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## MORPHOLOGY AND STRUCTURE OF ENDELLITE AND HALLOYSITE

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### ABSTRACT

An electron microscope study of the minerals of the kaolinite group has revealed that halloysite (metahalloysite) crystals consist of hollow tubes which have commonly collapsed, or have split and partially or completely unrolled. There is no apparent morphological transition from these crystals to the pseudohexagonal plates characteristic of kaolinite, dickite, and nacrite. The mineral endellite (halloysite) is believed to consist of well-developed tubes which split upon dehydration to halloysite (metahalloysite). It is suggested that this change in morphology explains the irreversibility of the dehydration process.

Halloysite (metahalloysite) specimens from different localities show notable morphological differences due to original variation in tube size and the degree of subsequent split-

ting and unrolling. This may be a partial explanation of the discrepancies in optical data on this mineral which exist in the literature.

X-ray, optical, and crystal growth data indicate the relation of the tubular morphology to the sheet structure of the minerals.

The tubular form of endellite (halloysite) is explained by (1) the "misfit" of the silicon-oxygen and aluminum-hydroxyl layers in the 1:1 structural unit, (2) the larger intervening distance between the 1:1 units in endellite (halloysite) as compared with kaolinite, and (3) the presence of water between the units in endellite (halloysite). According to this picture the morphological change which occurs when halloysite (metahalloysite) is formed is a logical result of the removal of interlayer water. Values obtained from the electron micrographs for the inner diameters of the tubes are of the same order of magnitude as those obtained by calculations based on the proposed structure.

The structural interpretation of the morphology indicates that in a given tube the randomness of orientation (in the *a* and *b* crystallographic directions) of successive cylindrical sheets is partial rather than complete.

### INTRODUCTION

The application of the electron microscope to the study of the clay minerals has posed a number of interesting problems. In the kaolinite

TABLE 1. PARTICLE SIZE AND HABIT OF THE KAOLIN MINERALS

Minerals of the Kaolin Group			
Mineral	Formula	Habit	Particle Size in Microns
NACRITE	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$	pseudo-hexagonal plates	1000-5000
DICKITE	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$	pseudo-hexagonal plates	1.0-500
KAOLINITE	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$	pseudo-hexagonal plates	0.25-3000
ENDELLITE (HALLOYSITE)	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$	tubes	0.01-15
HALLOYSITE (METAHALLOYSITE)	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$	split tubes	0.01-15
ALLOPHANE	$(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10} \cdot n\text{H}_2\text{O}$	irregular particles	<1

group one of the most perplexing of these is the structural explanation of the morphological relationship between kaolinite and halloysite (metahalloysite).\* The so-called laths of halloysite (metahalloysite) contrast markedly with the well-known pseudo-hexagonal plates of kaolinite despite the chemical similarity of the two minerals (see Table 1).

\* The writers feel that the nomenclature of the kaolinite group is still problematical and that final solution of the problem should rest with an international committee. To avoid confusion both terms will be used for each of the minerals involved. The American usage is given preference because this article has been published in an American Journal.

The present paper deals with the morphology of kaolinite, halloysite (metahalloysite), and endellite (halloysite) and proposes a structural relationship to explain the physical and chemical properties and behavior of these minerals. The data were obtained by electron microscope and *x*-ray diffraction studies of 83 specimens from 66 localities.

A report of these investigations was presented at the meetings of the Mineralogical Society of America in November 1948 (Bates, Hildebrand, Swineford, 1949). Most data and theory in the following pages were given at that time.

#### PREVIOUS MORPHOLOGICAL STUDIES

Berthier described and named halloysite (metahalloysite) in 1826, and from that time until 1934 the mineral was regarded as an amorphous substance with no characteristic shape. An early worker (Mellor, 1908) described it in detail as irregularly shaped, amorphous granules, with irregular surfaces and a sponge-like structure. Rogers (1917) as a result of optical studies, listed halloysite (metahalloysite) in his review of the amorphous minerals. *X*-ray studies by Hofmann, Endell, and Wilm in 1934 indicated the crystalline nature of halloysite (metahalloysite). In the same year Ross and Kerr (1934, p. 142) concluded from *x*-ray data that halloysite (metahalloysite) "occupies a state of crystallinity intermediate between the microcrystalline particles of kaolinite and the finely divided, almost completely dispersed allophane." A study of dityn-dallism of various clay minerals by Marshall (1941) led him to the conclusion that halloysite (metahalloysite) forms platy particles with only slight elongation.

Early study of halloysite (metahalloysite) with the electron microscope (Dittler, 1941) revised the earlier concepts of its morphology. Shaw and Humbert (1941) observed from electron micrographs that the mineral typically occurs as split rods, each rod seemingly composed of twin sections. They concluded: "The marked differences in structure of kaolinite and halloysite are far greater than has been suspected on the basis of other evidence. . . . The split character of halloysite rods is of extreme interest. It is evident that crystal structures that have been proposed for halloysite do not explain its observed features."

In 1942 Kelley and Shaw determined the dimensions of halloysite (metahalloysite) particles from Maiden, Catawba County, N. C., by a combination of electron micrograph studies (for length and breadth) and hydrodynamic theory (for thickness). In calculating the third dimension they assumed that the halloysite (metahalloysite) particles are rod-shaped ellipsoids. They differentiated the two smaller axes on the basis of density in the electron micrograph and concluded that in some

particles the breadth,  $b$ , is much greater than the thickness,  $c$ , whereas in others the  $b$  and  $c$  dimensions are about equal. By calculations from the  $a$  and  $b$  dimensions of halloysite (metahalloysite) particles in the 0.56 to 0.22 micron fraction, they found the ratio of  $c:b$  to be between 1:5 and 1:1. On the other hand, the mean axial ratio for the 2 to 1 micron fraction of kaolinite was found to be 1:6.7.

In the same year Kelley and Page (1942, p. 176) described halloysite (metahalloysite) as "needle-like crystals." They concluded, as had Shaw and Humbert, that the electron microscope has "revealed peculiarities in the form of halloysite . . . , which do not seem to be explained by our present picture of [its] crystal structure and so may lead to a revision, or, at least, to a reconsideration of the validity of the structures that are accepted at the present time."

Eitel (1943, p. 43) wrote that halloysite (metahalloysite) crystals are not flaky, but show in electron micrographs a pronounced lath-shaped habit resembling that of the serpentine minerals. A later paper (Eitel and Radczewski, 1943) discussed the possibility of a chain structure of the type  $(\text{Si}_4\text{O}_{10-10.5})_n$  as an explanation for the lath-like appearance of the particles.

Alexander, et al. (1943), observed in electron micrographs of halloysite (metahalloysite) from Lawrence County, Indiana, "geometrical arrangements of laths, serrations on the lath edges, and indentations of lath ends not hitherto noted." They called attention to lath intersections and terminations showing  $60^\circ$  angles and suggested that the halloysite (metahalloysite) fragments are "relic laths" of a larger plate-like unit. In electron microscope studies of morphology of these and other workers (Callaghan, 1948, pp. 20, 32) it has been assumed or stated that the morphology of the particles does not change upon dehydration in the electron microscope. In this connection Alexander, et al., also pointed out that halloysite (metahalloysite) has essentially the same morphological characteristics as endellite (halloysite), and this was considered to be one line of evidence indicating that halloysite (metahalloysite) forms from endellite (halloysite). The dark edges and notched ends of the particles were tentatively attributed by them to "longitudinal division."

## MORPHOLOGY

### *Kaolinite*

Characteristic kaolinite crystals are euhedral pseudo-hexagonal flakes such as those illustrated in Fig. 1. The range in particle size (long diameter of the hexagonal plate) is given in Table 1. Since the morphological relationship of kaolinite and halloysite (metahalloysite) is of primary

concern, particular emphasis in the following discussion is placed upon the departure of kaolinite particles from the ideal pseudo-hexagonal form. The most outstanding deviations observed in the present study are as follows:

- (1) Euhedral crystals with prominent elongation in one direction (Fig. 2A);
- (2) groups of overlapping oriented plates (Fig. 2B);

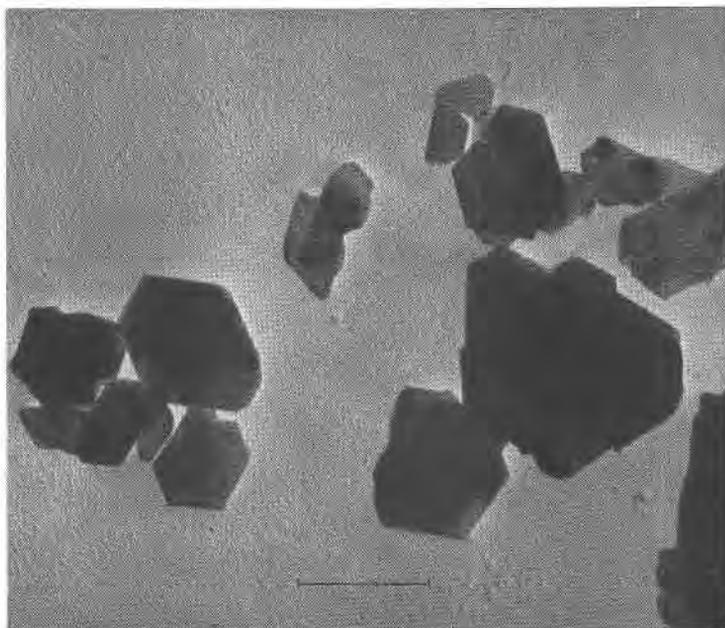


FIG. 1. Kaolinite from Banda, India, showing pseudo-hexagonal flakes.  
(The scale on all micrographs represents one micron.)

- (3) subhedral to anhedral particles of small to medium size;
- (4) pseudo-hexagonal plates with ragged edges and perforations suggestive of solution.

Two other facts may be noted about the morphology of kaolinite which have an important bearing on the relation of this mineral to endellite (halloysite) and halloysite (metahalloysite).

- (1) There is no tendency for euhedral kaolinite particles to curl or roll up even though they may be appreciably elongated in one direction;
- (2) there is no apparent morphological transition between kaolinite and halloysite (metahalloysite) crystals.

#### *Halloysite (metahalloysite) and endellite (halloysite)*

The present study shows that halloysite (metahalloysite) exists in the form of hollow tubes many of which are split longitudinally or have

collapsed to form laths or ribbons. Structural considerations lead to the hypothesis that endellite (halloysite) crystals take the form of well-developed tubes and that strain produced by dehydration to halloysite (metahalloysite) causes the tubes to collapse, split, and commonly unroll. The large variation in morphology of different specimens of halloy-

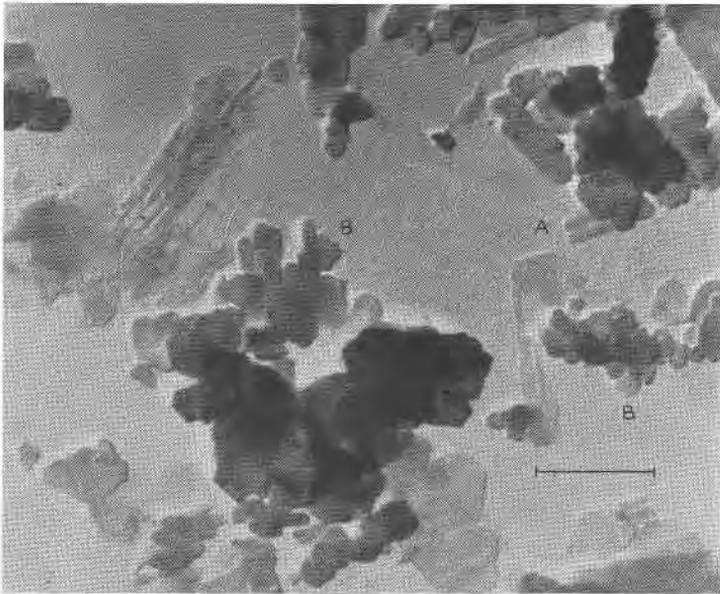


FIG. 2. Kaolinite from Zettlitz, Austria, showing (A) elongated, euhedral crystals, and (B) overlapping, oriented plates.

site (metahalloysite) results from initial differences in particle size and from the degree of splitting and unrolling produced by dehydration.

Tubes which on dehydration have apparently been modified only slightly or not at all are shown in halloysite (metahalloysite) from Leaky, Real County (formerly Edwards County), Texas, Fig. 3. Tubes at positions marked (A) show an oblique view of an end section. Double tubes, which are not uncommon, are seen at two positions marked (B). In such particles there is commonly an "empty" space between the inner and outer tubes, and if the particles are sufficiently translucent, the inner tube can be seen running the length of the outer one and in some cases projecting at both ends.

Splitting and unrolling may result in departure from the tubular shape. In Fig. 3 at (C) is a tube which has split and partly unrolled at one end. Such unrolling may produce a spatula-like form (Fig. 4A).



FIG. 3. Halloysite (metahalloysite) from Real County, Texas. (A) Oblique view of end section; (B) double tubes (tube in tube); (C) split and partially unrolled tube.

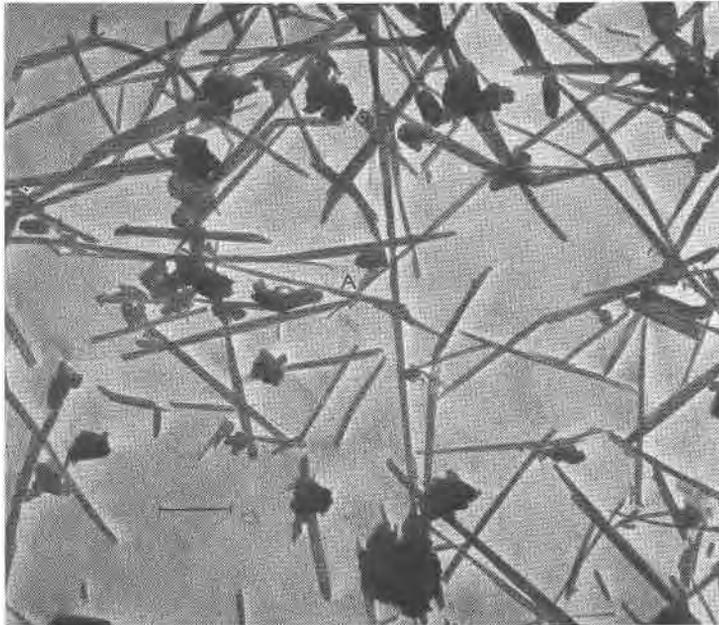


FIG. 4. Halloysite (metahalloysite) from Webster, Jackson County, North Carolina, showing long hollow tubes, some of which have collapsed. (A) Spatula produced by splitting and unrolling.

The width of the spatula "blade" in relation to the circumference of the "handle" affords a measure of the degree of unrolling. The diameter of the tube is  $440 \text{ \AA}$  and therefore its circumference or the width of the resulting spatula blade should be  $1382 \text{ \AA}$ . The measured width of the

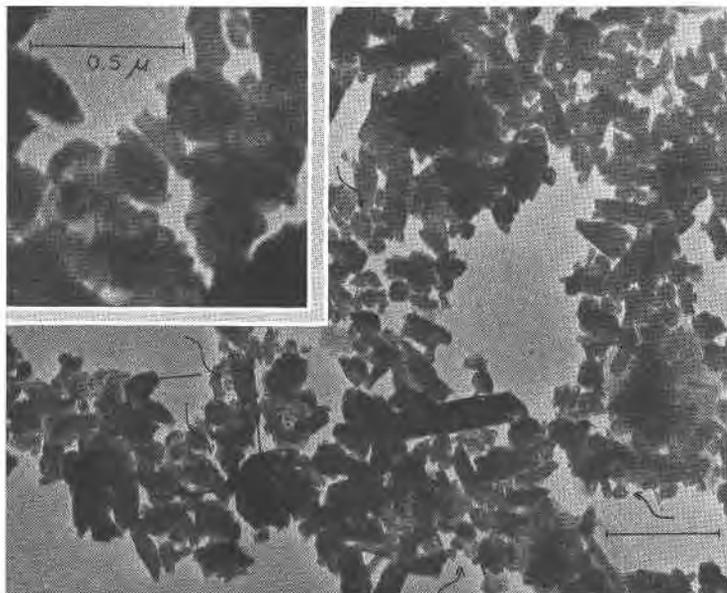


FIG. 5. Halloysite (metahalloysite) from Beuthen, Silesia.  
Arrows indicate some of the tubular cross-sections.

blade is  $1000 \text{ \AA}$ . The discrepancy indicates that complete unrolling has not been achieved.

Figure 5 of halloysite (metahalloysite) from Beuthen, Silesia, shows many tubes in cross section. The latter are observed most frequently in halloysite consisting of short, poorly developed crystals since these have a better chance of standing "on end" when they settle on the collodion film than do the more elongated tubes.

A number of other features in the micrographs are of interest. In some samples the surfaces of the tubes show semicircular concavities or indentations (Fig. 6). Since many of these indentations are of similar radius of curvature to that of other tubes, it is believed that each concavity represents the place where an intergrown tube, crossing at an angle, has been broken out. If such is the case the shape of the indentation is further evidence that the particles are cylindrical. A few of the larger tubes have a cottony appearance possibly resulting from shredding at the surface.

Although splitting and unrolling may result in the formation of well-defined rectangular laths, no example has been found of a hexagonal-shaped flake which was the consequence of such a process. Furthermore, the tubes do not show terminations of a uniform character. The ends are jagged and commonly frayed as if the tubes had been broken. Even in



FIG. 6. Halloysite (metahalloysite) from Chatham County, North Carolina. Arrows point to semicircular concavities in some tube surfaces suggesting former presence of inter-grown tubes.

those particles in which the ends are smooth and possibly not the result of fracturing, the angle of termination of the tube with its axis is not constant.

Table 2 presents data on diameter and wall thickness of 26 tubes selected from 7 micrographs and of necessity chosen for their clarity and ease of measurement. The outside diameters of the tubes measured range from 400 to 1900 Å, with a median value of 700 Å. The diameters of the holes range from 200 to 1000 Å and average 400 Å. The thickness of the walls has a narrower range of 100 to 700 Å and averages 200 Å.

Measurement of the widths of 1120 halloysite (metahalloysite) particles in 26 electron micrographs, regardless of the degree of collapse or unrolling, shows a range of from 100 to 6700 Å, and a median width of 860 Å. The frequency distribution tends to be log normal.

The morphological variations in halloysite (metahalloysite) resulting from initial differences in particle size and degree of splitting and unrolling are shown in Figs. 4, 7, and 8. Figure 4 of halloysite (metahalloysite) from Webster, North Carolina, illustrates long, thin, well-defined

TABLE 2. MEASUREMENTS OF OUTSIDE DIAMETER, INSIDE DIAMETER, AND WALL THICKNESS OF 26 HALLOYSITE (METAHALLOYSITE) TUBES

Locality	Outside Diam. (Angstroms)	Inside Diam. (Angstroms)	Wall Thickness	
			(Angstroms)	No. of 1:1* Units
Beuthen, Silesia	1000	600	200	28
Beuthen, Silesia	1600	600	500	69
Beuthen, Silesia	600	200	200	28
Beuthen, Silesia	600	200	200	28
Beuthen, Silesia	1700	700	500	69
Beuthen, Silesia	1700	300	700	99
Beuthen, Silesia	600	400	100	14
Beuthen, Silesia	1900	500	700	99
Beuthen, Silesia	400	200	100	14
Beuthen, Silesia	500	300	100	14
Beuthen, Silesia	600	400	100	14
Beuthen, Silesia	600	400	100	14
Beuthen, Silesia	500	300	100	14
Beuthen, Silesia	1400	600	400	56
Beuthen, Silesia	700	300	200	28
Beuthen, Silesia	600	300	200	28
Beuthen, Silesia	800	400	200	28
Beuthen, Silesia	800	400	200	28
Beuthen, Silesia	1700	300	700	99
Beuthen, Silesia	400	200	100	14
Real County, Texas	800	400	200	28
Real County, Texas	1200	1000	100	14
Hickory, North Carolina	700	500	100	14
Ely, Nevada	400	200	100	14
Nelson County, Virginia	900	600	200	28
Maiden, North Carolina	400	200	100	14

\* Based on (001) spacing of kaolinite.

tubes, whereas halloysite (metahalloysite) from Lookout, Alabama, Fig. 8, consists of irregularly shaped flaky particles many of which appear to be the result of the splitting and unrolling of short tubes. Most halloysites have crystals which, from the standpoint of morphology, fall between these two extremes.

Because of the ease with which endellite (halloysite) changes to hal-

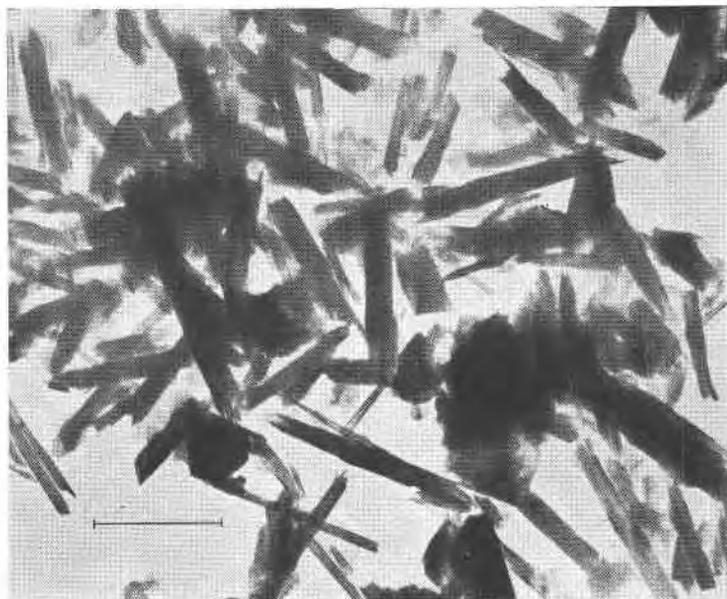


FIG. 7. Halloysite (metahalloysite) from Real County, Texas.

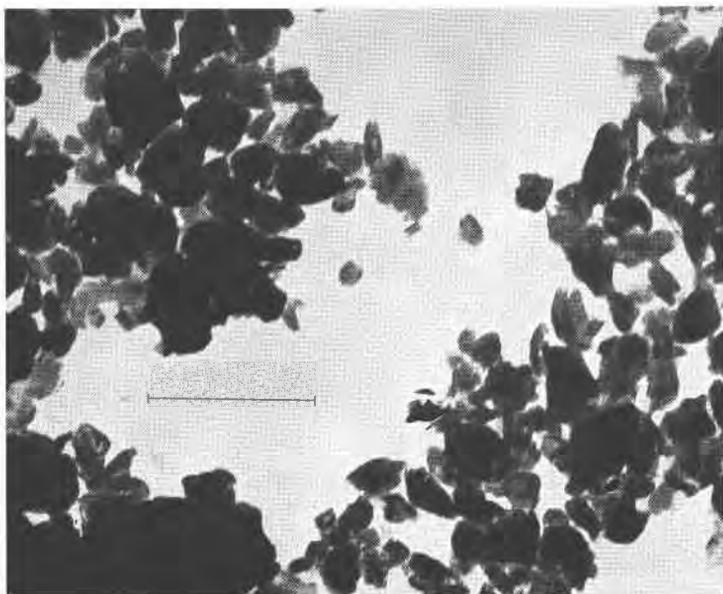


FIG. 8. Irregularly shaped flaky particles of halloysite (metahalloysite) from Lookout, Alabama, formed by splitting and unrolling of short tubes.

loysite (metahalloysite) it has been assumed by previous workers (Alexander, et al., 1943; Callaghan, 1948) that the heat of the electron beam and the vacuum of the electron microscope effect immediate dehydration of endellite (halloysite) when the mineral is placed in the instrument for observation, and further that, in spite of the loss of water, the morphology of the particles does not change. The present writers agree that dehydration probably occurs, but, as a result of structural relationships to be discussed later in this paper, do not concur in the belief that the morphology of the particles remains unchanged. It is hoped that in subsequent electron microscope work using replica techniques the morphology of endellite (halloysite) may be observed and studied.

#### CORRELATION OF EXPERIMENTAL DATA WITH MORPHOLOGY

X-ray, optical, and crystal growth data suggest the following relationships between the tubular form of the crystals and the sheet structure which has been assigned to endellite (halloysite) and halloysite (metahalloysite) (Mehmel, 1935; Hendricks, 1938; Edelman and Favejee, 1940). These relationships are represented diagrammatically in Fig. 9.

1. The wall of the tube consists of curved sheets which in the micas and kaolinite are planar.
2. The  $c$  axis for any section of the tube is nearly perpendicular to a plane tangent to the tube at that point.

#### *X-Ray*

The differences in the x-ray patterns of kaolinite, halloysite (metahalloysite), and endellite (halloysite) have been studied recently by Brindley and Robinson (1948). Diffraction peaks from the (001) planes are symmetrical but more diffuse in halloysite (metahalloysite) than in kaolinite. Other peaks in halloysite (metahalloysite) take the form of asymmetric bands formed by diffraction from two-dimensional gratings as a result of random structure in the  $a$  and  $b$  directions.

The diffuse character of the (00 $l$ ) diffractions may be explained by the curvature of the (001) planes, as brought out in exaggerated form in Fig. 9. The ratio of height to breadth of the (001) peak at 7.5 to 7.1Å from x-ray spectrometer patterns of dickite, kaolinite, and halloysite (metahalloysite) is shown in Table 3. Variation in particle size affects this ratio and is probably responsible for part of the difference between kaolinite and dickite. However, electron micrographs of kaolinite and halloysite (metahalloysite) indicate that here the particle size difference is too small to account for the entire variation in peak height to breadth ratios. The (001) diffractions from badly split and unrolled halloysites (metahalloysites) are similar to those from nearly tubular particles,

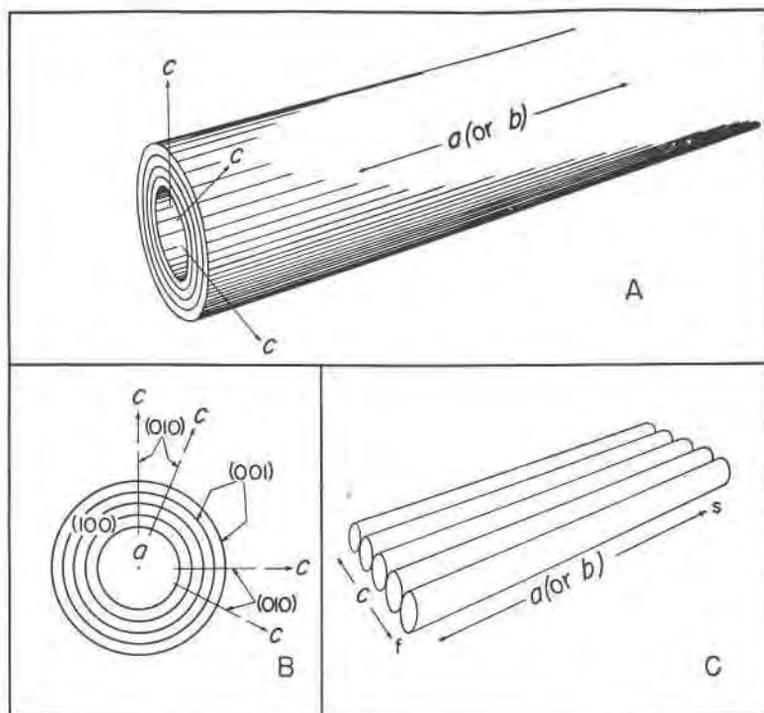


FIG. 9. Proposed relation of morphology to structure in endellite (halloysite).

A. Tube in perspective.

B. Cross section showing crystallographic axes and major planes.  $c = n\alpha$ ,  $a = n\beta$ ,  $b = n\gamma$  (assuming optical similarity to kaolinite).

C. Character of optical elongation in oriented aggregate.  $f$  = fast vibration direction,  $s$  = slow vibration direction.

TABLE 3. RATIOS OF HEIGHT TO BREADTH OF THE (001) PEAK IN X-RAY SPECTROMETER PATTERNS OF DICKITE, KAOLINITE AND HALLOYSITE (METAHALLOYSITE)

Mineral	Number of Specimens	Height — (001) peak Breadth		
		Maximum	Minimum	Average
Dickite	6	35.6	20.0	27.6
Kaolinite	13	32.4	9.0	17.9
Halloysite (Metahalloysite)	34	13.0	0.8	5.1

suggesting that some curvature of the sheet remains even though the tube has split or collapsed.

It is doubtful if the arrangement of sheets in concentric cylinders would, of itself, produce the asymmetric bands found in  $x$ -ray patterns of halloysite (metahalloysite) and endellite (halloysite) for all reflections except those from (001). Without additional randomness of structure, reflections from planes (100) perpendicular to the tube axis (see Figure 9B) would be sharp and symmetrical while those from (010) would probably be diffuse but would show no asymmetry.

#### *Petrographic Microscope*

Grim (1942, p. 248) wrote that "careful optical work with halloysite shows certain peculiarities difficult to explain on the basis of suggested structures." In the present study, petrographic microscope work on oriented aggregates indicates that the tubes have positive elongation, and the measured birefringence is  $0.002 \pm .001$ . If it is assumed that the indices of halloysite (metahalloysite) bear the same relationship to each other and to the structure as do those of kaolinite, this elongation and a similar birefringence are to be expected from a sheet structure developed in tubular form. The probable relationships are shown in Fig. 9C and are discussed in more detail later in this report.

#### *Crystal Growth*

It is well established that growth in the micas and in kaolinite, nacrite, and dickite takes place most rapidly at the edges of the sheets, extending them outward. Since the tubes of endellite (halloysite) apparently grow most rapidly in length, it is logical that the ends of the tubes represent the edges of the sheets.

### STRUCTURE

#### *Present Concept and Proposed Structure of Endellite (Halloysite)*

Figure 10 gives a diagrammatic picture of the structure of endellite (halloysite) proposed by Hendricks (1938). As in the other kaolin minerals there is a 1:1 structure in which a modified gibbsite sheet is bonded to a silicon-oxygen sheet. The height of the resulting unit in the  $c$  direction is 4.51 Å in each of the minerals. In the mineral gibbsite the six hydroxyl ions on one side of the unit cell occupy a distance of 8.62 Å, while in the silicon-oxygen sheet in kaolinite the corresponding six oxygen ions occupy a distance of 8.93 Å. Thus, as Pauling (1930) pointed out, the two sheets which make up the structure are not a perfect fit. A hypothetical single 1:1 unit of kaolinite, free of neighboring ions, might have a  $b_0$  dimension of 8.93 Å compatible with the spacing of the oxygen

ions on one side and a similar dimension of  $8.62 \text{ \AA}$  typical of the hydroxyl ions on the other. In actual fact, however, since adjoining units are less than  $3 \text{ \AA}$  away the six oxygen ions of one unit apparently "stretch" the opposing hydroxyl ions to fit the cell dimension of  $8.93 \text{ \AA}$ .

It is here proposed that in endellite (halloysite) (Fig. 11B) as a result

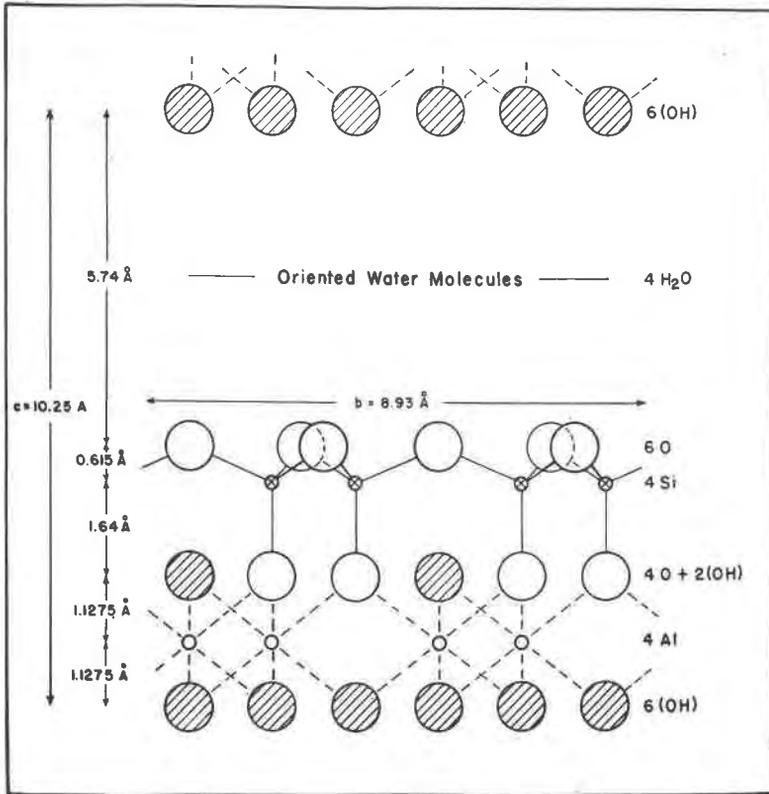


FIG. 10. Structure of endellite (halloysite) according to Hendricks.

of the greater distance of  $5.74 \text{ \AA}$  and the presence of water molecules between the 1:1 units, the hydroxyl ions are only slightly, if at all, subject to "stretching" forces from opposing oxygen layers of neighboring units. The six hydroxyl ions are, therefore, free to approach their normal spacing of  $8.62 \text{ \AA}$  while the six oxygen ions on the opposite side of the same unit occupy a distance of  $8.93 \text{ \AA}$ . If it is assumed that the "vertical" bonds within the unit remain of equal length relative to each other, a curvature must result such as that shown in exaggerated form in Fig. 11C. A simple calculation shows that the inner diameter of the resulting

cylinder would be 250.8 Å. This is of the same order of magnitude as the inner diameter of the smallest tubes as shown in Table 2.

These structural relationships are to be expected in a tube with a wall of unit cell thickness.\* If the diameter is smaller or larger the lattice

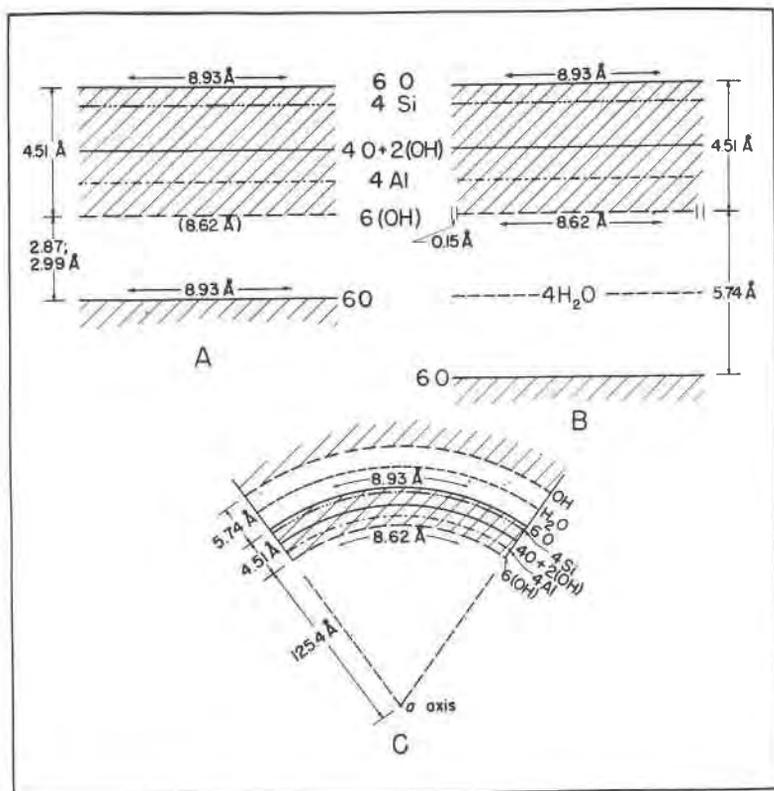


FIG. 11. Diagrammatic representation of the structure of kaolinite and endellite (halloysite).

- Arrangement of layers in kaolinite.
- Arrangement of layers in endellite (halloysite) according to Hendricks.
- Proposed arrangement of endellite (halloysite) layers.

would be strained as a result of the departure from the ideal relationship of oxygen to hydroxyl spacings. If the inner diameter is smaller, the six hydroxyl ions would have to be compressed to occupy a distance less than 8.62 Å relative to the 8.93 Å spacing of the oxygen ions. Because of this limiting condition, a hollow structure would be expected. On the

\* On the basis of the unit cell of kaolinite established by Brindley and Robinson (1946).

other hand, for tubes with a larger radius of curvature, the hydroxyl ions must occupy a distance greater than 8.62 Å. The resulting strain makes the addition of subsequent layers more difficult. The fuzzy appearance of the edges of some of the largest tubes possibly indicates that the limiting radius of curvature has been reached and that additional units tend to shred off because they are under too great a tensional strain.

The foregoing analysis explains curvature about the  $a$  axis and the units apply to the length of the unit cell in the  $b$  direction. If the  $a_0$  values are used, the oxygen ions extend 5.14 Å, the corresponding hydroxyl ions 5.06 Å (as in gibbsite) and the resulting tube diameter would be 570 Å. Perhaps the differences in radius of curvature about  $a$  and about  $b$  have some bearing upon the existence of double tubes (Fig. 3B).

#### *Significance of the Tubular Structure*

*Relation of endellite (halloysite) to halloysite (metahalloysite).*—This concept of the structure of endellite (halloysite) readily accounts for the longitudinal splitting of the tubes when the material dehydrates to halloysite (metahalloysite). Upon loss of the oriented water molecules between the layers, adjoining units come together from a distance of 5.4 Å to approximately 3 Å. The hydroxyl ions, which in the tubular form occupied approximately their normal spacing along  $b_0$  of 8.62 Å and were presumably under little strain in this direction, now become subject to the forces of the closer oxygen ions and are "stretched" to a distance approaching 8.93 Å. As a result the curved sheets tend to become planar and must either split or collapse. Once started, a split would continue along the length of the tube. Unrolling presumably further relieves the strained condition.

The incomplete reversibility of the change from endellite (halloysite) to halloysite (metahalloysite) has never been adequately explained. The picture presented here suggests that the splitting or collapse of the tubes not only relieves the strain set up on dehydration but also tends to prevent return to the hydrated state. It is conceivable that in some crystals the tubular structure might be sufficiently strong to prevent opposing oxygen and hydroxyl layers of adjacent units from coming together when the intervening layer of oriented water molecules is removed. Such tubes would be pseudomorphs of halloysite (metahalloysite) after endellite (halloysite) and could presumably be completely rehydrated. Whether or not they might be abundant in a particular sample or could indeed exist at all would depend upon the structural rigidity of the tubes, but no data are available on this point. Bradley (1945, p. 706) and MacEwan (1948, pp. 356, 357) have shown that when the interlayer water of endellite is replaced with various organic complexes the strong

diffraction effect from the (001) planes is displaced from 10.1 Å to values as high as 11.6 Å. This indicates that the tubes may be flexible enough to "absorb" a thirteen per cent increase in radius, and Hendricks (personal communication) has suggested that the crystals may actually be made up of many overlapping curved sheets which can shift slightly over one another. In any case, the well-defined nature of the longitudinal splitting indicates that upon dehydration all the concentric cylindrical sheets of the tube act as a unit.

*Random structure in endellite (halloysite) and halloysite (metahalloysite).*—It has been shown that if the tubes are developed parallel to the  $a$  axis the minimum inner diameter is theoretically 250 Å; if parallel to  $b$ , 570 Å. Conceivably the tube axis might be parallel to some intermediate direction in the plane of the sheet in which case the theoretical minimum inner diameter would be between these two extremes. In any of these cases, however, it is likely that in any single crystal the tube axis is parallel to the same crystallographic direction in each of the successive cylindrical sheets which form the tube. This means that the orientation of one unit with respect to others above and below it along the  $c$  axis is not completely random but must be partially ordered. Thus, in a tube developed parallel to the  $a$  axis, disorder produced by shifting of successive cylindrical sheets parallel to the tube axis (translation parallel to  $a$ ) or produced by revolution about the tube axis (translation parallel to  $b$ ), would be permissible. On the other hand, if complete disorder were produced by random rotation about the normal to the sheet (with or without random translation) the tube axis could not have the same crystallographic direction in successive 1:1 units.

As brought out indirectly by Warren (1941, p. 693), in discussing  $x$ -ray diffraction effects in random layer lattices, there is no difference in the powder pattern from layers related by random translation and the pattern from those related by random translation plus random rotation. Therefore, this picture of partial rather than complete disorder in the orientation of units stacked parallel to the  $c$  axis supplements interpretations of the  $x$ -ray data (Hendricks, 1942; Brindley and Robinson, 1948, p. 399).

The case for partial rather than complete disorder in the stacking of 1:1 units is strengthened by birefringence measurements on oriented aggregates. If randomness of successive units were complete, compensation would take place, and no interference color would be visible. Many workers have measured birefringence on oriented aggregates of halloysite (metahalloysites) and, as mentioned previously, present work yielded a value for  $n_\gamma$  (or  $n_\beta$ )  $- n_\alpha$  equal to  $0.002 \pm .001$ .

*Effect of tubular structure on optical properties.*—Optical data on

halloysite (metahalloysite) and endellite (halloysite) are conflicting. Published values for the indices of refraction vary from 1.528 to 1.648 (Correns and Mehmel, 1936, p. 337; Ross and Kerr, 1934, p. 138; Alexander, et al., 1943, p. 12). The birefringence is usually described as less than 0.001, although measurements of the double refraction of endellite suspensions oriented by an electric field (Whiteside and Marshall, 1944, p. 33) gave values of  $0.0050 \pm$  for hydrogen saturated halloysite (metahalloysite) and 0.0112 for the same material when sodium saturated. Because of conflicting results obtained from studies of aggregates of halloysite (metahalloysite) crystals, Grim (1942, p. 249) points out that "... it would seem ... that halloysite is composed of units that may easily vary from definite alignment to a random orientation."

It is not unlikely that the birefringence of halloysite (metahalloysite) is similar to that of kaolinite (0.006) and that the observed variation is the result of the tubular structure and of the degree of splitting and unrolling which has taken place in different specimens. In a complete tube, because of the variable direction of the  $c$  axis in a plane approximately perpendicular to the tube axis (Fig. 9B), the birefringence would change from a minimum value of  $n_\gamma - n_\beta$  (0.001 in kaolinite) along the crest of the tube to a maximum value of  $n_\gamma$  (or  $n_\beta$ ) -  $n_\alpha$  along each edge. In an aggregate of oriented tubes (Fig. 9C) the resultant value would probably lie between these extremes. A tube that had completely unrolled or collapsed would have a birefringence of only  $n_\gamma - n_\beta$  so that even in oriented aggregates the material would appear nearly isotropic.

*Dehydration characteristics.*—The role of adsorbed and interlayer water has been carefully evaluated by Brindley and Robinson (1948). The tubular structure suggests that in future dehydration studies the possible effect of capillary water should also be considered.

#### APPLICABILITY OF PROPOSED CONCEPT TO OTHER MINERALS

The two fundamental structural conditions which exist in endellite (halloysite) and cause the crystals to be tubular are: (1) a sheet structure of the 1:1 type in which the sheets have slightly different dimensions in the  $a_0$  and  $b_0$  directions; and (2) bonds between the 1:1 units which are not sufficiently strong to overcome this discrepancy by "stretching" the ions on the "bottom" of one unit to fit the dimensions of the ions on the "top" of the opposing unit. Similar conditions may well exist in other 1:1 sheet structure minerals and a number of possibilities are being investigated. Serpentine appears to be the most promising, for Warren and Hering (1941) and Aruja (1945) have shown that both antigorite and chrysotile possess layer structures. It would seem likely that a morphological and structural analogy to the kaolin minerals may exist, in which

case chrysotile fibers would actually be hollow cylindrical crystals similar to those discussed in this paper.

### CONCLUSION

Electron microscope studies show that halloysite (metahalloysite) occurs as modified hollow tubes. Because of the vacuum and the heat of the electron beam endellite (halloysite) has not been observed directly in the electron microscope but structural evidence combined with these studies of halloysite (metahalloysite) suggests that endellite (halloysite) consists of well-developed tubes which collapse, spilt, and unroll upon dehydration. Although it is possible that some crystals do not change form upon dehydration because of the structural strength of the cylindrical 1:1 units which form the tube, true pseudomorphs of halloysite (metahalloysite) after endellite (halloysite) are probably rare. In general, the presence of split or collapsed rather than complete tubes is judged to be one of the major differences between the two minerals. The present work not only supports the conclusion of others that halloysite (metahalloysite) is formed by dehydration of endellite (halloysite) but indicates that this is the only way in which it is produced.

Data on the minerals lead to the belief that (1) the wall of the tube consists of curved (001) sheets, and (2) the *c* axis for any point on the tube is nearly perpendicular to a plane tangent to the tube at that point. The axis of the tube may be parallel to either the *a* or *b* axis, or possibly to any intermediate crystallographic direction in the plane of the sheets.

The proposed explanation of the tubular structure takes account of (1) the discrepancy of dimensions of the silicon-oxygen sheets as opposed to the modified gibbsite sheets, (2) the larger intervening distance between the 1:1 units in endellite (halloysite) as compared to kaolinite. Removal of the water layers on dehydration of endellite (halloysite) brings the hydroxyl layer of one unit closer to the oxygen layer of the next and causes readjustment of the spacing of the hydroxyl ions. The resulting strain manifests itself in the form of collapsed or split and partially unrolled tubes of halloysite (metahalloysite).

It has been shown that the inner diameters of halloysite (metahalloysite) tubes measured from electron micrographs range from 200 to 1000 Å and are of the same order of magnitude as the values obtained by calculations based on the proposed structure, namely 250 to 570 Å. As would be expected from the structural picture, the spread of the outside diameters is somewhat greater—400 to 1900 Å.

As a result of the tubular form and the optical birefringence of oriented aggregates, it is proposed that the orientation of successive cylindrical 1:1 units in a given tube is not, as hitherto believed, completely random.

Rather, there is partial randomness produced by translation along and rotation about the tube axis.

The varied indices of refraction and birefringence assigned to halloysite (metahalloysite) by previous workers are explained on the basis of the difference in optical orientation produced by tubes in various states of splitting and unrolling.

Finally, in clays of natural occurrence no morphological transition has been observed between the typical pseudo-hexagonal plates of kaolinite and the hollow tubes of endellite (halloysite) and halloysite (metahalloysite).

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#### REFERENCES

- ALEXANDER, L. T., FAUST, G. T., HENDRICKS, S. B., INSLEY, H., AND McMURDIE, H. F. (1943), Relationship of the clay minerals halloysite and endellite: *Am. Mineral.*, **28**, 1-18.
- ARUJA, ENDEL (1945), An  $x$ -ray study on the crystal structure of antigorite: *Mineral. Mag.*, **27**, 65-74.

- BATES, T. F., HILDEBRAND, F. A., AND SWINEFORD, A. (1949), Electron microscopy of the kaolin minerals: *Am. Mineral.*, **34**, 274.
- BERTHIER, P. (1826), Analyse de l'halloysite: *Ann. Chim. Phys.*, **32**, 332-335.
- BRADLEY, W. F. (1945), Diagnostic criteria for clay minerals: *Am. Mineral.*, **30**, 704-713.
- BRINDLEY, G. W., AND ROBINSON, K. (1946), The structure of kaolinite: *Mineral. Mag.*, **27**, 242-253.
- (1948), X-ray studies of halloysite and metahalloysite. Part I, The Structure of metahalloysite, an example of a random layer lattice: *Mineral. Mag.*, **28**, 393-406.
- CALLAGHAN, EUGENE (1948), Endellite deposits in Gardner Mine Ridge, Lawrence County, Indiana: *Indiana Dept. of Conservation, Division of Geol., Bull.* **1**, p. 1-47.
- CORRENS, C. W., AND MEHMEL, M. (1936), Über den optischen und röntgenographischen Nachweis von Kaolinit, Halloysit und Montmorillonit: *Zeits. Krist.*, **94**, 337-348.
- DITTLER, E. (1941), More recent knowledge of the nature of clay: *Tonind.-Ztg.*, **65**, p. 515, 528.
- EDELMAN, C. H., AND FAVEJEE, J. CH. L. (1938), On the crystal structure of montmorillonite and halloysite: *Zeits. Krist.*, **102**, 417-431.
- EITEL, W. (1943), Das Elektronmikroskop und seine Anwendung auf keramische Probleme: *Berichte der Deutschen Keramischen Gesellschaft*, **24**, 37-53.
- EITEL, W., AND RADZIEWSKI, O. E. (1943), Zur Kenntnis des Metahalloysite: *Abhandl. Preuss. Akad. Wiss. Jahrgang. Math.-naturw. Klasse. Nr. 5*,
- GRIM, R. E. (1942), Modern concepts of clay materials: *Jour. Geol.*, **50**, 225-275.
- HENDRICKS, S. B. (1938), On the crystal structure of the clay minerals: Dickite, halloysite, and hydrated halloysite: *Am. Mineral.* **23**, 295-301.
- (1942), Lattice structure of clay minerals and some properties of clays: *Jour. Geol.*, **50**, 276-290.
- HOFMANN, U., ENDELL, K., AND WILM, D. (1934), Röntgenographische und kolloidchemische Untersuchungen über Ton: *Angew. Chem.*, **47**, 539-547.
- KELLEY, O. J., AND SHAW, B. T. (1942), Studies of clay particles with the electron microscope. III, Hydrodynamic considerations in relation to shape of particles: *Soil Sci. Soc. Am., Proc.*, **7**, 58-68.
- KELLEY, W. P., AND PAGE, J. B., (1942) Criteria for the identification of the constituents of soil colloids: *Soil Sci. Soc. Am., Proc.*, **7**, 175-181.
- MACEWAN, D. M. C. (1948), Complexes of clays with organic compounds. I. Complex formation between montmorillonite and halloysite and certain organic liquids: *Faraday Soc. Trans.*, **44**, 349-368.
- MARSHALL, C. E. (1941), Studies in the degree of dispersion of the clays. IV. The shapes of clay particles: *Jour. Phys. Chem.*, **45**, 81-93.
- MEHMEL, M. (1935), Über die Struktur von Halloysit und Metahalloysit: *Zeits. Krist.*, **90**, 35-42.
- MELLOR, J. W. (1908), A note on the nomenclature of clays: *Trans. Eng. Cer. Soc.*, **8**, 23-30.
- PAULING, L. C. (1930) The structure of micas and related minerals: *Nat. Acad. Sci. Proc.*, **16**, 123-129.
- ROGERS, A. F. (1917), A review of the amorphous minerals; *Jour. Geol.*, **25**, 515-541.
- ROSS, C. S., AND KERR, P. F. (1934), Halloysite and allophane: *U. S. Geol. Survey, Prof. Paper* **185-G**, 135-148.
- SHAW, B. T., AND HUMBERT, R. P. (1941), Electron micrographs of clay minerals: *Soil Sci. Soc. Am. Proc.*, **6**, 146-149.
- WARREN, B. E., AND HERING, K. W., (1941), The random structure of chrysotile asbestos: *Phys. Rev.*, **59**, 925.
- (1941), X-ray diffraction in random layer lattices: *Phys. Rev.*, **59**, 693-698.
- WHITESIDE, E. P., AND MARSHALL, C. E. (1944), Mineralogical and chemical studies of the Putnam silt loam soil: *Univ. of Missouri Agricultural Exp. Station Res. Bull.* **386**, 1-48.