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## RELATIONSHIP OF THE CLAY MINERALS HALLOYSITE AND ENDELLITE

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### ABSTRACT

A study was made of the clay mineral halloysite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , and the more highly hydrated related mineral,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , for which the name endellite is proposed. By means of chemical, electron-microscopic, x-ray diffraction, and petrographic methods, it was found that: (1) halloysite is formed by a partial dehydration of endellite; (2) halloysite has the same type of aluminum silicate layers as kaolinite, but the layers are usually superimposed in a less orderly manner in the former than in the latter; (3) endellite has a structure in which kaolinite-type layers alternate with single layers of water molecules; and (4) endellite may be formed by alteration of the constituents of a basic igneous rock, or its metamorphic equivalent.

The naming and identification of halloysite by Berthier in 1826<sup>1</sup> was based on type material from Angleur, Liege, Belgium, which closely resembles kaolinite in composition. Hofmann, Endell, and Wilm in 1934<sup>2</sup> described a more hydrous mineral from Djebel Deber, Libya, which apparently forms, by partial dehydration, the mineral called halloysite by Berthier. Hofmann, Endell, and Wilm, however, called their mineral halloysite and the original mineral from Belgium, metahalloysite. This shifting of names has caused considerable confusion which has been increased by Hendricks' suggestion<sup>3</sup> that the more hydrous material be called "hydrated halloysite." In an attempt to eliminate this confusion, and still preserve the original usage of the term halloysite, we suggest that the more hydrous mineral be called endellite in recognition of one of its discoverers.<sup>4</sup>

<sup>1</sup> Berthier, P., *Ann. Chim. Phys.*, **32**, 332 (1826).

<sup>2</sup> Hofmann, U., Endell, K., and Wilm, D., *Angew. Chem.*, **47**, 539 (1934).

<sup>3</sup> Hendricks, S. B., *Am. Mineral.*, **23**, 295 (1938).

<sup>4</sup> The name hofmannite has previously been given to a hydrocarbon; Dana, *System of Mineralogy*, p. 1013.

The nature as well as the names of the minerals endellite and halloysite have been the subject of much controversy. It has generally been agreed, although without satisfactory evidence, that the formula of endellite is approximately  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ . Three publications have appeared on the crystal structure of endellite, in each of which a different structure is proposed.<sup>3,5,6</sup>

The present study, which clarifies most of the questions which have been raised, was made possible only by the development of the electron microscope. The investigation was facilitated by the discovery of several new deposits of endellite, in two of which its mode of formation could be followed.

#### SOURCES OF MATERIALS

The halloysite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) samples studied were obtained from Dr. Clarence S. Ross, of the United States Geological Survey. These included specimens already described in a paper by Ross and Kerr<sup>7</sup> and designated by them as follows:

- No. 2 from Angleur, Liege, Belgium (type material)
- No. 3 from Lawrence County, Indiana ("indianaite")
- No. 8 from Adams County, Ohio
- No. 9 from Rankin County, Mississippi
- No. 10 from Real County, Texas

Undescribed samples, also supplied by Dr. Ross, were from Iyo, Japan, Washoe County, Nevada, and Victor, Colorado. All of these specimens were porcelain-like in appearance with a conchoidal fracture. The least dimension of any one of the specimens was 1 centimeter and all probably occurred in much larger masses.

Four samples of endellite which had been kept under water were available for examination. Of these No. 21 was the type material from Djebel Deber, Libya, kindly sent by Professor Hofmann of the University of Rostock. Specimen No. 22 from the vicinity of Anamosa, Iowa, was obtained through the courtesy of Dr. P. G. Nutting of the United States Geological Survey. Some of the best material (No. 23) was obtained from the Dragon Consolidated mine, near Eureka, Utah. This apparently authigenic hydrothermal deposit has recently been described by Schroter and Campbell.<sup>8</sup> These endellite samples contained large areas of translu-

<sup>5</sup> Mehmel, M., *Zeits. Krist.*, **90**, 35 (1935).

<sup>6</sup> Edelman, C. H., and Favejee, J. Ch. L., *Zeits. Krist.*, **102**, 417.

<sup>7</sup> Ross, C. S., and Kerr, P. F., *Prof. Paper 185-G*, U. S. Geol. Survey, Washington (1934).

<sup>8</sup> Schroter, G. A., and Campbell, I., *Am. Inst. Mining and Met. Engrs., Tech. Pub. No. 1139-H*, 31 pp. (1940).

cent porcelain-like material with conchoidal fracture and, after drying at 100°C., closely resembled the halloysite specimens.

A somewhat more impure sample (No. 24) was collected in the vicinity of Rockdale, near Baltimore, Md., where endellite had been formed by alteration of plagioclase feldspar in an epidote amphibolite. Endellite persisted in the "C" horizon of the associated soil.

#### ELECTRON MICROSCOPE PHOTOGRAPHS

Electron microscope photographs of halloysite and endellite were made in the laboratories of the National Bureau of Standards, using the apparatus manufactured by the Radio Corporation of America. The initial magnifications were usually about 10,000 diameters, but a few photographs were taken at about 18,000 diameters.

The specimens examined were first ground for a few minutes in an agate mortar and then dispersed in water. In some instances it was necessary to use a few drops of dilute ammonium hydroxide as a dispersing agent. After allowing the coarser material to settle, the suspended sample was diluted to such a concentration that a drop would give a mount of the desired density when applied to a thin collodion membrane. The membrane, which had been prepared by the spreading of a dilute collodion solution on water, was supported on an electroplated 200-mesh gauze. After drying at room temperature, the mounted sample was introduced into the electron microscope. Since the microscope is necessarily evacuated, the endellite samples were probably completely changed to halloysite, but this should not have interfered with observations on the morphology of individual particles.

Although the typical lath-shaped form of the halloysite fragments, well shown in Figs. 1, 2, and 3, has previously been observed in electron microscope images by Shaw and Humbert,<sup>9</sup> the halloysite from Lawrence County, Indiana (Fig. 1, 1) exhibits geometrical arrangements of laths, serrations on the lath edges, and indentations on the lath ends not hitherto noted. Thus, the portion of the object indicated by *A* in Fig. 1, 1, appears to be formed from a number of related fragments between which an angle of about 60° frequently occurs. This is perhaps more clearly shown in Fig. 4 where the oriented portion of the photograph is sketched. This arrangement was noted in other electron micrographs of the material. It is probable that the related fragments are only part of a much larger system that had been degraded since the formation of the mineral.

<sup>9</sup> Shaw, B. T., and Humbert, R. P., *Proc. Soil Sci. Soc. Am.*, **6**, 146-149 (1941).

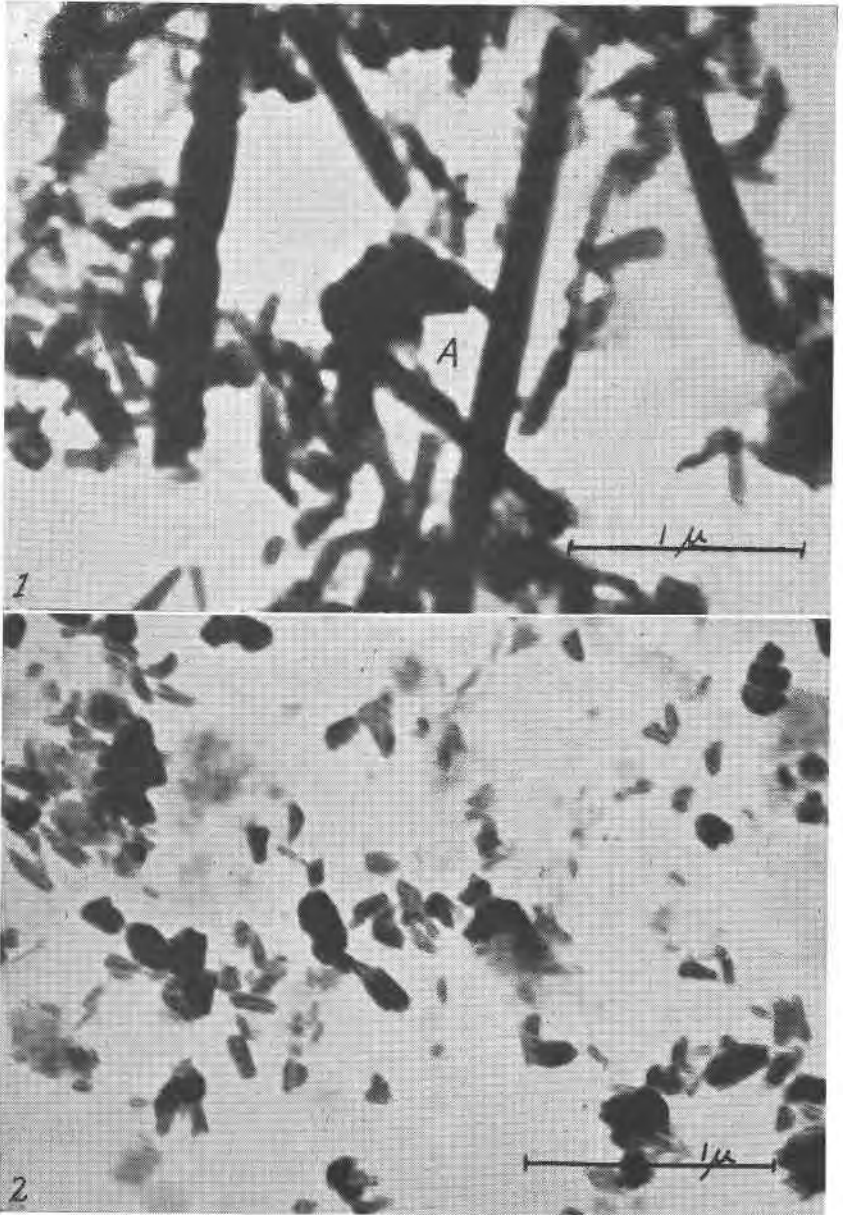


FIG. 1. (1) Halloysite ("indianaite"), Lawrence County, Indiana.  
(2) Endellite, Rockdale, Maryland.

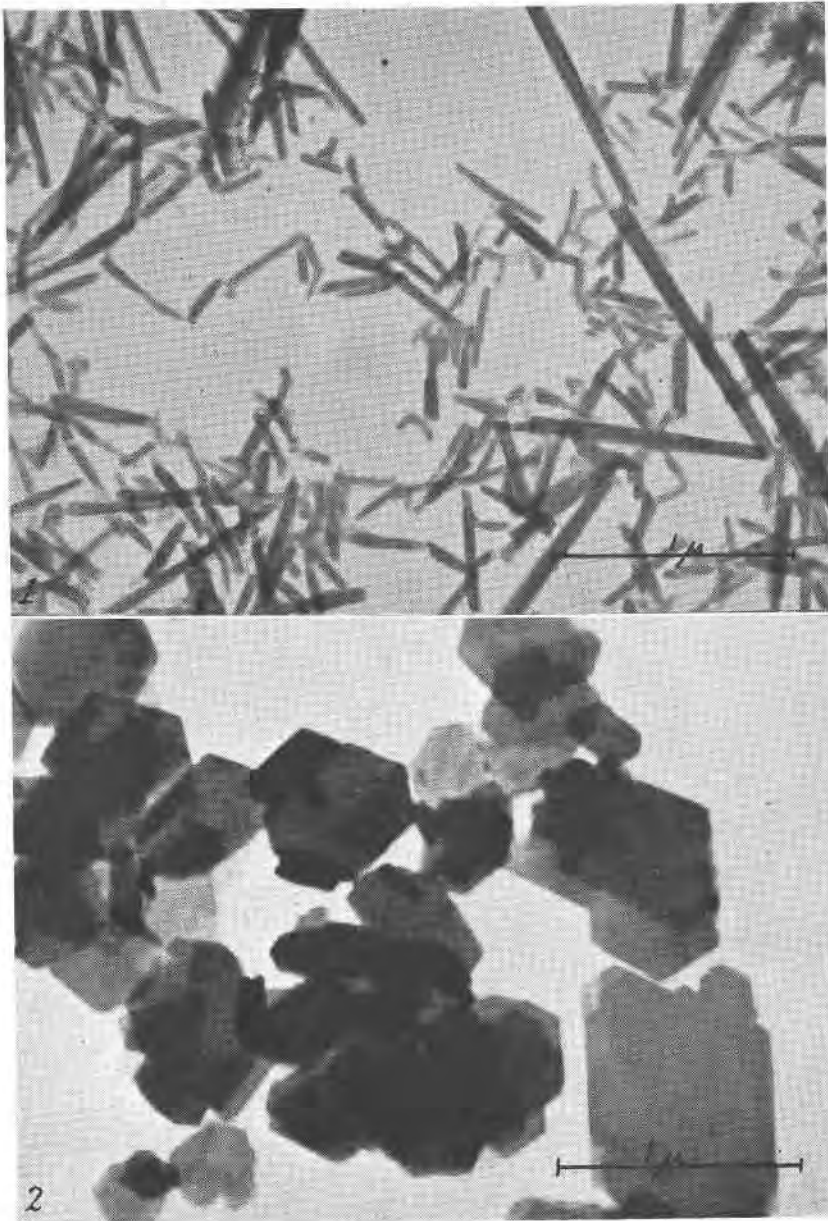


FIG. 2. (1) Endellite, Anamosa, Iowa. (2) Kaolinite, Georgia.

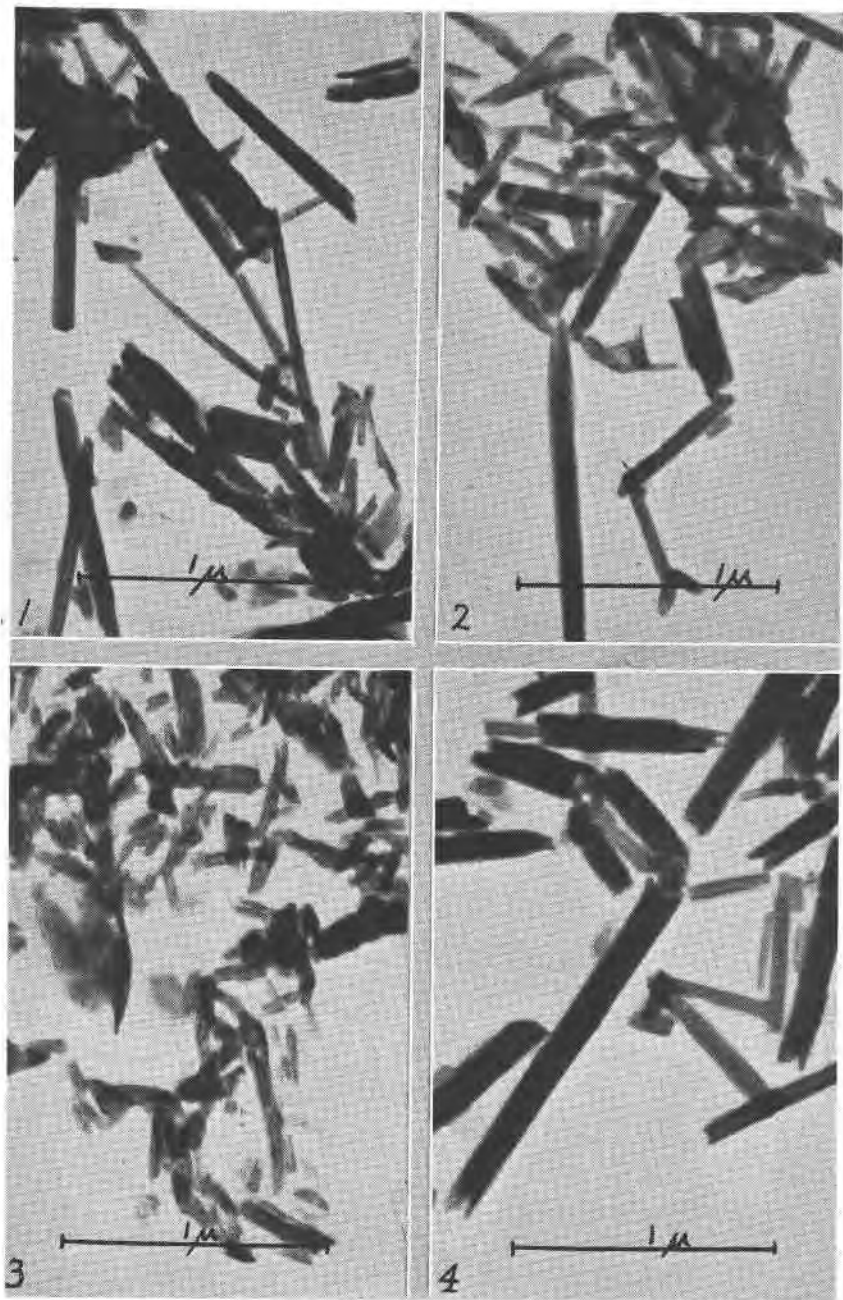


FIG. 3. (1) Halloysite, Iyo, Japan.  
(2) Endellite, Djebel Deber, Libya.  
(3) Halloysite, Liege, Belgium.  
(4) Halloysite, Real County, Texas.

The endellite specimen from the vicinity of Rockdale, Md., was known to contain a mixture of several clay minerals. Endellite relic laths are numerous in the photograph reproduced as Fig. 1, 2, but some hexagonal plates may also be observed. None of the endellite specimens gave results essentially different from those obtained for halloysite. Authentic specimens of kaolinite usually contain hexagonal plates and none has been found to have the lath-like fragments of endellite and halloysite. A typical kaolinite photograph is reproduced in Fig. 2, 2.

Many of the endellite and halloysite fragments display a true or ap-

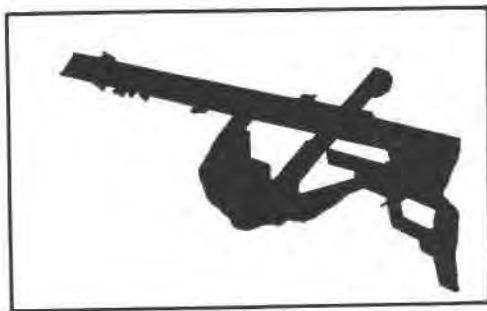


FIG. 4. A tracing of a portion of Fig. 1 (1) showing related fragments of halloysite.

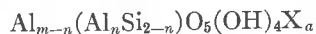
parent longitudinal division as shown in Fig. 3. Although some of the fragments do not appear to be divided, their indented or notched ends may be indicative of such division. Fragments of endellite or halloysite from any particular specimen have a tendency to be similar in dimensions. This feature, observed repeatedly, is probably a characteristic of the material.

#### COMPOSITION OF HALLOYSITE AND DEHYDRATED ENDELLITE

Chemical formulas for halloysite and dehydrated endellite which express the relationship between ions in tetrahedral and octahedral coordination can be developed after certain assumptions are made. These assumptions are:

1. There is a fixed ratio, 5:4, of oxygen to hydroxyl ions.
2. The ratio of ions in tetrahedral coordination to oxygen ions is 2:5.
3. All silicon ions are in tetrahedral coordination.
4. Possible isomorphous substitution of  $Mg^{++}$ ,  $Fe^{+++}$ ,  $Na^+$  or  $Li^+$  for  $Al^{+++}$  is neglected.

The formula then is of the type



in which  $m$  represents the total  $Al^{+++}$  present,  $n$  the number of ions to be

added to  $\text{Si}^{++++}$  to bring the number of cations in tetrahedral coordination to 2, and  $\text{X}_a$  represents the replaceable base. The value of  $a$  in the expression  $\text{X}_a$  is 0.02, corresponding to the usual exchange capacity of the kaolin minerals, i.e., about 0.08 milliequivalent per gram.

To illustrate the calculation of the formula, the analysis given by Ross and Kerr<sup>7</sup> of their sample No. 3 may be used. The analysis and the corresponding atomic equivalents of  $\text{Si}^{++++}$  and  $\text{Al}^{+++}$  are:

	<i>Per cent</i>	<i>Atomic equiv.</i>
$\text{SiO}_2$	40.26	$\text{Si}^{++++}$ 0.670
$\text{Al}_2\text{O}_3$	37.95	$\text{Al}^{+++}$ 0.744
$\text{Fe}_2\text{O}_3$	0.30	
$\text{CaO}$	0.22	
$\text{Na}_2\text{O}, \text{K}_2\text{O}$	0.74	
$-\text{H}_2\text{O}$	4.45	
$\text{H}_2\text{O}$	15.94	

Since

$$(m)/0.744 = (2 - y)/0.670$$

and

$$3(m) + 4(2 - n) + a = 14$$

in order to balance the charge; consequently

$$3(2 - n) \cdot 0.744/0.670 + 4(2 - n) + a = 14.00.$$

The formula, therefore, is  $\text{Al}_{2.024}(\text{Al}_{1.092}\text{Si}_{1.908})\text{O}_5(\text{OH})_4\text{X}_{.02}$ , which, considering the limits of analytical accuracy and the validity of assumptions concerning base exchange and isomorphous substitution, may be simplified to  $\text{Al}_{2.02}(\text{Al}_{1.09}\text{Si}_{1.91})\text{O}_5(\text{OH})_4\text{X}_{.02}$ . Relative amounts of  $\text{Al}^{+++}$  in tetrahedral and octahedral coordination are not significantly affected by the above assumptions. The formulas for nine of the 13 halloysite specimens, the analyses of which are published by Ross and Kerr,<sup>7</sup> are given in Table 1.

TABLE 1. FORMULAS OF HALLOYSITE SPECIMENS

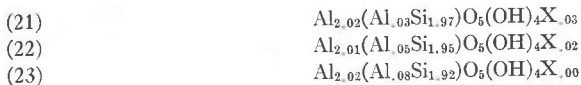
Ross-Kerr no.	Formula
3	$\text{Al}_{2.02}(\text{Al}_{1.09}\text{Si}_{1.91})\text{O}_5(\text{OH})_4\text{X}_{.02}$
4	$\text{Al}_{2.00}(\text{Al}_{1.02}\text{Si}_{1.98})\text{O}_5(\text{OH})_4\text{X}_{.02}$
5	$\text{Al}_{1.99}(\text{Si}_{2.00})\text{O}_5(\text{OH})_4\text{X}_{.02}$
6	$\text{Al}_{2.01}(\text{Al}_{1.04}\text{Si}_{1.96})\text{O}_5(\text{OH})_4\text{X}_{.02}$
7	$\text{Al}_{2.00}(\text{Al}_{1.08}\text{Si}_{1.97})\text{O}_5(\text{OH})_4\text{X}_{.02}$
8	$\text{Al}_{2.02}(\text{Al}_{1.08}\text{Si}_{1.92})\text{O}_5(\text{OH})_4\text{X}_{.02}$
9	$\text{Al}_{2.00}(\text{Al}_{1.02}\text{Si}_{1.98})\text{O}_5(\text{OH})_4\text{X}_{.02}$
12	$\text{Al}_{2.01}(\text{Al}_{1.04}\text{Si}_{1.96})\text{O}_5(\text{OH})_4\text{X}_{.02}$
13	$\text{Al}_{2.02}(\text{Al}_{1.08}\text{Si}_{1.92})\text{O}_5(\text{OH})_4\text{X}_{.02}$



The foregoing method does not give a satisfactory formula for sample 2, the type material from Liege, Belgium, since the  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of this material is 2.06:1.00 and, therefore, is in excess of the 2.00:1.00 limitation imposed by the formula. This high ratio may be the result of a slight amount of silica as an impurity, either as a separate phase or as an anauxite type material. Ross and Kerr's sample 11, from Newton County, Arkansas, probably contains diaspore or gibbsite as an impurity, since the water lost above  $110^\circ$  is relatively high, the  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio is low and other samples from that locality contain such impurities. The amounts of alkali in the samples, which were usually low and in some cases not reported, were not considered in the calculation of the formulas. The formula of sample No. 10 has not been calculated because of the unusually high content of alkalis (1.19 per cent).

Although halloysite has approximately the same formula as kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ,<sup>7</sup> analyses of halloysite always show more than 14.4 per cent of water lost above  $110^\circ\text{C}$ ., whereas pure kaolinite samples have very nearly the 13.9 per cent required by the formula.

Analyses of five endellite samples dried at  $100^\circ\text{C}$ ., from the four localities described above, are listed in Table 2. Formulas for samples Nos. 21, 22, and 23, after drying at  $110^\circ\text{C}$ ., are:



Sample No. 22a, the fine fraction of the Anamosa, Iowa, material, was shown by differential thermal analysis to contain about 20 per cent of gibbsite. The material from Rockdale, Maryland, sample 24, contains both kaolinite and the iron-bearing clay mineral, nontronite, as shown by examination with a petrographic microscope.

TABLE 2. ANALYSES OF ENDELLITE SAMPLES DRIED AT  $110^\circ\text{C}$ .

	21	22	22a	23	24
$\text{SiO}_2$	45.20	44.51	35.26	44.35	45.46
$\text{Al}_2\text{O}_3$	38.96	39.90	45.24	40.35	36.69
$\text{Fe}_2\text{O}_3$	0.21	0.21	0.44	0.21	3.51
CaO	0.00	0.00	0.00	0.00	0.00
MgO	0.08	0.05	0.34	0.04	0.32
Ignition loss	15.35	15.44	19.46	15.54	14.34
Total	99.80	100.11	100.74	100.49	100.32

- 21 Djebal, Deber, Libya.
- 22 Anamosa, Iowa, translucent piece.
- 22a Anamosa, Iowa, fraction less than 2 microns in size.
- 23 Eureka, Utah.
- 24 Rockdale, Md., fraction less than 2 microns in size.

The base exchange capacities of samples Nos. 22, 23, and 24 were determined by first saturating the clay at  $pH$  7.0 with  $Ba^{++}$ , from 0.2 N.  $BaCl_2$  which was then displaced by treatment with  $NH_4Cl$ . The displaced  $Ba^{++}$  was determined gravimetrically as the sulfate. Observed capacities are: No. 22, 0.08; No. 23, 0.01; No. 24, 0.21 m.e. per gram. The high exchange capacity of the material from Rockdale, Md., No. 24, was due to the nontronite in it.

These several samples of dehydrated endellite have very nearly the same composition as found for halloysite by Ross and Kerr.

#### IDENTIFICATION OF ENDELLITE BY X-RAY DIFFRACTION, WATER CONTENTS, REFRACTIVE INDICES, AND DENSITIES

Mehmel<sup>5</sup> gives x-ray powder diffraction data for halloysite and endellite. Endellite has an intense reflection with a spacing of  $10.1\text{\AA}$ , while the greatest spacing of halloysite is  $7.2\text{\AA}$ . Otherwise the diffraction patterns are closely similar. Hofmann, Endell, and Wilm<sup>2</sup> first showed, and others have verified their observations, that drying endellite even at room temperatures causes it to give the diffraction pattern of halloysite. Efforts to obtain endellite by hydrating halloysite have not been successful.

The four endellite specimens examined in this work gave mixed diffraction patterns of endellite and halloysite. All of the samples showed varying water contents, depending upon the humidity. Typical results, obtained from the Eureka, Utah, sample (No. 23) that had been ground to pass a 325-mesh screen, are reproduced in Fig. 5. The sample was brought to equilibrium at  $30^\circ\text{C}$ ., first at 75 per cent and subsequently at lower relative humidities. The results of duplicate experiments are shown by circles in Fig. 5. After equilibration at the lower relative humidities, the samples were again brought to equilibrium at 75 per cent relative humidity. The amounts by which they failed to regain their initial weights are indicated by circles with attached arrows.

The endellite samples examined are partially reversible in their hydration. When samples of endellite (Eureka, Utah) were dried at  $300^\circ\text{C}$ . and again brought to equilibrium at  $30^\circ\text{C}$ . and 75 per cent relative humidity, they reabsorbed about 50 per cent of the water lost, but the intense diffraction line at  $10.1\text{\AA}$ , characteristic of endellite, did not reappear. It

would seem that this water taken up by the dehydrated endellite is merely adsorbed, as also is a part of the water in the original samples.

Somewhat different results for the dehydration characteristics of endellite were obtained by Hofmann, Endell, and Wilm<sup>2</sup> and by Correns and Mehmel.<sup>10</sup> The endellite used by Hofmann, Endell, and Wilm probably contains gibbsite as an impurity, as indicated by the weight loss of 19 per cent at temperatures above 200°C., while that of Correns and Mehmel contained less admixed halloysite (their metahalloysite) than did the material from Eureka, Utah.

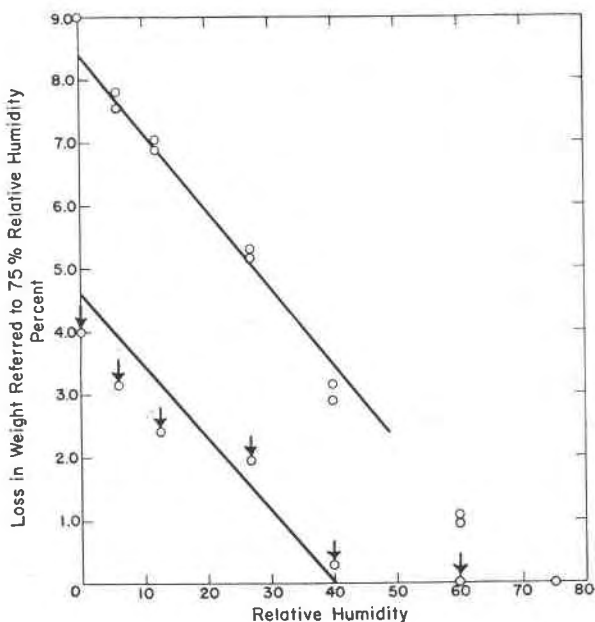


FIG. 5. Effect of relative humidity at 30°C. upon loss of water from partially dehydrated endellite.

Although Correns and Mehmel<sup>10</sup> indicate that the refractive index of endellite determined by use of the immersion method depends upon the immersion liquid, careful measurements by one of the present authors (G. T. Faust), using several liquids, failed to show this effect (Table 3). When care was used to insure penetration of the specimen by the liquid, no change was noted in the refractive index either with the liquid used or with the length of time in contact with the liquid, after displacement of the surface water in the first few seconds. If the surface film of water

<sup>10</sup> Correns, C. W., and Mehmel, M., *Zeits. Krist.*, **94**, 337 (1936).

were not completely removed, as in case of a totally immiscible liquid, values too low would be obtained.

TABLE 3. APPARENT REFRACTIVE INDICES OF ENDELLITE SPECIMENS FOR  $\text{Na}_D$  LIGHT

	(a) Rohrbach's solution in glycerin	(b) Glycerine and quinoline	(c) Mineral oil and monochloro- naphthalene	Dehydrated endellite or halloysite in (c)
21	1.543	1.543	1.540-1.545	1.556
22	1.543	1.541		
23		1.542		1.551
24	1.551	1.552		1.556

The values of the refractive indices of endellite listed by Correns and Mehmel<sup>10</sup> vary between 1.528 and 1.550, which includes the range shown in Table 3. While Correns and Mehmel consider these values to be those of endellite, they probably are values for mixtures of endellite and halloysite. The true value, as shown later, is probably  $1.490 \pm .005$ . Using this figure for pure endellite, none of the specimens so far measured contains more than 50 per cent of endellite, the remainder being its dehydration product, halloysite.

There appears to be no unequivocal method of determining directly the water content of endellite because no samples unmixed with halloysite seem to be available. An indirect method was adopted, however, based on the assumptions that the halloysite in the samples was derived from endellite, that no volume change in the specimen accompanied the change from endellite to halloysite, and that the submicroscopic pores produced by the change are completely refillable with water. Dense, coherent, and porcelain-like specimens were chosen as most nearly fulfilling these conditions and density determinations were made on such samples by determining their weights after drying at  $110^\circ$ , the weights after the pores were filled with water, and the water displacement of the wet samples. The percentages of water lost by wet specimens when dried at  $110^\circ\text{C}$ . as shown in Table 4, column 4, agree within the limits of experimental error with the water loss accompanying the change of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  to  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . The results provide evidence that the composition of endellite is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ .

Specimens with lower densities when the pores are water-filled, such as that from Washoe County, Nevada, with density of 2.03 and that from Adams County, Ohio, with density of 2.02, are less coherent and porce-

lain-like than those listed in the table, indicating that the original samples of endellite were not free from voids.

TABLE 4. DENSITIES FOR HALLOYSITE AND DEHYDRATED ENDELLITE SPECIMENS

Source of specimen	Density		Per cent of water in wet specimen lost by drying at 110°C.
	Specimen with pores filled with water	Specimen dried at 110°C.	
Eureka, Utah	2.11; 2.13	2.58	13.7
Iyo, Japan	2.17	2.60	12.4
Lawrence County, Indiana	2.16	2.59	12.5
Calculated values	2.12 <sup>1</sup>	2.61 <sup>3</sup>	12.24 <sup>2</sup>

<sup>1</sup> Calculated for  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  with

$$a_0 = 5.1\text{\AA}, b_0 = 8.9\text{\AA}, c_0 = 10.25\text{\AA}, \beta = 100^\circ 12'.$$

<sup>2</sup> Calculated for loss of  $2\text{H}_2\text{O}$  from  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ .

<sup>3</sup> Calculated for  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  (halloysite) with

$$a_0 = 5.1\text{\AA}, b_0 = 8.9\text{\AA}, c_0 = 7.2\text{\AA}, \beta = 100^\circ 12'.$$

#### CRYSTAL STRUCTURE OF ENDELLITE AND HALLOYSITE

The atomic arrangement in endellite was first studied by Mehmel,<sup>5</sup> who suggested that it is formed of alternate  $\text{Al}_2(\text{OH})_6$  and  $\text{Si}_2\text{O}_3(\text{OH})_2$  layers. Hendricks<sup>3</sup> showed that this type of structure does not account for the intensities of the (001) reflections and proposed in its place one in which  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  layers, similar to those of kaolinite, are interleaved with layers of water molecules. For the latter structure the computed and observed intensities are in agreement.

An alternative structure for endellite was proposed by Edelman and Favejee,<sup>6</sup> who considered it made up of  $\text{Al}_2\text{Si}_2\text{O}_4(\text{OH})_6$  layers with possibly some water adsorbed between layers. There are a number of objections to the structure. It does not explain the intensities of the (001) reflections and, in addition, calculations show that the second order should have an appreciable intensity. Actually, this reflection, which should appear with a spacing of  $5.05\text{\AA}$ , is not present. This proposed structure, moreover, leads to a composition of  $\text{Al}_2\text{Si}_2\text{O}_4(\text{OH})_6 \cdot X\text{H}_2\text{O}$ , which is not in agreement with the probable water content as adduced in the last section. Perhaps worst of all, it is not a structure that by loss of water could form halloysite with a separation of silicate layers near  $7.2\text{\AA}$ .

Part of the confusion concerning the structure of these minerals arises from the fact that the powder patterns of kaolinite and halloysite differ only in the character and strength of the reflections from lattice planes oblique to the base. They are always diffuse and weak in halloysite, whereas the corresponding reflections in kaolinite are usually sharp.<sup>11</sup> These diffuse reflections are evidence of great disorder in the stacking of the  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  layers. There appears to be no essential objection to the structure of endellite originally proposed by Hendricks<sup>3</sup> and to the conclusions that halloysite is a kaolin-type mineral and that it usually has considerable disorder in the stacking of the silicate layers.

The refractive index calculated for  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ , assuming a unit structure having  $a_0 = 5.1\text{\AA}$ ,  $b_0 = 8.9\text{\AA}$ ,  $c_0 = 10.25\text{\AA}$ ,  $\beta = 100^\circ 12'$ , with  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$  having the molecular refractivity found for kaolinite and that of water, is  $1.490 \pm .005$ .

#### GENESIS OF ENDELLITE AND HALLOYSITE

Evidence that halloysite is formed from endellite is:

1. Samples of halloysite and endellite subjected only to changes brought about by pressure and temperature conditions within the electron microscope have identical geometrical arrangements, crystal habits, and shapes.

2. These habits and shapes are quite different from those of kaolinite, although the latter is almost identical with halloysite in  $x$ -ray structure.

3. Many porcelain-like specimens of endellite-halloysite when their pores are filled with water have the density calculated for endellite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ).

4. The content of the water lost above  $110^\circ$  is always greater in halloysite than in kaolinite.<sup>12</sup>

Ross and Kerr's<sup>7</sup> discussion of the origin of halloysite thus really refers to endellite. To this can be added the surmise that endellite is formed only in the presence of liquid water or an almost saturated vapor.

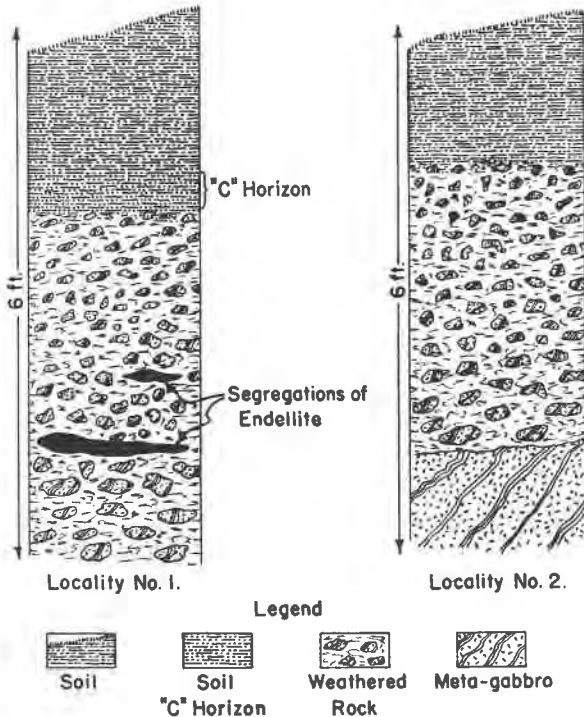
The absence of preferred orientation in a number of the halloysite fragments is shown by the nature of the  $x$ -ray diffraction photographs made on a Weissenberg goniometer, and also by the lack or very low order of birefringence observed in the polarizing microscope. Thus, while the large original pieces probably did not contain voids, they were poly-

<sup>11</sup> Some samples of kaolinite also give diffuse reflections from these planes (private communication from H. F. Carl of the United States Bureau of Mines).

<sup>12</sup> This additional water is probably adsorbed on the very fine material left by dehydration of the endellite since measurements of surface area by the nitrogen adsorption method made by R. A. Nelson on dehydrated endellite from Eureka, Utah, gave 90 sq. meters per gram, which is greater than that of any kaolinite yet measured.

crystalline on a microscopic or possibly sub-microscopic scale. The connected remnants of the crystal shown in Fig. 1, and sketched in Fig. 4, indicate that the original platelike crystal of endellite was at least 2 microns in greatest dimensions.

The genesis of endellite is well illustrated in the occurrence near Rockdale in Baltimore County, Maryland. Here the rocks consist of gabbros



Columnar sections at localities in Baltimore Co., Maryland.

FIG. 6. Columnar sections illustrating occurrence of endellite near Rockdale, Baltimore County, Maryland.

which have undergone varying degrees of metamorphism. Endellite occurs as segregations in the zone of weathered rock, or as small pockets disseminated in the weathered rock itself. Columnar sections illustrating the occurrence are given in Fig. 6.

*Locality No. 1.* The specimen was taken from a trench, along the west side of the road from Rockdale to Scotts Level, at a point 250 feet south of the intersection of the road and the stream. The site is on the wooded flank of a hill along which a trench about 6 feet deep had been dug for some distance up the hill. The rock from which the endellite was derived

is an epidote amphibolite. This rock has a porphyroblastic texture, a fine to medium grain size, and a blackish green-gray color. The principal constituent is hornblende with a well developed prismatic cleavage and strong pleochroism (Z= deep bluish green, Y= Yellowish green, X= pale greenish yellow). Some of the crystals possess schiller inclusions, a relic of the former hypersthene. It is biaxial negative, with  $2V$  almost  $90^\circ$ , and the  $\beta$  index of refraction 1.661. Epidote occurs as subhedral grains and is abundant in the plagioclase, from which it is derived through metamorphism. The epidote is optically biaxial;  $2V$  is variable but near  $90^\circ$ , and  $\beta$  is 1.734. Plagioclase of bytownite composition,  $Ab_{24}An_{76}$ , occurs as lath-shaped crystals showing good twinning. It contains epidote grains and tiny needles of actinolite showing extinction angles up to  $21^\circ$ . The accessories are sphene and magnetite. A micrometric analysis made with the Wentworth-Hunt recording micrometer is given in Table 5, and a photomicrograph of a typical thin section is shown in Fig. 7, b.

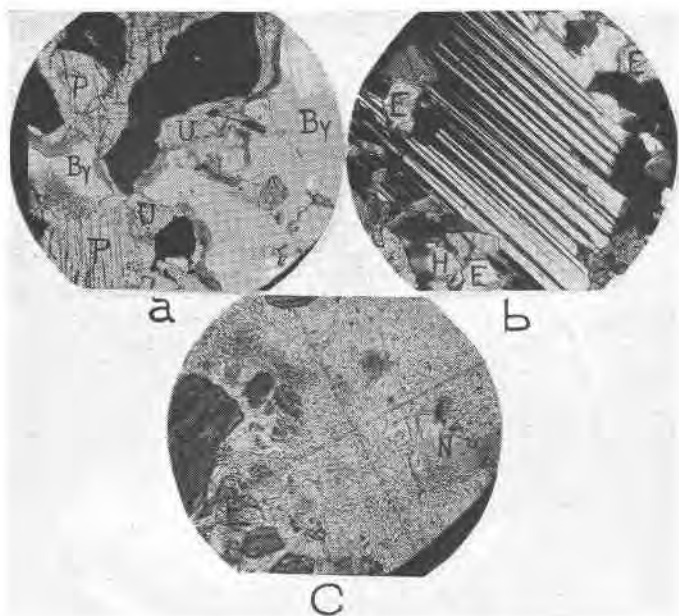


FIG. 7. Photographs of thin sections from rocks occurring at Rockdale, Maryland.  
 (a) *Uralitized hyperite*. Opaque areas are magnetite, pyroxene (P), showing uralite (U) rims, set in a bytownite (By) base.  
 (b) *Epidote amphibolite (meta-gabbro)*: Epidote (E) developing at the expense of plagioclase through metamorphism. Hornblende (H) exhibits lower relief.  
 (c) *Weathered epidote amphibolite*. Displaying "worms" of kaolinite in a base of endellite and halloysite with some nontronite.

As this rock weathers, its color lightens and it develops a mottled appearance of white areas in a grayish green base. The hornblende, still the dominant constituent, is similar to that in the fresh rock except for incipient alteration, in part to a brownish aggregate which is here considered to be nontronite, and in part to iron oxides. The plagioclase is in various stages of freshness, but is being replaced by the clay minerals. The magnetite and sphene



are accessories. The mineralogical composition is given in Table 5, and a photomicrograph of a thin section is shown in Fig. 7, *c*.

The suite of clay minerals is distinctly unique. "Worms" of kaolinite are embedded in a colorless base made up in part of a slightly birefringent halloysite and in part of isotropic endellite. It was from such pockets as these that endellite was obtained for the various physical and chemical measurements here described. The other minerals show little if any evidence of alteration. There is some nontronite in this section. It has a dirty brown color, a more or less speckled appearance, aggregate polarization, and a fibrous crenulated structure. Small spherulites of nontronite were observed. The kaolinite has the following optical properties:  $\alpha = 1.565$ ,  $\beta = 1.572$ .

Mottled boulders of this weathered rock, originally containing endellite, had been excavated and left by the side of the road. Within the course of several weeks the boulders had disintegrated to white powdery halloysite and the unlocked accessories.

*Locality No. 2.* This is roughly 600 feet up the hill in the direction of Rockdale. A columnar section at this station is shown in Fig. 6. The rocks dip gently into the hill and lie above the epidote amphibolite of locality No. 1. The rock here is a uralitized hyperite (Fig. 7, *a*). A single pegmatite dike of variable width, averaging two feet, was found cutting the uralitized hyperite and dipping into the hill at an angle of about  $75^\circ$ . It consists of coarse muscovite, quartz, and feldspar, the whole mass being stained somewhat by iron oxides.

The uralitized hyperite is purplish gray in color, medium in grain size, and xenomorphic in texture. It consists of pleochroic hypersthene ( $Z =$  grayish green,  $Y =$  almost colorless,  $X =$  light pink), diallage, and a bytownite of slightly variable composition but approximately  $Ab_{21}An_{79}$ . The hypersthene grains are frequently surrounded by coronas of secondary fibrous hornblende (uralite). The accessories are magnetite, biotite, and apatite. The mineralogical composition of this rock is given in Table 5. This rock weathers to give endellite. It is thus apparent that the so-called gabbros and meta-gabbros of Baltimore County may yield endellite on weathering. Both rocks described here contain a highly calcic plagioclase (bytownite) that is altering in place to form endellite. At one of the localities the endellite has partially segregated among the weathered rock fragments. At both localities it is disseminated throughout the weathered rock and either it or halloysite is present in the "C" horizon of the soil.

The pH of the weathering rock was near 6.4 and the weathering material was wet even after a prolonged dry period of the preceding summer. The location was near the bottom of quite a long hill and the presence of rather solid rock near the surface might have caused drainage through the weathering zone. The presence of characteristic "worms" of kaolinite in a base of endellite and halloysite suggests that kaolinite may have been formed by reorganization of the halloysite which, in turn, was the product of partial dehydration of the endellite. Plagioclase feldspars, in a neutral or slightly acid system, and in the presence of water, can weather to give endellite. The tiny specks of alteration products, frequently observed on feldspars and called kaolinite, may be in part endellite or halloysite. The chemical character of the liquid phase and the ions in solution probably play an important part in determining the course of kaolinization of feldspathic materials.

#### SUMMARY

Halloysite,  $Al_2Si_2O_5(OH)_4$ , and endellite,  $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ , have been studied by means of chemical, electron-microscopic, x-ray diffraction, and petrographic methods. The observations indicate that halloysite is formed by dehydration of endellite.

TABLE 5. MICROMETRIC ANALYSES, EXPRESSED IN WEIGHT PER CENT, OF THE SEVERAL ROCKS OCCURRING AT ROCKDALE, MD.

	Epidote amphibolite	Weathered epidote amphibolite	Uralitized hyperite
	Per cent by weight	Per cent by weight	Per cent by weight
Hornblende	69.6	53.4	10.6 (uralite)
Plagioclase	10.3 Ab <sub>24</sub> An <sub>76</sub>	5.7 Ab <sub>26</sub> An <sub>74</sub>	48.3 Ab <sub>21</sub> An <sub>79</sub>
Epidote	18.6	3.3	
Sphene	0.4	1.0	
Magnetite	1.1	0.3	5.0
Endellite	—		
Halloysite	—	28.6	
Kaolinite	—		
Nontronite and small amounts of iron oxide stains	—	7.7	
Biotite	—		0.4
Pyroxenes	—		35.7
	100.00	100.00	100.00

Halloysite has the same type of aluminum silicate layers as kaolinite, but the layers usually are superimposed in a less orderly manner. Endellite has a structure in which kaolinite-type layers alternate with single layers of water molecules.

It is proposed that halloysite be retained as the name for materials similar to the type mineral first described by Berthier. For the more highly hydrated mineral, which has variously been called halloysite and hydrated halloysite, the name endellite is suggested in recognition of one of its discoverers.