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## ON THE CRYSTAL STRUCTURE OF THE CLAY MINERALS: DICKITE, HAL- LOYSITE AND HYDRATED HALLOYSITE

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DICKITE,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

Four distinct clay minerals, kaolinite, nacrite, dickite,<sup>1</sup> and halloysite,<sup>2</sup> are formed by superposition of layers having the ideal composition,  $[(\text{OH})_4\text{Si}_2\text{Al}_2\text{O}_5]_n$ . The structure within the layer was suggested by Pauling,<sup>3</sup> and Gruner<sup>4</sup> using powder photographs worked out more detailed structures for the first three minerals. His result for dickite has been questioned by Ksanda and Barth<sup>5</sup> who obtained excellent data from single crystals. Mr. Ksanda of the Geophysical Laboratory, Carnegie Institution of Washington, has kindly furnished unpublished x-ray diffraction data on dickite for this further study.

Gruner, and Ksanda and Barth are in essential agreement on the dimensions of the unit of structure. Ksanda and Barth, however, consider the mineral to be monoclinic holohedral since it failed to show a piezoelectric effect, the suggested space group being  $C_{2n}^6-C2/c$ . This possibility is eliminated since single crystals show a strong pyroelectric effect when tested by the Martin method.<sup>6</sup> Since the absent reflections require a glide reflection plane the space group must be  $C_s^4-Cc$  as found by Gruner.

That the structure is really formed by polar superposition of  $[(\text{OH})_4\text{Al}_2\text{Si}_2\text{O}_5]_n$  sheets is shown by the intensities of  $(00l)$  reflections. Barth and Ksanda noted up to the 20th order from this plane and showed that calculated and observed intensities were in moderate agreement. The following parameter values lead to excellent agreement as shown by Table 1; all atoms in general positions with  $c$  parameters for  $\text{Si}_1$ ,  $\text{Si}_2 = .00$ ;  $\text{O}_3$ ,  $\text{O}_4$ ,  $\text{O}_5 = .037$ ;  $\text{O}_1$ ,  $\text{O}_2$ ,  $(\text{OH})_1 = -.110$ ;  $(\text{OH})_2$ ,  $(\text{OH})_3$ ,  $(\text{OH})_4 = -.258$  and  $\text{Al}_1$ ,  $\text{Al}_2 = -.191$ . It follows from these parameter values and the close approach of the  $a_0$  and  $b_0$  dimensions to the ideal values that the structure of the layer must be close to that suggested by Pauling.

TABLE 1. OBSERVED AND CALCULATED INTENSITIES FOR (00*l*) OF DICKITE,  $\text{CuK}\alpha$  RADIATION

Order of reflection	Calc. Int.	Order of intensities		Estimated intensities
		observed	calculated	
2	53.0	2	2	9
4	77.0	1	1	10
6	13.7	3	3	5
8	13.0	4	4	5
10	6.9	6-7	6	3
12	4.1	6-7	7	3
14	2.2	8	8	2
16	10.5	5	5	4
18	0.4	9	9	1

There are four possible ways of superimposing the  $[(\text{OH})_4\text{Si}_2\text{Al}_2\text{O}_5]_n$  layers, neglecting translations along the  $y$  axis, and these are schematically represented by figure 1, where the arrows represent reflection planes of the layers. The layers moreover can be shifted either by  $+x$  or  $-x$  along the  $a$  axis, the value but not the sign of the shift being fixed by the crystallographic angle  $\beta$ . Gruner's suggested dickite and kaolinite

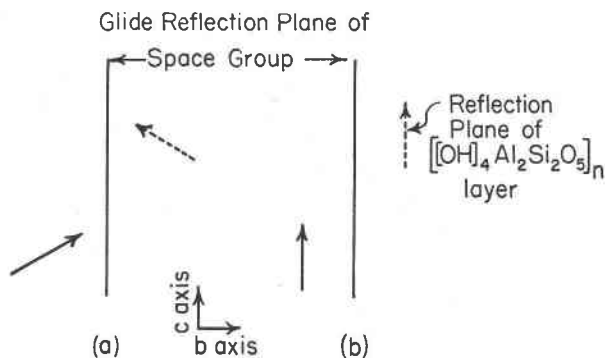


FIG. 1

structures are of type 1, and for convenience the first is designated by  $Aa$ ; the second by  $Bb$ . Shift of the aluminum atoms alone by  $\frac{1}{3}b_0$  within the layers gives structures  $Aa'$  and  $Bb'$  of type 2.

Arrangements  $Bb$  and  $Bb'$  require  $(400) > (200)$  and thus are eliminated for dickite. Both  $Aa$  and  $Aa'$  correctly account for the intensities of the  $(h00)$  and  $(20l)$  reflections as Barth and Ksanda have shown. This is also true for the  $(40l)$  reflections save that  $(40\bar{6})$  absent has too high a

calculated intensity, which, however is quite sensitive to choice of parameters. A most striking feature of the data from dickite is the absence of reflections from  $(06l)$ , with  $l$  odd and from  $(h3l)$  with  $l$  even. This and the high intensity of  $(060)$  requires the layers to be shifted by  $(2n+1)/6$  along the  $b$  axis with respect to each other. Moreover, it is to be noted that intensities of reflections for  $(h3l)$  with  $l$  odd, calculated for any value of  $n$  (Ksanda and Barth's Table 8) are in approximate agreement with the observed values.

Intensities of  $(0kl)$  reflections unfortunately cannot be explained by any choice of  $n$ . This can be seen by consideration of  $(020)$ ,  $(021)$ , and  $(022)$ , Table 2, which have approximately the same intensities and values of  $\sin \theta$ . One is thus left in the position of having eliminated all possible structures strictly compatible with space group requirements.

TABLE 2. CALCULATED VALUES OF  $F^2/16 F^2_{A1}$  FOR SOME PLANES OF DICKITE

Plane	(020)	(021)	(022)
Intensity	ms	ms	ms
$Aa, n=1$	1.5	0.7	3.5
2	0.04	3.2	3.3
3	2.2	2.0	0.4
$Aa', n=1$	7.2	0.0	0.9
2	1.5	3.5	0.2
3	2.0	3.0	0.3
$S, n=1$	2.9	0.0	2.6
2	0.7	2.0	0.6
3	0.9	2.0	0.8

The only escape seems to be that the actual structure is one having an average arrangement required by space group  $Cc$ . In any case the averaged structure would be one based upon arrangements  $Aa$  and  $Aa'$  with shifts of one layer over the other in the  $b$  direction of  $(2n+1)/6$ . The radiation scattered from different parts of the crystal might or might not be coherent, thus the possibility must be borne in mind of summing amplitudes or their squares.

A logical structure might be one in which the aluminum atoms were equally distributed in the positions of  $Aa$  and  $Aa'$ . Intensities calculated assuming coherence of scattered radiation are shown under  $S$  of Table 2, and they are not satisfactory. Statistical structures with all values of  $n$  equally probable would require  $(hkl)$  with  $k$  odd to be absent if the scattered radiation was coherent. Structures  $Aa$  or  $Aa'$  with all possible shifts equally probable but without coherent scattering

from parts of the crystal of different structure would explain the ( $h3l$ ) intensities. Intensities of (020), (021), and (022) are explained by  $Aa$  on this basis but not by  $Aa'$ , the latter making (022) far too weak as can be seen by summing  $Aa'$ ,  $n=1, 2$ , and 3 of Table 2. However, calculations for (023) and (027) eliminated  $Aa$  since the calculated intensities are too great.

Many combinations were tried with assumed coherence of the scattered radiation but none of these was satisfactory. It would seem, therefore, that the presumptive evidence is in favor of structure  $Aa$ , which was selected by Gruner, but  $Aa'$  is not eliminated. In the former structure, as Gruner has pointed out, the hydroxyl groups in the bottom of one layer would be equidistant from two oxygen atoms on top of another layer irrespective of the value of  $n$ . In any case a statistical structure would not be unexpected since forces between the layers are quite small. This is rather similar to the observation that  $CdBr_2$  and  $NiBr_2$  can form structures<sup>7,8</sup> in which the layers are superimposed in a random manner while preserving a close packing of the large bromine ions.

HYDRATED HALLOYSITE,  $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ ,  
AND HALLOYSITE,  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ .

The relationship of halloysite to the other clay minerals has been discussed by Mehmel.<sup>2</sup> Hofmann, Endell and Wilm<sup>9</sup> recognized that a mineral of the ideal composition  $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$  could be obtained but that it readily dehydrates even at 50°C. Mehmel called the dehydrated product "metahalloysite" and indicated that its structure was formed by superposition of  $[(OH)_4Si_2Al_2O_5]_n$  layers as are the other kaolin minerals. The great ease with which this dehydration takes place has not generally been recognized and as a consequence there is some confusion in the literature, but as a rule Mehmel's "metahalloysite" is the usual halloysite of others.

In attempting to verify Mehmel's experimental results a number of x-ray powder diffraction photographs were made of "halloysite" samples kindly placed at my disposal by Dr. Clarence S. Ross, of the United States Geological Survey. The specimens, many of which had been in the laboratory for more than a year, had predominantly the diffraction pattern of kaolinite. Samples 5, 6, 10, 11, 14, 16, and 21 described by Ross and Kerr<sup>10</sup> as halloysite according to microscopic examination, proved to be kaolinite, while samples 2, 8, and 9 were halloysite. Inherent difficulty in differentiating the two by microscopic methods was recognized by Ross and Kerr. A sample of "halloysite" from Anamosa Iowa, supplied by Dr. Ross, while predominantly halloysite, contained some of the hydrated material described by Hofmann, Endell and Wilm.

Professor Hofmann of the Chemical Institute of the University of Rostock most kindly sent me a sample of halloysite from Djebel Debar. Its diffraction pattern agreed entirely with that of hydrated halloysite as described by Mehmel<sup>2</sup> and shown by Hofmann, Endell and Wilm.<sup>9</sup> Moreover, heating to 50° overnight, or exposure for a week to the laboratory air, was sufficient to change the diffraction pattern to that of halloysite. Neither the samples of halloysite from Dr. Ross' collection nor the dried material from Djebel Debar formed hydrated halloysite upon three months' standing in water at room temperature.

TABLE 3. ELECTRON DIFFRACTION DATA FROM HALLOYSITE

Spacing in Å units	Intensity <sup>1</sup>	Probable indices
4.35	vs	(110)(020)
2.56	s	(200)(130)
	A region of broad scattering	
1.654	m	(310)(240)(150)
1.483	ms	(060)(330)
1.298	m	(260)
1.226	m	(170)(350)(420)
1.105	w	(080)(440)
1.023	vw	(280)(370)
0.973	mw	(190)
0.956	mw	(460)(530)
0.872	w	(550)
0.842	vw	(390)(600)(2.10.0)
0.801	vw	(1.11.0)

<sup>1</sup> Abbreviations: v, very; s, strong; m, medium; w, weak.

Electron diffraction data from halloysite are summarized in Table 3. These results were obtained after the manner described in similar work on kaolinite and thus only reflections from (*hk*0) appear. Patterns of halloysite and kaolinite while closely similar have some distinct differences, particularly at the larger angles of scattering. Shishacow<sup>12</sup> has recently reopened the discussion as to whether or not such data are obtained from single layers, which he prefers to consider (Si<sub>2</sub>O<sub>5</sub>)<sub>n</sub> rather than [(OH)<sub>4</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>]<sub>n</sub>. He, however, apparently was not familiar with the experiments on anauxite<sup>13</sup> and mica<sup>14</sup> which demonstrated why only (*hk*0) reflections appear from superimposed layers. Since Mehmel observed (*hkl*) reflections, by *x*-ray diffraction, and these were verified, the question of how the [(OH)<sub>4</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>]<sub>n</sub> layers are superimposed in halloysite is still open.

Electron diffraction photographs were taken using the diffraction pat-

tern of gold for reference and spacings are accurate to about 0.5 per cent on this basis. Shishacow<sup>12</sup> contends that use of gold for reference can lead to errors as great as 1 per cent in the wave length, but the point is not accepted.

Mehmel suggested that the structure of hydrated halloysite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$  consists of  $\text{Al}_2(\text{OH})_6$  and  $\text{Si}_2\text{O}_3(\text{OH})_2$  layers superimposed with the symmetry of the space group  $C_s^3-Cm$ . Dehydration to halloysite was assumed to take place by interaction of hydroxyl groups in one layer with those of another. This appears unlikely since such reactions generally require a large activation energy and thus would not be expected to take place readily at such low temperatures. The reaction would be analogous to the dehydration of gibbsite which takes place at a quite high temperature.

An alternative structure to that suggested by Mehmel would be one in which neutral  $[(\text{OH})_4\text{Si}_2\text{Al}_2\text{O}_5]_n$  layers similar to those of the other clay minerals are interleaved with layers of  $[2\text{H}_2\text{O}]_n$  molecules. Such a structure would be similar to that suggested for the vermiculites by Gruner.<sup>15</sup> A choice between the two possibilities can be made from con-

TABLE 4. CALCULATED INTENSITIES FOR SOME ORDERS OF REFLECTION FROM (00 $l$ ) OF HYDRATED HALLOYSITE

Order	$\frac{\sin \theta}{\lambda}$	C	$F^2/4 \times C^1$		Observed intensity
		$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \times 10^{-3}$	Mehmel	Hendricks	
$n$	.0495	.350	110	720	vs
$2n$	.099	.085	172	7	a
$3n$	.1485	.040	18	73	
$4n$	.198	.019	31	26	

Values of  $z$  parameters

Mehmel			Hendricks		
	at			at	
4Al		.00	4A1		.00
6(OH)		.118	2(OH)+4 O		.11
6(OH)		-.118	6(OH)		-.11
4Si		-.445	4Si		.27
4OH		.40	6O		.33
6O		-.375	4H <sub>2</sub> O		.61 <sup>2</sup>

<sup>1</sup> Scattering factors used are those listed in "The International Tables for Determination of Crystal Structures," Chemical Catalogue Company, New York, 1935.

<sup>2</sup> This value of the  $\text{H}_2\text{O}$   $z$  parameter places the water molecules midway between (OH) groups and oxygen atoms along the axis. Its exact value does not greatly affect the calculated intensities, particularly for  $n$  and  $2n$  reflections.

sideration of the intensities of  $x$ -ray reflections from (00 $l$ ). Relative calculated intensities of reflections according to the two postulates are shown in Table 4; parameter values also being listed.

An intense reflection from a plane with a spacing of 10.1Å is observed on powder photographs of hydrated halloysite. The large value of this spacing, its change upon dehydration, and its orientation in samples of hydrated halloysite formed by settling from water, all suggest that it is an order of (00 $l$ ). Mehemel called it the first order reflection consistent with the requirements of the space group  $C_s^3-Cm$ . The second order reflection is absent. Now Mehemel's structure requires a weak first order reflection and a stronger second order one; his calculated intensity for (00 $l$ ) is apparently in error. The alternative structure correctly explains these intensities. Data are hardly sufficient to permit further analyses of the structures of halloysite or hydrated halloysite.

#### SUMMARY

Dickite is shown to have an atomic arrangement based on space group  $C_s^4-Cc$ . Independent  $[(OH)_4Si_2Al_2O_5]_n$  layers are superimposed in some random manner in which a shift of  $(2n+1/6) b_0$  of one layer with respect to another is preserved.

Hydrated halloysite,  $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ , probably has a structure in which neutral  $[(OH)_4Al_2Si_2O_5]_n$  layers are interleaved with  $[(H_2O)_2]_n$  layers.

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