

DENSITY AND STRUCTURE OF ENDELLITE

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ABSTRACT

The tubular structure that has been proposed for endellite $[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}]$ will contain considerable space not occupied by the solid phase. Based on the tubular dimensions which have been reported for this material, void space of 30 to 40 percent of the total volume of massive endellite would be anticipated.

Experimental determination of the void space in several samples of an endellite specimen by means of density measurements made on water-saturated samples indicates that the massive mineral contains 10 percent or less void space. It is concluded that endellite does not exist in a tubular form.

When endellite dehydrates to form halloysite $[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]$ there is no appreciable change in the gross volume of the material. The massive halloysite formed, however, contains more than 40 percent void space which is refillable with water. It is hypothesized that endellite may exist in the form of laths with some displacement of the fundamental layer structure. When the endellite dehydrates the laths undergo considerable shrinkage and distortion to give the structures observed in electron micrographs and shadow-cast replicas.

INTRODUCTION

In this paper the term endellite refers to the mineral with the formal composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The term halloysite is used to describe the mineral composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The nomenclature of these minerals has been the subject of conflict for several years (Faust, 1955). The selection of terminology in this work has been made for the sake of clarity and without special regard to the merits of the nomenclature arguments.

One of the early attempts to define endellite structurally by means of x-ray diffraction patterns appears to have been made by Hendricks (1938) although Hofmann, Endell and Wilm (1934) and Mehmel (1935) had previously shown that the hydrated mineral (i.e., endellite) differed from the dehydrated form (i.e., halloysite). Hendricks proposed that endellite consisted of neutral $[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]_n$ layers interleaved with $(2\text{H}_2\text{O})_n$ layers. Brindley and his co-workers (Brindley and Robinson, 1948; Brindley and Goodyear, 1948; Brindley, Robinson, and Goodyear, 1948) extended the structural study of endellite and halloysite and demonstrated that endellite with a normal basal spacing of 10.1Å can be dehydrated readily to form halloysite having a basal spacing of about 7.2Å at temperatures of about 400°C. In fact, endellite partially dehydrates at room temperature if the relative humidity is less than 100 percent. Under these conditions the dehydration is a function of the relative humidity, and Brindley and Goodyear (1948) reported that below 15 percent relative humidity only halloysite with some residual interlayer water was observed.

Through 1948 it was generally held that endellite had a flat-sheet type of

structure, although some workers who had made electron micrographs of the mineral suggested that the observed morphology did not agree too well with the proposed flat-sheet structure (Shaw and Humbert, 1942; Kelley and Page, 1942). However, in 1948 Bates, Hildebrand, and Swineford (1949) presented a new concept of the structure of endellite based on electron micrographs of many samples of the material. Their hypothesis, which is stated more completely in a later paper (1950), depicted endellite in the form of hollow tubes. When the endellite dehydrated to form halloysite, as it appeared to do in the electron microscope, these tubes tended to split and unroll. Measurement of the dimensions of the tubes appearing in electron micrographs indicated that the outer diameters varied from 1900Å to 400Å, and the inner diameters varied from 1000Å to 200Å, depending upon the source of the sample.

With a material that dehydrates as readily as endellite, it is unavoidable in direct electron microscope work on this substance and in replica techniques involving vacuum treatment of the samples that the material actually observed is either completely or partially dehydrated endellite. In fact, the ease with which endellite dehydrates below 100 percent relative humidity makes difficult any observations on "pure" endellite. In order to postulate anything about the morphology of endellite it is necessary to infer a relatively high degree of correspondence between the dehydrated morphology observed and the original hydrated material. This problem has long been recognized by workers in the field, but until a satisfactory replica technique (which does not dehydrate the endellite) is developed the problem remains. However, another approach which may establish the probability of a tubular structure for endellite is based on the determination of void volume (i.e., space not occupied by endellite) in massive endellite. Superficially, at least, the method involves a relatively direct density measurement on fully hydrated endellite. The procedure (Pundsack, 1956) is based on the premise that a massive structure composed of efficiently packed hollow tubes will contain a relatively large and measurable void volume.

CHARACTERIZATION OF SAMPLES

A number of samples of endellite from different localities were obtained. All the samples were received in a well-moistened condition and precautions were taken to prevent any dehydration of the specimens. The initial characterizations were made by means of x-ray spectrometer patterns of the materials. The samples were maintained in an atmosphere saturated with water vapor while the spectrometer patterns were obtained. Endellite and halloysite can be distinguished readily by the basal spacing of about 10.1Å in the former compared to a basal spacing of about 7.2Å in the latter. Despite the precautions taken to prevent dehydration, all the samples contained some halloysite as evidenced by the presence of the 7.2Å spacing in the x-ray spectrometer patterns. The purest endellite sample proved to be a specimen from the Dragon Mine, Eureka, Utah, and density measurements were confined to it. The fact that all the endellite specimens contained halloysite is consistent with the observations of Brindley

and Goodyear (1948) who noted the same phenomenon in their samples. Whether the halloysite was present in the original material at the time of collection or formed in the sample as a result of dehydration during subsequent handling is not known. The difficulty of obtaining endellite free from halloysite created a problem concerning the usefulness and meaning of void space determinations made on samples of mixed composition. This problem will be discussed in the next section. X-ray diffraction data for the Eureka, Utah, specimen are listed in Table 1 and the analysis of the specimen is shown in Table 2.

TABLE 1. — X-RAY DIFFRACTION DATA, ENDELLITE, DRAGON MINE, EUREKA, UTAH

<i>d</i> , Å	<i>l</i>
10.14	V.S.
7.08	W. (halloysite)
4.39	}
4.35	
4.19	M.S.
3.57	M.
3.35	M.S.
2.55	M.
2.49	M.
2.45	V.W.
2.34	W.
1.68	}
1.67	
1.64	
1.48	M.S.
1.28	V.W.
1.23	V.W.

TABLE 2. — CHEMICAL ANALYSIS, ENDELLITE, DRAGON MINE, EUREKA, UTAH

	Percent
SiO ₂	37.70
Al ₂ O ₃	33.52
Fe ₂ O ₃	0.04
MgO	0.01
CaO	0.01
Na ₂ O	0.09
TiO ₂	0.01
P ₂ O ₅	0.62
H ₂ O*	28.0
	100.0

* This analysis is based on a saturated sample of endellite at 100 percent relative humidity. If the sample is dehydrated to approximate equilibrium (520 hours) over anhydrous Mg(ClO₄)₂ it loses water to the extent of 15.6 percent by weight of the original sample.

THEORETICAL

It can be shown that when hollow cylindrical tubes with an outer radius r_1 and an inner radius r_2 are placed in hexagonal close-packing the relationship between the gross volume V_G occupied by a bundle of the tubes and the volume of solid material V_S is

$$\frac{V_G}{V_S} = \frac{2\sqrt{3}}{\pi} \left(\frac{r_1^2}{r_1^2 - r_2^2} \right) \quad (1)$$

When specific density values are substituted for specific volumes Equation 1 becomes

$$D_S = \frac{2\sqrt{3}}{\pi} D_G \left(\frac{r_1^2}{r_1^2 - r_2^2} \right) \quad (2)$$

In order to use Equation 2 to make some approximate calculations for hypothetical endellite tubes of various dimensions it is necessary to know the absolute density, D_S for endellite. The unit-cell dimensions for endellite may be employed to calculate D_S . The unit-cell dimensions published by Mehmel (1935) lead to a density of 2.11 g/cc for endellite. This is the value used by Alexander and others (1943) in their investigation of endellite. The unit-cell dimensions proposed by Brindley and Robinson (1948) yield $D_S = 2.14$ g/cc. The density of endellite computed as an additive value of 87.75 percent halloysite plus 12.25 percent water is about 2.19 g/cc. Unit-cell dimensions from our own x-ray data agreed with those of Brindley and Robinson; therefore, the absolute density of endellite was taken as 2.14 g/cc. Subsequent data will show that the choice of a density value from those listed above is not highly critical to the final conclusions drawn in this work.

The values for void fractions in endellite listed in Table 3 were calculated using some of the outer and inner radii that have been reported for endellite. It can be seen that tubular structures lead to massive structures having appreciable void space. The D_G values in Table 3 are calculated assuming that all the void space is occupied by air. Since endellite appears to exist only in a water-saturated condition it is probable that any void space in the sample will be occupied by water rather than air. Thus, the total volume of a block of massive endellite is best represented by

$$V_T = xV_S + (1-x)V_W + V_V \quad (3)$$

where V_T = total volume of block of endellite (cc/g)

V_S = specific volume of endellite (cc/g) = $1/2.14 = 0.468$ cc/g

V_W = specific volume of water occupying voids (1.0 cc/g)

V_V = volume of air-filled voids per gram sample

x = mass of solid endellite per gram sample

From Equation 3 it appears that measurement of the density of a water-saturated sample of endellite will indicate whether the specimen contains void space. By assuming that all the void space is occupied by water (i.e., $V_V = 0$), the ex-

TABLE 3. — MINIMUM VOID FRACTIONS IN "TUBULAR" ENDELLITE OF VARIOUS DIMENSIONS

$r_1(A)$	$r_2(A)$	D_a	Percent Void Space
200	100	1.46	31.8
300	200	1.08	49.5
400	200	1.46	31.8
500	300	1.25	41.6
800	500	1.19	44.3

perimental data can be used to calculate the "free" water present in the sample, and this value can then be checked experimentally by means of an ignition loss determination. For example, if one hypothesizes the existence of an endellite sample with 30 percent void space the measured density would be 1.49 g/cc assuming air-filled voids and no liquid penetration of the voids during the density determination. However, if the voids were filled with water prior to the density determination, the observed density would be 1.80 g/cc. The saturated sample would contain 16.7 percent by weight "free" water, a quantity which would show up readily on an ignition loss determination. If the saturated sample contained a mixture of water-filled and air-filled voids the experimental density would be between 1.49 and 1.80 g/cc and the "free" water content would be less than 16.7 percent.

EXPERIMENTAL

Experimental determinations of density values for the Eureka, Utah, endellite were made by shaking a moist porcelainlike solid piece of the specimen as free of excess water as possible and then carefully sorbing any large visible drops of water from the surface of the solid with the corner of absorbent paper. The sample then was weighed and covered with water in a pycnometer unit. This entire operation was accomplished in less than two minutes. After vacuum outgassing the sample in contact with water to remove air from the system, the density of the sample was determined. The densities of two different blocks of the Eureka, Utah, material determined in this way were 2.09 g/cc and 2.10 g/cc, respectively. These values compare well with a density of 2.11 g/cc reported for endellite by Alexander and others (1943). After the density had been determined, both samples were removed from the pycnometer, shaken free of excess water and reweighed. In both specimens the weights were within 1 percent of the original weights of the samples. This indicates that the samples had not sorbed any more water than they contained originally. The saturated endellite was ignited at 1050°C and found to have an ignition loss of 28.0 percent based on the saturated sample weight.

If the samples examined were "pure" endellite the use of Equation 3 to calculate void space and "free" water content would be valid without further justification. However, the x-ray diffraction pattern of this material indicates that it

contains some halloysite (i.e., the dehydrated form of endellite). This would invalidate void space determinations using Equation 3 were it not for the following relationship. Alexander and others (1943) have shown that when endellite in a given specimen dehydrates to form halloysite there is no over-all volume change in the sample and the submicroscopic voids that are formed are completely refillable with water. Thus, a specimen of halloysite formed by dehydrating endellite will have the same over-all water content and density as the original endellite if the halloysite is resaturated with water.¹ This observation by Alexander and his co-workers was confirmed with the material employed in this work. A sample of endellite was dehydrated over anhydrous magnesium perchlorate to form halloysite. The water loss during this operation was 15.6 percent. The density of the halloysite determined in water was 2.56 g/cc. The density of the original endellite was 2.10 g/cc; hence the density of 2.56 g/cc for the dehydrated material is in the range which one would expect for the loss of 15.6 percent water with a specific volume of 1 cc/g from the original material. The fact that this value was observed in experimental studies meant that in the density determination water was penetrating the voids in the halloysite equivalent to the space created by the loss of 15.6 percent water from the original endellite. This was demonstrated by the simple expedient of pouring off the excess water from the saturated halloysite sample and weighing the wet specimen. It had a weight within 3 percent of the original endellite from which it was formed.

CONCLUSIONS

Thus, it appears that any halloysite in the Eureka, Utah, sample behaves as if it were endellite insofar as density determinations made on the water-saturated material are concerned. Equation 3, therefore, may be used to calculate void space in the endellite specimens from Eureka, Utah. Taking the experimental density of 2.09 g/cc and substituting the reciprocal of this in Equation 3 (letting $V_v = 0$)

$$\begin{aligned} 0.479 &= 0.467x + 1 - x \\ x &= .521/.533 = 0.978 \end{aligned}$$

On the basis of density measurements, then, the sample is 97.8 percent endellite,² and it contains a maximum of 2.2 percent "void" water (i.e., water in excess of formula water). Ignition of this sample yielded an over-all water loss of 28.0 percent. The theoretical total formula water content of endellite is 24.5 percent. Thus, the ignition loss value indicates an excess water content of about 4.6 percent compared to a value of 2.2 percent calculated from the density measurements. Considering the uncertainties and assumptions involved these values

¹ The halloysite does not rehydrate to form endellite. The saturated halloysite specimen merely contains "free" water equivalent in weight to that present in the original endellite specimen.

² Endellite is used here to refer to the endellite-halloysite mixture of the original sample since water-saturated halloysite behaves as if it were endellite in the density measurements.

are in good agreement. The 2.2 percent excess water value indicates a void fraction of 4.6 percent and the 4.6 percent water value leads to a void fraction of about 9.4 percent. The significant point about these void fraction values is that neither one is close to the void fractions required by hollow tubes. Thus, it can be concluded that endellite does not possess a tubular structure.

A plausible structure for endellite may be advanced by considering the solid to exist as laths made up of sheets of the composition proposed by Hendricks (1938) and more fully elaborated by Brindley and Robinson (1948). Probably these highly elongated sheets have a certain degree of randomness in the direction of stacking. At least the x-ray diffraction pattern shows some evidence of randomness in the endellite structure. When the endellite undergoes dehydration the laths are subjected to considerable shrinkage and distortion. This leads to the structures that are viewed in halloysite samples.

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