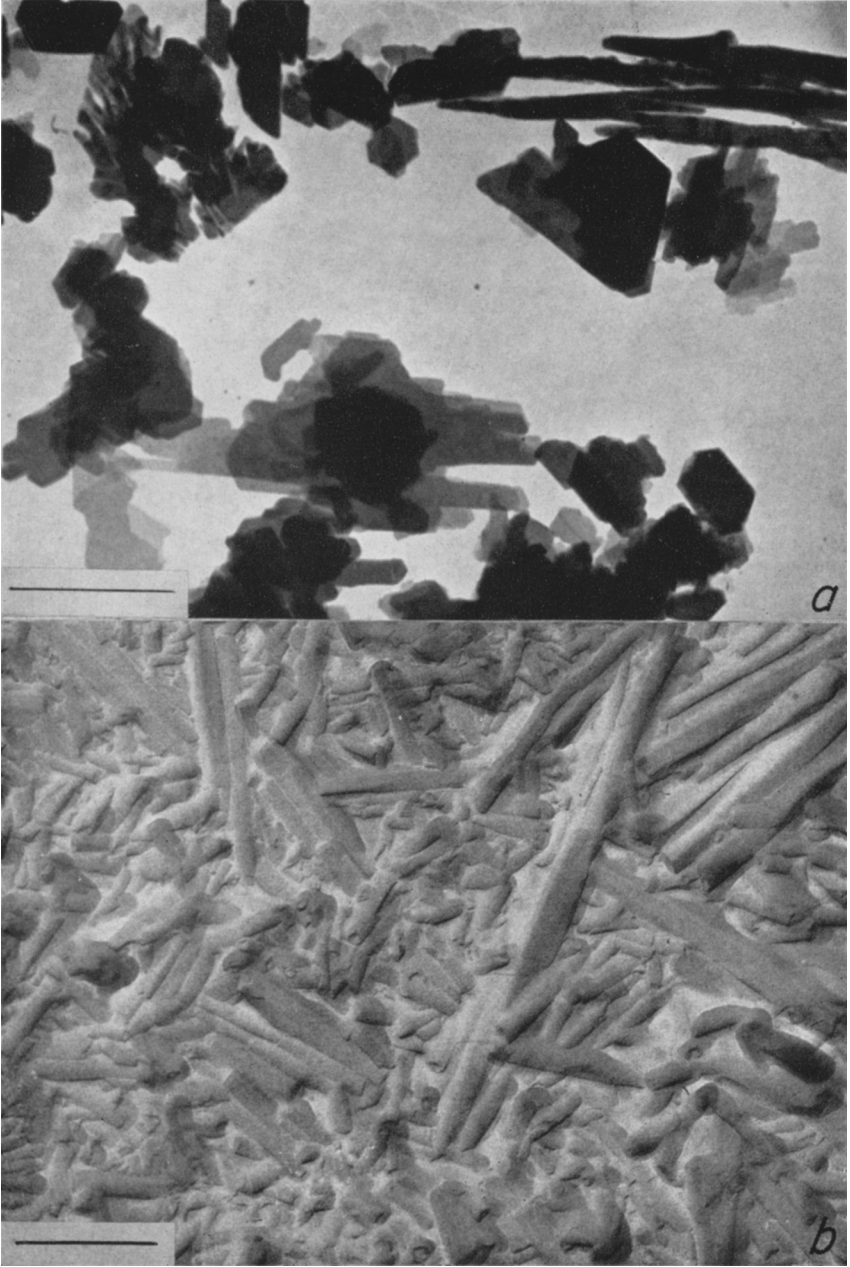


FIGURE 4.—*a*, Kaolinite, South Mountain, Pennsylvania : skeletal and elongate shapes possessing the normal degree of crystallinity of kaolinite. *b*, Halloysite ($4\text{H}_2\text{O}$), Wendover, Utah : Replica of fracture surface of clay lump showing tubes of varying size and shape.

tubes (C) have been noted in earlier accounts. Figure 3b shows, in addition, several "Y" shapes (D) where a single tube splits into two others. Of particular interest in both pictures is the fact that the inner diameter of the tubes is fairly uniform (21–100 Å) in spite of the many varying shapes and a much larger variation in the outside diameters not only from tube to tube (130–820 Å) but also along the length of many individual tubes. This supports the original hypothesis (Bates, Hildebrand and Swineford, 1950) that the inner diameter of halloysite and chrysotile tubes is controlled by the structural misfit of the tetrahedral and octahedral sheets of the layer lattice. The outer diameter, on the other hand, depends more on conditions of growth, amount of disordered material, and number of concentric layers.

The electron microscope evidence that chrysotile fibers are tubular is further supported by studies of surface chemistry of Canadian asbestos made at Lehigh University (Healey and Young, 1954; Young and Healey, 1954). In the latter paper the authors concluded from gas adsorption and heat of wetting experiments that :

1. The individual fibers in chrysotile are for the most part bound in fiber bundles ; thus, a large portion of their external surface is not available to adsorbed molecules.
2. Chrysotile has an internal capillary structure.
3. These capillaries appear to be within the individual fibers themselves ; indeed it is possible that the capillaries may be identified with the apparent hollow tubular structure shown by electron photomicrographs.
4. The capillaries appear to be blocked in some manner with strongly sorbed water plugs. These plugs are permeable to water vapor and ammonia but not to less polar gases.
5. The water plugs are removed by activation at 425° at 10⁻⁵ mm pressure. There is no change in the bulk chrysotile structure after heating to temperatures up to 500°; however, changes in the surface occur at temperatures greater than ca. 450°.
6. The water plugs may be reformed in samples activated at less than 425° by saturation with water vapor.

This evidence of the formation of " water plugs " appears to be compatible with the electron microscope evidence of " amorphous-appearing material " in the tubes in that such material might be expected to absorb water and swell thus blocking the capillaries to entry of " less polar gases."

INTERRELATION OF MORPHOLOGY AND BULK DENSITY

The authors believe that the values obtained by Pundsack (1956, 1958) and Kalousek and Muttart (1957) for the density of bulk samples of chrysotile and halloysite (4H₂O) are to be expected in the light of the observed morphological data and the detailed structural picture originally proposed to account for the formation and existence of tubular crystals. The latter postulates that only a single 1 : 1 layer in each tube will have the correct radius of curvature resulting from the misfit of tetrahedral and octahedral sheets. The atoms in this layer (referred to as the " ideal tube ") will have the most regular (but not planar) arrangement attainable for this particular environment. Here the position of an atom with respect to its neighbors is determined by the crystal

chemistry of the two sheets which make up the 1 : 1 layer and is not greatly affected by the weakly bonded adjacent layers. Unless there is a progressive change from the inside to the outside of a tube in chemical composition or structural arrangement, concentric layers inside and outside the "ideal layer" mentioned above will have radii of curvature that are too small and too large respectively to permit a perfect fit of the two sheets within each layer. Thus, it is to be expected that the arrangement of atoms will become less regular both inward and outward from some point within the wall of the tube. It is hypothesized that in the process of crystallization, material "trapped" inside and subsequent layers outside the "ideal tube" will have less regularity in atomic arrangement finally filling "intertube" and "intratube" areas with "amorphous-appearing" material.

If this picture is correct the amount of void space in a specimen may be nearly nonexistent where inter- and intratube regions are filled, or attain a maximum value where such regions are empty and tubes of similar dimensions are in random arrangement. In "practice" it seems probable that these "extreme" situations will be rare and that most samples will yield intermediate values. The material from Globe, Arizona, which represents some of the best commercial "fiber" available, yields electron micrographs showing tubes of remarkable length/width ratio and uniformity of size and shape. Nevertheless, pictures such as Fig. 2b show that even in this chrysotile there is considerable variation in the diameter of the fibers and the amount of "amorphous-appearing" material present on and in them. Coupled with the probability that no two samples are alike (1) with respect to tube diameters (both inside and outside), (2) with respect to the detailed manner in which the tubes are packed, and (3) with respect to the percentage of "perfect" versus "imperfect" tubes (collapsed tubes, curved laths, etc.); it is not surprising that measurements of void space on a material as well crystallized as that from Globe range from a few percent to 12.5 percent of the total volume (Pundsack, 1956, p. 363; Kalousek and Muttart, 1957, p. 11).

MORPHOLOGY OF KAOLINITE AND HALLOYSITE

Material having the chemical, structural, and thermal characteristics of halloysite ranges morphologically from twisted curls and fibers intimately associated with amorphous-looking rounded grains of allophane (Sudo and Takahashi, 1956) to well defined tubes that split upon dehydration to give more irregular shapes (Bates, Sand and Mink, 1950; Bates and Comer, 1955). The work of Brindley and Comer (1956) suggests and the present study confirms that this range can be extended from tubes toward "hexagonal" kaolinite plates as a result of the existence of curved laths and laths with "hexagonal tendencies" seen in electron micrographs of replicas of fractured surfaces of a number of halloysite clays and halloysite-kaolinite mixtures.

In this paper the term halloysite is used for material which appears in electron micrographs in the form of tubes, or of laths with a large enough ratio of length/width to suggest a genetic relationship to tubes. The term

kaolinite refers to platy particles that show "pseudohexagonal" angles and vary from equidimensional to elongate. The morphological data presented show that there is an area of overlap between halloysite laths and elongate kaolinite plates.

The characteristic morphology of kaolinite crystals is well known. Figure 4a illustrates some elongate and skeletal shapes that are observed more rarely.

The existence of tubes of $4\text{H}_2\text{O}$ halloysite projecting from fractured surfaces of clay lumps has been demonstrated in an earlier paper (Bates and Comer, 1955). Photographs such as the one reproduced here in Fig. 4b show that the individual tubes in the specimens studied vary considerably in length and width and approach random, as opposed to parallel, orientation. Some tubes appear flattened and many are slightly twisted and warped in order to conform better to their surroundings. In replicas of the Wendover, Utah, halloysite, such as Fig. 4b, which contains the smallest tubes of any halloysite studied, the inner diameters vary from 80 to 200 Å and the outer diameters from 220 to 420 Å. It will be noted, however, that few of the measurable cross sections are as broad as many of the particles lying in the fracture surface.

Electron microscope studies of dispersions of halloysite tubes demonstrate a large amount of variation within and between samples in the lengths and widths of the tubes or of the laths genetically related to them. Measurement of the width of 1120 particles (Bates, Hildebrand and Swineford, 1950, p. 471) showed a range of from 100 to 6700 Å and an average width of 860 Å. Subsequent unpublished work sponsored by the Filtról Corporation and done by M. A. Rosenfeld, J. C. Griffiths, and the present authors involved the measurement of 400 particles from each of thirteen samples from nine halloysite deposits in Utah, Texas, Georgia, and North Carolina. The results are summarized in Table I.

Of 5200 particles measured the range in width was from 150 to 6360 Å and the average width was 810 Å. A very high correlation ($r = 0.944$) between mean tube length and mean tube breadth of the thirteen samples indicates a structural relationship between the two parameters, particularly in the light of statistically designed experiments which showed that the various disaggregation procedures did not affect tube length. It is of interest that the mean width of the Wendover particles, measured on dispersed material, is larger than that obtained from measurements of tubes in replica (220–420 Å). The discrepancy is probably due in part to inadequate sampling (in replica measurements) and in part to unrolling of the tubes in the disperse sample.

Some of the largest tubes viewed by the authors were found in material from British Guiana and were described in 1952 at the First National Clay Conference (Bates, 1955, pp. 132, 133). Selected areas from the micrographs are shown in Fig. 5. The appearance of "hexagonal" kaolinite plates having rolled edges (A), tubes with crystallographic angles at the terminations (B), and other tubes showing polygonal rather than round or oval cross sections (C), indicated at that time that more detailed study of the morphological relations of halloysite and kaolinite was needed.

TABLE I.—MEAN WIDTH AND LENGTH OF 400 HALLOYSITE PARTICLES FROM EACH OF THIRTEEN SAMPLES

Locality	Type of Halloysite (As Received)	Mean Width	Mean Length
Wendover, Utah	4H ₂ O	440 Å	2220 Å
New Park, Utah	4H ₂ O	470	1850
Dragon Mine, Eureka, Utah (earthy type)	4H ₂ O	510	2400
Dragon (porcelain type)	4H ₂ O	560	2490
Dragon (assoc. pyrite)	4H ₂ O	630	2970
Dragon (high alumina)	4H ₂ O	790	4620
Taylor's Ridge, Ga. (stained)	4H ₂ O	850	3290
Taylor's Ridge (white)	4H ₂ O	910	3220
Raddatz Deposit, Eureka, Utah	2H ₂ O, K*	960	4590
Clayton, Texas	4H ₂ O, K	1090	5160
Gusher Knob, N. C.	4H ₂ O, K	1230	4690
Dodge, Texas	2H ₂ O, K	1320	7460
Fox, Utah	2H ₂ O	1750	10,690
Mean of all 5200 particles	—	810	3810

* K indicates the presence of kaolinite in the sample.

Additional uncertainty that the relationship between kaolinite and halloysite is a simple one, was raised by single crystal electron diffraction studies of "tubular kaolin" by Honjo, Kitamura and Mihama (1954) who stated (p. 139) that their observations "suggest that there exists in the kaolins of tubular habit a structure which contains two kaolin layers in a unit cell like dickite but is triclinic like kaolinite and persists, more or less, even when a sample gives rise to an x-ray powder pattern of apparently two dimensional features as with Bedford kaolin."

Visconti, Nicot and Goulart de Andrade (1956) have pointed out that certain Brazilian kaolins give x-ray patterns of kaolinite but appear as tubes in the electron microscope. Similar data obtained in the study of a kaolin clay from Les Eyziez, France, by DeKeyser and Degueldre (1954) was shown by Brindley and Comer (1956) to result from a mixture of kaolinite and halloysite in the sample. However, the latter authors noted (p. 64), from electron microscope replicas of bulk material, that

the surfaces of the tubes show unusual features which have not been described previously. They often appear to be fracturing into fragments having hexagonal outlines. Others appear to be rolled sheets rather than tubes, with the edges of the sheets showing hexagonal forms along the length of the roll.

Oberlin and Tehoubar (1957) and Oberlin (1957) have shown that under special conditions involving alternating periods of dehydration and rehydration characteristic of the surface in certain parts of the Sahara and successfully reproduced in their laboratories, well-formed kaolinite hexagons become

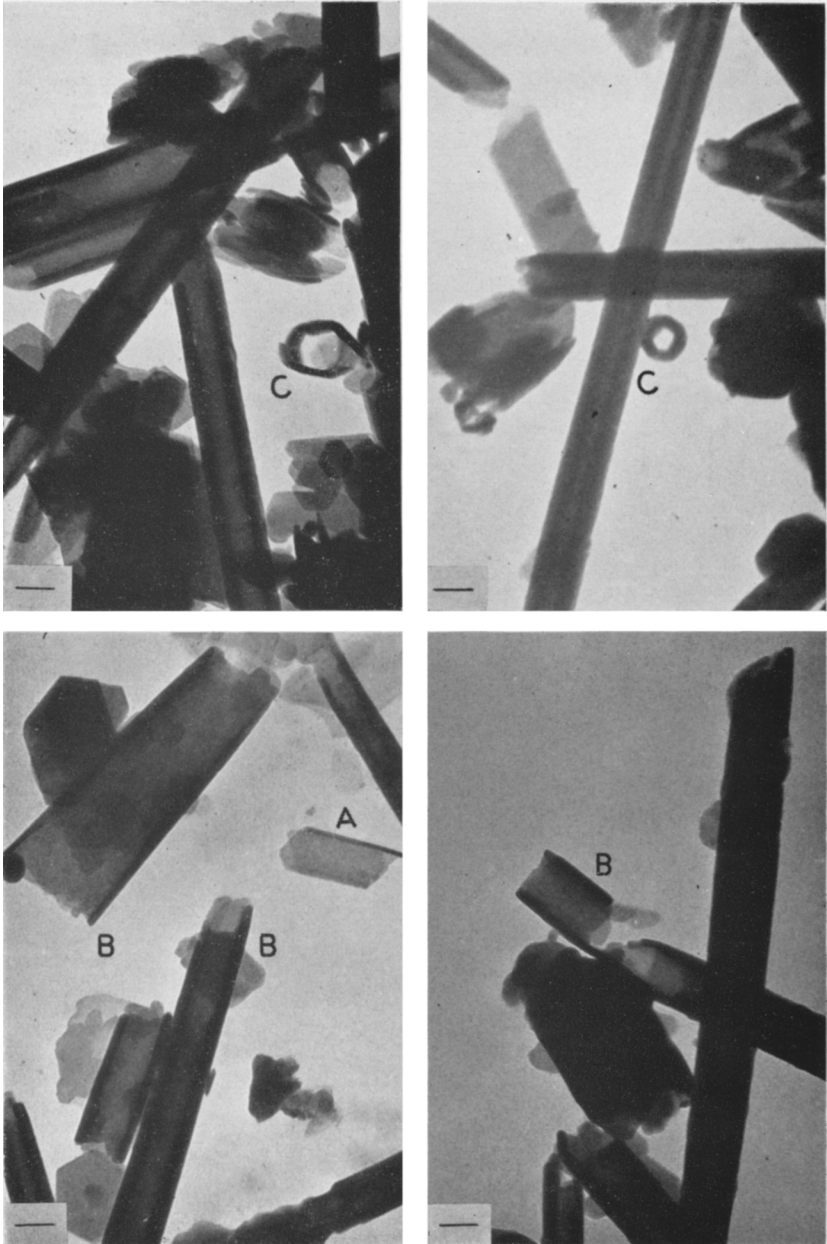


FIGURE 5.—Kaolinite-halloysite mixture, Maria Elizabeth bauxite deposit, British Guiana : A. Plate with curled edge, B. Tubes and laths with angular terminations, C. Polygonal cross-sections. Scale is 0.1μ .

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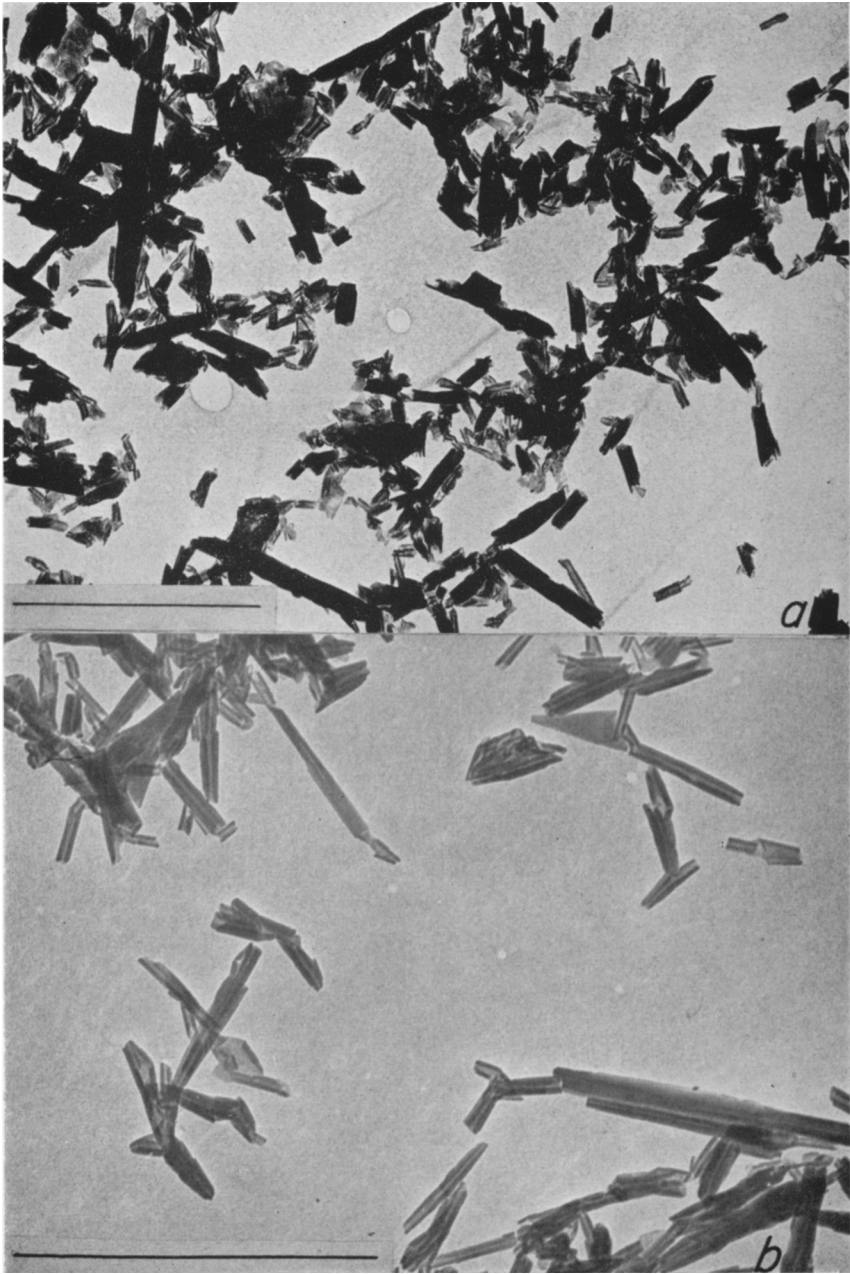


FIGURE 6.—*a*, Halloysite (4H₂O), Dragon Mine, Eureka, Utah. *b*, Halloysite (4H₂O), Wendover, Utah.

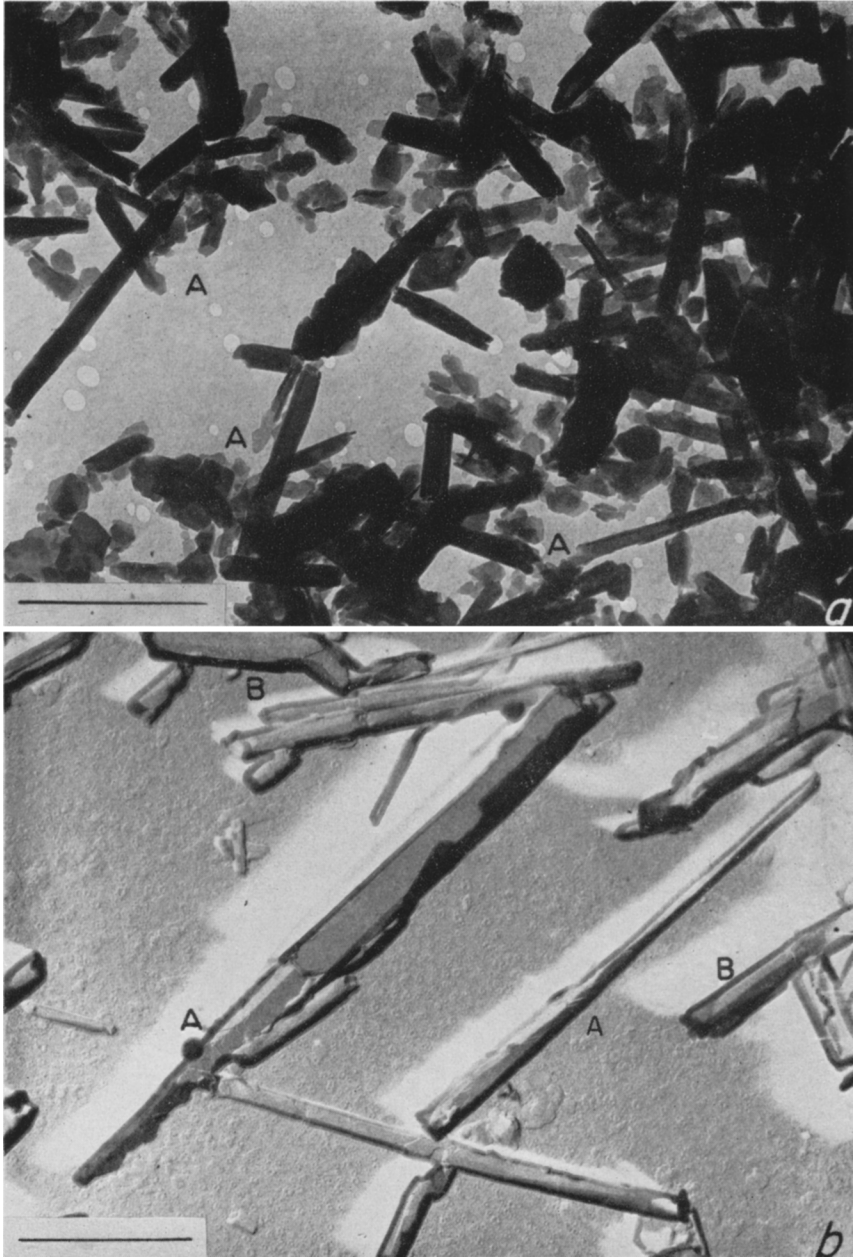


FIGURE 7.—*a*, Halloysite ($2\text{H}_2\text{O}$), Raddatz, Utah : A. Tubes and laths with “ hexagonal ” terminations. Kaolinite is also present. *b*, Halloysite ($2\text{H}_2\text{O}$), Fox deposit, Utah : A. “ Crystallographic ” striations on lath surfaces ; B. Laths with longitudinal angular displacements suggesting bending along structural lines. (Replica of material dispersed on glass slide.)

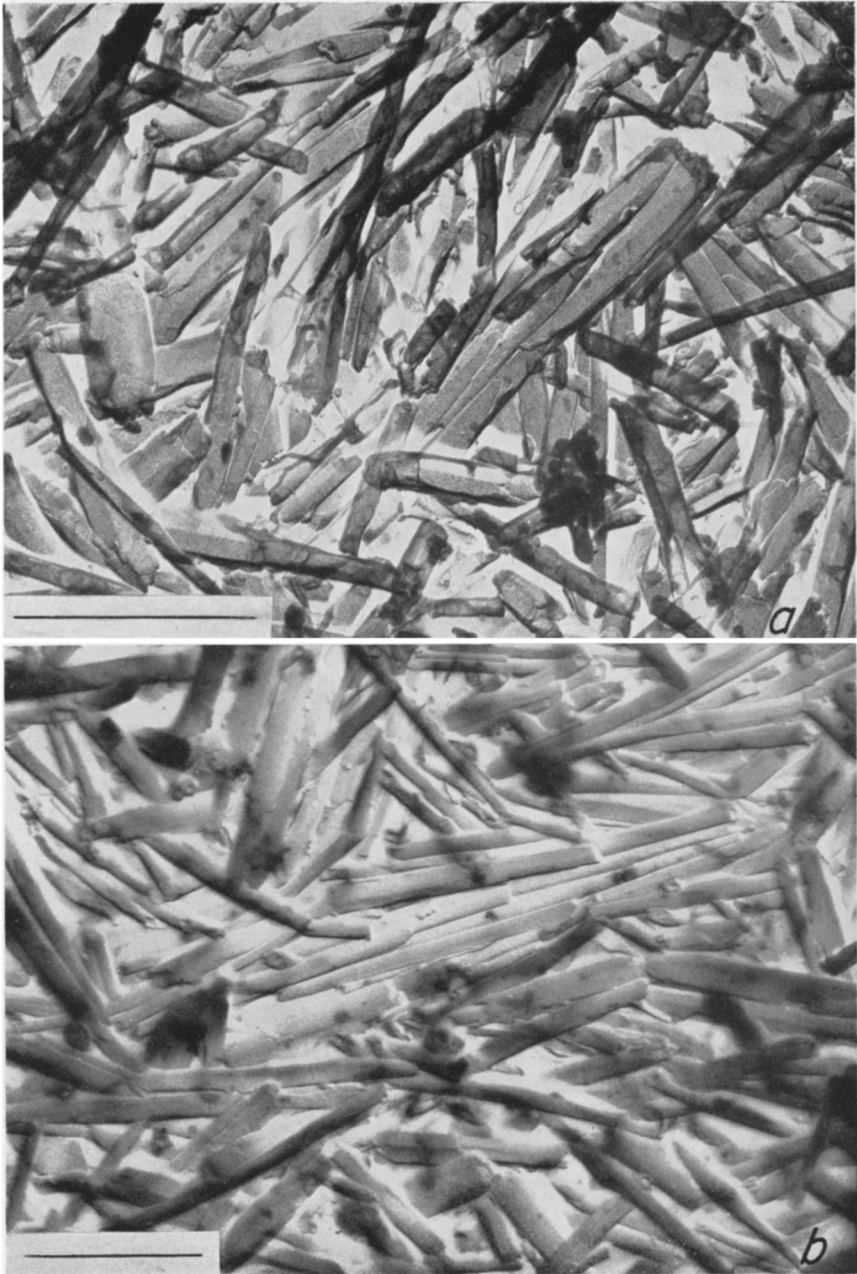


FIGURE 8.—Halloysite Fox Deposit, Utah : *a*, laths seen in replica of fracture surface. *b*, tubes and laths suggest a mixture of $2\text{H}_2\text{O}$ and $4\text{H}_2\text{O}$ material.

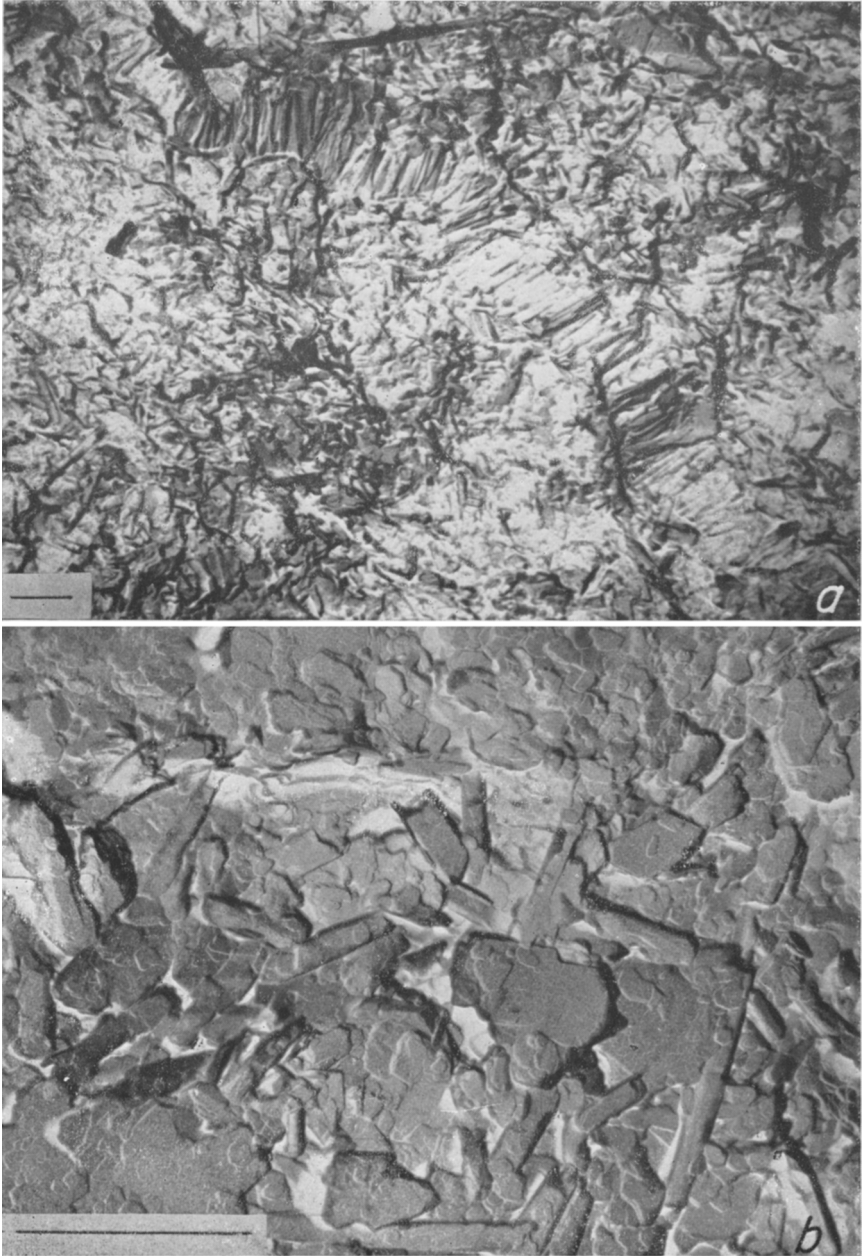


FIGURE 9.—*a*, “Veinlet” of halloysite ($2\text{H}_2\text{O}$) laths in a kaolinite–halloysite matrix, Raddatz deposit, Utah. *b*, Halloysite ($2\text{H}_2\text{O}$) laths and kaolinite plates from Raddatz deposit, Utah.

cleaved into flakes which are thin enough to roll up and form tubes as order between successive layers is destroyed. According to these authors the resulting crystals have the form and structure of halloysite.

In an effort to learn more of the frequency of occurrence of tubes and laths having "hexagonal" terminations, edge features, and polygonal cross sections, the authors restudied hundreds of electron micrographs of dispersed samples of halloysite. Most showed no evidence of "hexagonal tendencies" but characteristically showed features such as those pictured in Figs. 6a and 6b. Such tubes vary considerably in regularity and thickness, and when unrolled become irregularly shaped flakes commonly with curled edges.

In contrast, close inspection showed that a few of the pictures showed hexagonal features similar to those observed in the British Guiana material. Figure 7a shows numerous tubes ending in hexagonal shaped crystals (A), and laths commonly appear to be made up of an agglomeration of smaller hexagonal units. Halloysite ($2\text{H}_2\text{O}$) from the Fox deposit in Utah County, Utah, illustrates some of the characteristic features particularly well. In Fig. 7b the particles were dispersed on a glass microscope slide and then replicated using the platinum-carbon technique to bring out surface features. Crystallographic outlines can be seen on the upper surfaces (A) as well as along the edges of the elongate particles. It is also apparent that curvature results from pronounced angular displacements (B) which run lengthwise along the crystals and would give rise to a polygonal outline if a complete tube were seen in cross section.

Replicas of fractured surfaces of this clay are shown in Figs. 8a and 8b. The former establishes the fact that many of the crystals are laths and not tubes in the bulk clay. As in Fig. 7b, the crystals tend to fracture and bend along straight lines possibly related to crystallographic directions. On the other hand they are much more elongate and uniform in width than "typical" kaolinites, and they have a much greater tendency to curl and form tubes when dispersed. Figure 8b shows that definite tubes as well as laths occur in the untreated material.

Figures 9a and 9b show replicas of fractured clay lumps from the Raddatz deposit, Eureka, Utah. In Fig. 9a a "veinlet" of lath-shaped particles is seen at relatively low magnification in a nondescript matrix of tubes, laths, and plates. Figure 9b shows a mixture of laths and typical kaolinite plates at higher magnification.

The existence of lath-shaped crystals in the kaolinite group may represent either a distinct variety or simply a stage in a continuous morphological transition between kaolinite and halloysite ($4\text{H}_2\text{O}$). The Fox and Raddatz samples discussed gave the x-ray reflections of only the $2\text{H}_2\text{O}$ form even though care was taken to keep the material moist during and after collection. An electron diffraction study of single laths and tubes is in progress, and preliminary results indicate that the laths from the Fox deposit possess some of the features of both kaolinite plates and halloysite tubes.

As a result of these and other observations, the authors believe that it is logical to have in the kaolinite group a complete morphological series from

hexagonal plates to elongate plates to "laths with hexagonal tendencies" to curved laths to tubes to the more amorphous curls and rounded grains of allophane.

SUMMARY AND CONCLUSIONS

High magnification electron micrographs of chrysotile reveal that tubes are present in bulk samples. Replicas show that material exists between the tubes, and the pictures of dispersed fibers reveal "fuzzy" material both on the outside and inside of both natural and synthetic tubes. These observations suggest that at some point in the wall of the tube an "ideal layer" with a high degree of atomic regularity exists where the misfit of octahedral and tetrahedral sheets determines the ideal radius of curvature. It is hypothesized that from this point toward the center of the tube, the arrangement of atoms becomes less regular finally giving way to amorphous material inside the tube. Proceeding outward from the "ideal layer" the radius of curvature increases resulting in either (1) a less perfect fit of the octahedral and tetrahedral sheets in each successive concentric layer, or (2) the breaking of each subsequent layer into a series of scallops, each having the ideal radius of curvature but fitting imperfectly on the layer beneath. In either case the regularity of atomic arrangement decreases as compared to that exemplified by the ideal layer until the material in the outer part of the wall differs little from the fuzzy, "amorphous-looking" material that fills the inter-tube spaces. The fact that the material breaks around rather than across the tubes, plus the fact that dispersions reveal tubes of definite wall thickness, suggests that the change in regularity of atomic arrangement is discontinuous rather than continuous.

The presence of poorly crystallized material within and between the tubes explains why the measured density of bulk chrysotile and halloysite samples is not the same as that calculated for a hypothetical specimen consisting of regular, close-packed hollow tubes. In this connection the replicas also show that the tubes are not regular but vary considerably in size, shape and degree of perfection, particularly in halloysite. "Outer shells" seen on some of the tubes probably provide many of the laths, and even some platy fragments, observed in micrographs of dispersed material.

Lath-shaped crystals observed in replicas of clay specimens from several localities are believed to represent an intermediate morphological state between plates of kaolinite and tubes of $4\text{H}_2\text{O}$ halloysite. The x-ray diffraction data are those of halloysite ($2\text{H}_2\text{O}$) but more accurate structural information is expected from single crystal electron diffraction studies. The laths commonly are characterized by hexagonal terminations and angular projections along the edges, and by a tendency to bend along straight lines roughly parallel to the long dimension of the lath.

In the two morphological series, (1) between the "flattest" plates and thinnest tubes of serpentine and (2) from kaolinite "hexagons" to $4\text{H}_2\text{O}$ halloysite tubes to allophane spheres, it is to be expected that various structure states will exist.

REFERENCES

- Bates, T. F. (1951) Morphology of layer lattice silicates : *J. Sci. Labs. Denison Univ.*, v. 42, pp. 83–92.
- Bates, T. F. (1955) Electron microscopy as a method of identifying clays : in *Clays and Clay Technology*, Calif. Div. Mines Bull. 169, pp. 130–150.
- Bates, T. F. and Comer, J. J. (1955), Electron microscopy of clay surfaces : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council pub. 395, pp. 1–25.
- Bates, T. F., Hildebrand, F. A. and Swineford, Ada, 1950, Morphology and structure of endellite and halloysite : *Amer. Min.*, v. 35, pp. 463–484.
- Bates, T. F., Sand, L. B. and Mink, J. F. (1950) Tubular crystals of chrysotile asbestos : *Science*, v. 111, pp. 512–513.
- Behne, W. and Müller, W. (1954) Elektronenmikroskopische Untersuchungen über die Morphologie von Halloysite : *Naturwiss.*, v. 41, p. 138.
- Brindley, G. W. and Comer, J. J., 1956, The structure and morphology of a kaolin clay from Les Eyzies, France : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council pub. 456, pp. 61–66.
- Comer, J. J. and Turley, J. W. (1955) Replica studies of bulk clays : *J. Appl. Phys.*, v. 26, pp. 346–350.
- DeKeyser, W. L. and Deguedre, L. (1954) Relations between the morphology and structure of kaolins and halloysites : *Bull. Soc. Belge. Geol., Paleontol. et Hydrol.*, v. 63, pp. 100–110.
- Fleischer, M. (1957) New mineral names : lizardite, ortho-chrysotile, clino-chrysotile, para-chrysotile : *Amer. Min.*, v. 42, p. 585.
- Gillery, F. H. (1958) x-Ray study of synthetic Mg–Al serpentines and chlorites : in press.
- Healey, F. H. and Young, G. J. (1954) The surface properties of chrysotile asbestos : *J. Phys. Chem.*, v. 58, pp. 885–886.
- Honjo, G., Kitamura, N. and Mihama, K. (1954) A study by means of single crystal electron diffraction diagrams—the structure of tubular kaolin : *Clay Minerals Bull.*, v. 2, pp. 133–140.
- Honjo, G. and Mihama, K. (1954) A study of clay minerals by electron diffraction diagrams due to individual crystallites : *Acta Cryst.*, v. 7, pp. 511–513.
- Jagodzinski, H. and Kunze, G. (1954) Die Rollchenstruktur des Chrysotils : *Neues Jahrb. Min., Mh.* 1954, pp. 95–108, pp. 113–130, pp. 137–150.
- Kalousek, G. L. and Muttart, L. E. (1957) Studies on the chrysotile and antigorite components of serpentine : *Amer. Min.*, v. 42, pp. 1–22.
- Nagy, B. (1953) The textural pattern of the serpentines : *Econ. Geol.*, v. 48, pp. 591–597.
- Nagy, B. and Faust, G. T. (1956) Serpentine : natural mixtures of chrysotile and antigorite : *Amer. Min.*, v. 41, pp. 817–837.
- Noll, W. and Kircher, H. (1950) Zur Morphologie des Chrysotilasbestes : *Naturwiss.*, v. 37, pp. 540–541.
- Noll, W. and Kircher, H. (1951) Über die Morphologie von Asbesten und ihren Zusammenhang mit der Kristallstruktur : *Neues Jahrb. Min., Mh.* 10, pp. 219–240.
- Noll, W. and Kircher, H. (1952) Veränderungen von Chrysotilasbest im Elektronenmikroskop : *Naturwiss.*, v. 39, p. 188.
- Oberlin, A. M. (1957) Altération des cristaux de kaolinite ; détermination par microdiffraction électronique, de la structure des produits altérés : *C.R. Acad. Sci., Paris*, v. 244, pp. 1658–1661.
- Oberlin, A. M. and Tchoubar, C. (1957) Étude en microscopie électronique de l'altération des cristaux de kaolinite : *C.R. Acad. Sci., Paris*, v. 244, pp. 1624–1626.
- O'Daniel, H. and Kedesdy, H. (1947) Über eine micellare Silikatstruktur : *Naturwiss.*, v. 34, p. 55.
- Pundsack, F. L. (1956) The properties of asbestos. II. The density and structure of chrysotile : *J. Phys. Chem.*, v. 60, pp. 361–364.
- Pundsack, F. L. (1958) The density and structure of endellite : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 566, pp. 129–135.

248 SIXTH NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS

- Sudo, T. and Takahashi, H. (1956) Shapes of halloysite particles in Japanese clays : in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council, pub. 456, pp. 67–79.
- Turkevich, J. and Hillier, J. (1949) Electron microscopy of colloidal systems : *Analyt. Chem.*, v. 21, pp. 475–485.
- Visconti, Y. S., Nicot, B. N. F. and Goulart de Andrade, E. (1956) Tubular morphology of some Brazilian kaolins : *Amer. Min.*, v. 41, p. 67–76.
- Whittaker, E. J. W. (1953) The structure of chrysotile : *Acta Cryst.* 6, pp. 747–748.
- Whittaker, E. J. W. (1954) the diffraction of x-rays by a cylindrical lattice. I : *Acta Cryst.*, v. 7, pp. 827–832.
- Whittaker, E. J. W. (1955) The diffraction of x-rays by a cylindrical lattice. II : *Acta Cryst.*, v. 8, pp. 261–265 ; III : *Acta Cryst.*, v. 8, pp. 265–271.
- Whittaker, E. J. W. and Zussman, J. (1956) The characterization of serpentine minerals by x-ray diffraction : *Min. Mag.*, v. 31, pp. 107–127.
- Young, G. J. and Healey, F. H. (1954) The physical structure of asbestos : *J. Phys. Chem.*, v. 58, pp. 881–884.
- Zussman, J., Brindley, G. W. and Comer, J. J. (1957) Electron diffraction studies of serpentine minerals : *Amer. Min.*, v. 42, pp. 133–153.