NOTE ON THE STRUCTURE OF DICKITE AND OTHER CLAY MINERALS

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Diffraction data from x-ray powder photographs of several clay minerals taken by Gruner in combination with the results of a structure analysis of mica as published by Pauling have enabled Gruner to propose plausible structures for kaolinite, dickite, nacrite, vermiculite, talc, and pyrophyllite. However, as is well known, diffraction data from powder photographs are, generally speaking, insufficient for establishing uniquely the crystal structure of monoclinic minerals with many parameters. Until verified by further experimental evidence the structures assigned to these minerals should therefore be regarded as tentative.

On account of the physical properties of the material, it is of course very difficult to obtain single crystal measurements from any of the clay minerals, which is the obvious reason why Gruner used only powder photographs in his investigation. Dickite, however, often seems to grow in somewhat better crystals than any of its congeners, and in a sample of dickite from Pine Knot Colliery, Schuylkill Co., Pa.,[1] we have been able to find individual crystals large enough for a röntgenographic study. A small crystal, 0.4 mm. long, 0.04 mm. broad, and 0.02 mm. thick was mounted on a Weissenberg goniometer,[2] and x-ray photographs were taken with the crystal rotating about the a-axis and also about the b-axis. A Laue photograph normal to the base was also taken. The present paper is concerned with the experimental data thus obtained, and with the agreement between these data and the structure proposed for dickite by Gruner.

OPTICAL PROPERTIES

The plane of the optical axes is normal to the plane of symmetry and inclined 16°, rear to the normal to (001); $b=\gamma$; $a:\beta=16°$;

[1] Beautiful samples of transparent but minute crystals of dickite (labeled Honess & Williams) were kindly sent to us by Dr. F. J. Williams, Pennsylvania State College, to whom we are indebted.

[2] We have used much smaller crystals than that of dickite in our x-ray work. They require a somewhat longer exposure, but the resulting photographs are uniformly more satisfactory than those from large-size crystals (see Fig. 1). Manipulation of such small crystals, however, requires a slightly modified technique compared with that of optical goniometry: the adjustment and orientation can be effected only photographically and with x-rays.

optically positive with $2V = 70°$; no perceptible dispersion. (These measurements were made with a Fedorov stage and are accurate to 2°.) The indices of refraction are: $\alpha = 1.562$, $\beta = 1.565$, $\gamma = 1.571$, all probably within ± 0.001 (Na-light). These properties identify the mineral as dickite.[3]

Unit Cell Dimensions

The geometrical elements of dickite, as derived from our x-ray measurements are given in Table 1. With them are compared the elements derived from measurements with the reflection goniometer by Miers,[4] and the planar spacings of Gruner,[5] who, however, had to use Miers' value of the angle β in order to arrive at the spacings.

Table 1
Geometrical Elements of Dickite

a_0	b_0	c_0	a		b	c		
5.145	8.882	14.337	0.5789	: 1 :		1.6142	96° 45′	Ksanda and Barth
—	—	—	0.5748	: 1 :		1.5997	96° 49′	Miers
5.14	8.94	14.42	—	—		—	—	Gruner

The accuracy of the spacings can be seen from Tables 2 to 5 in which the new x-ray measurements have been listed. The angle β has been determined with an accuracy of $\pm 10'$. Our values lead to a unit cell containing four molecules of the formula $Al_2Si_2O_5(OH)_4$; calculated density: ρ calc. $= 2.618$, density measured by immersion: $\rho = 2.62$.[6]

Atomic Arrangement

The correct space group of dickite, as indicated by the usual x-ray criteria, is either C_{2h}^6 or C_s^4. The difference between them is that C_{2h}^6 has a symmetry center which is lacking in C_s^4. A test for piezo-electricity[7] gave a negative result, which makes C_s^4 improb-

[3] Ross, C. S., and Kerr, P. F., The kaolin minerals: *U. S. Geol. Surv.*, Prof. Paper **165** E, pp. 151–180, 1931.

[4] Miers, H. A., *Mineral. Mag.*, vol. **9**, p. 4, 1890.

[5] Gruner, J. W., The crystal structure of dickite: *Z. Krist.*, vol. **83**, pp. 394–404, 1932.

[6] Dick, Allan B., On kaolinite: *Mineral Mag.*, vol. **8**, pp. 15–27, 1888.

[7] Kindly made by Dr. R. T. Milner of the U. S. Bureau of Chemistry and Soils on two samples of dickite, one from Pine Knot Colliery, Schuylkill Co., Pa., and the other from Red Mountain, Colo.

able. In his paper on dickite Gruner[8] has considered two different structural arrangements which he has called arrangement A and arrangement B, both isomorphous with C_s^4. For both arrangements he has calculated the product $j \cdot F^2$ (the frequency factor times the structure factor) for all reflections down to a spacing of 1.300 using for them the F-values given in Wyckoff's tables.[9] By multiplying

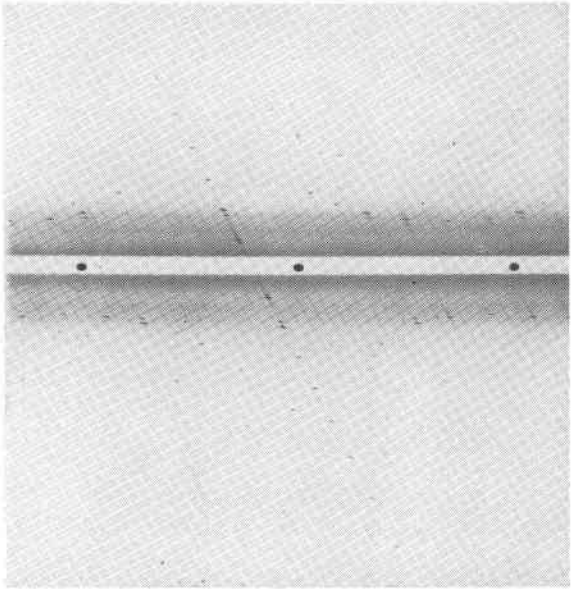

FIG. 1. Equatorial Weissenberg photograph of dickite rotated about the a-axis and taken with copper radiation.

this product by the function of the glancing angle and correcting for the difference in j, we should thus, if either of the two arrangements were correct, obtain figures which would be proportional to the observed intensities.

An inspection of the tables 2 to 8 shows that the agreement between calculated and observed intensities is not satisfactory;[10]

[8] *Op. cit.*

[9] Wyckoff, R. W. G., The Structure of Crystals, 2d ed., **1931**, pp. 95 and 100.

[10] The intensity data listed in Tables 2, 3, 4, and 6, 7, 8 are all based on Weissenberg photographs of one and the same crystal of dickite. Except in Table 6, 10 indicates the strongest and 1 the weakest intensity of any visible spot. The intensities obtained with Cu-radiation are not directly comparable with those obtained with Mo-radiation.

but certain sets of reflections are in better agreement with the calculations than others. In particular it is noticed that the reflections from the base and from the front pinacoid are in fair agreement with the calculations, whereas the reflections from the side pinacoid are very much off (see Tables 4, 5, and 2 respectively). A trial calculation also showed that a slight readjustment of some of the 13 parameter values along the *c*-direction would produce a still better fit between the observed and calculated intensities of the basal reflections.

The new *x*-ray data thus permit of the following conclusions:

(1) The shape and dimensions of the unit cell of dickite have been correctly determined by Gruner.

(2) Dickite is composed of discrete sheets of cations and anions parallel to the *a-b* plane stacked on top of each other in the manner described by Gruner.

(3) The two-dimensional arrangement of the several atoms within each sheet is, however, different from any of the arrangements considered by Gruner.

(4) Since the crystal structures of kaolinite,[11] nacrite,[12] vermiculite,[13] and halloysite[14] have been calculated on the basis of the incorrect structure of dickite, the proposed structures of all these minerals cannot be accepted as being correct without further proof.

TABLE 2

REFLECTIONS FROM THE SIDE PINACOID (EQUATORIAL PHOTOGRAPH OF A SINGLE CRYSTAL OF DICKITE, ROTATED ABOUT THE *a*-AXIS)

Indices	*CuK* radiation	*d*	d_{010}	Intensity		
				Calculated for position		Observed
				A	*B*	
020	β	4.431	8.862			
020	$\alpha_1+\alpha_2$	4.430	8.860	0.0	4.7	4
040	$\alpha_1+\alpha_2$	2.220	8.880	0.8	0.0	1+
060	β	1.478	8.868			
060	$\alpha_1+\alpha_2$	1.477	8.862	6.6	6.6	4+
			$b_0=d_{010}=8.867$Å			

[11] Gruner, J. W., *Z. Krist.*, vol. **83,** pp. 75–88, 1932.

[12] *Z. Krist.*, vol. **85,** pp. 345–354, 1933.

[13] *Am. Mineral.*, vol. **19,** pp. 557–575, 1934.

[14] Mehmel. M., Über die Struktur von Halloysit und Metahalloysit: *Z. Krist.*, vol. **90,** pp. 35–43, 1935.

TABLE 3
REFLECTIONS FROM THE FRONT PINACOID (EQUATORIAL PHOTOGRAPH OF A SINGLE CRYSTAL OF DICKITE ROTATED ABOUT THE *b*-AXIS)

Indices	*MoK* radiation	*d*	d_{100}	Intensity	
				Calculated	Observed
200	$\alpha_1+\alpha_2$	2.555	5.110	5.0	5
400	$\alpha_1+\alpha_2$	1.278	5.112	3.0	2
600	$\alpha_1+\alpha_2$			0.3	0
			$\overline{d_{100}}=5.111$ Å		
			$a_0 = 5.146$Å		

TABLE 4
REFLECTIONS FROM THE BASE

Indices	Radiation	*CuK*$_\alpha$ and *CuK*$_\beta$ radiation		Intensity		*MoK*$_\alpha$ radiation	
		d	d_{001}	Calc.*	Obs.	*d*	d_{001}
002	β	7.119	14.238				
002	$\alpha_1+\alpha_2$	7.120	14.240	17.8	9	7.118	14.236
004	β	3.555	14.220				
004	$\alpha_1+\alpha_2$	3.556	14.224	21.8	10	3.551	14.204
006	β	2.372	14.232				
006	$\alpha_1+\alpha_2$	2.371	14.226	6.0	8	2.376	14.256
008	β	1.780	14.240				
008	$\alpha_1+\alpha_2$	1.779	14.232	1.3	8	1.781	14.248
0010	β	1.422	14.220				
0010	α_1	1.422	14.220	2.0	5	1.423	14.230
0010	α_2	1.423	14.230				
0012	β	1.186	14.232				
0012	α_1	1.186	14.232	1.7	6	1.189	14.268
0012	α_2	1.186	14.232				
0014	β	1.017	14.238				
0014	α_1	1.016	14.224	0.6	3	1.019	14.266
0014	α_2	1.016	14.224				
0016	β	.890	14.240				
0016	α_1	.890	14.240	1.4	6	.890	14.240
0016	α_2	.890	14.240				
0018	α_1	.7915	14.247	0.7	2		
0018	α_2	.7918	14.252				
0020	β	.7126	14.252	.2	1		
		$d_{001}=14.233$ Å				$d_{001}=14.243$ Å	
		$c_0 = 14.332$ Å				$c_0 = 14.342$ Å	

* The calculated intensities of Gruner in this case have been checked by the use of Bragg's *F*-values and the theoretical chemical formula for dickite. This affects the intensities in the decimal place only; some intensities of low spacings have not been calculated by Gruner, for them also Bragg's *F*-values have been used.

TABLE 5

MEASUREMENTS FROM ROTATION PHOTOGRAPHS OF A SINGLE CRYSTAL OF DICKITE

The crystal of dickite rotated about *a*-axis, *CuK* radiation			The crystal of dickite rotated about *b*-axis, *MoK* radiation		
Layer-line	a_0/n	a_0	Layer-line	b_0/n	b_0
1	5.175	5.175	1	8.915	8.915
2	2.565	5.130	2	4.444	8.888
3	1.710	5.130	3	2.972	8.916
		$a_0=5.145$ Å	4	2.222	8.888
			5	1.782	8.910
			6	1.478	8.868
					$b_0=8.898$ Å

TABLE 6

INTENSITY DATA FROM AN EQUATORIAL PHOTOGRAPH OF A SINGLE CRYSTAL OF DICKITE, ROTATED ABOUT THE *a*-AXIS, *CuK* RADIATION

Indices	Calculated for position A	Calculated for position B	Observed
021	4.8	4.8	7
022	4.6	0.4	8
023	2.0	4.6	3+
024	0.7	0.7	6
025	0.6	0.5	2
026	0.4	0.3	3
027	0.2	0.7	0
028	0.4	0.0	3−
029	0.1	0.2	1
041	0.2	0.4	1
042	0.2	0.4	2
043	0.4	0.8	2−
044	0.8	0.0	5
045	0.5	0.6	3+
046	0.0	0.4	1
047	0.5	0.4	3+
048	0.5	0.1	4
061	0.0	0.0	0
062	1.3	1.3	1+
063	0.0	0.0	0
064	0.5	0.5	1

TABLE 7

INTENSITY DATA FROM AN EQUATORIAL PHOTOGRAPH OF A SINGLE CRYSTAL OF DICKITE ROTATED ABOUT THE *b*-AXIS, *MoK* RADIATION

Indices	Calculated	Observed
$20\bar{2}$	7.4	6
202	23.3	10
$20\bar{4}$	0.7	3
204	7.4	6
$20\bar{6}$	2.6	4
206	9.6	7
$20\bar{8}$	4.9	3
208	1.5	2

TABLE 8

INTENSITY DATA FROM THE THIRD LAYER-LINE PHOTOGRAPH OF A SINGLE CRYSTAL OF DICKITE ROTATED ABOUT THE *b*-AXIS, *MoK* RADIATION. DENOTATION OF SYMBOLS: *s*=STRONG; *m*=MEDIUM; *w*=WEAK

Indices	Calculated	Observed
130	0.0	0
$13\bar{1}$	4.3	*m*−
131	7.6	*s*
$13\bar{2}$	0.0	0
132	0.0	0
$13\bar{3}$	9.5	*s*−
133	1.0	*m*
$13\bar{4}$	0.0	0
134	0.0	0
$13\bar{5}$	5.8	*m*
135	2.2	*m*
$13\bar{6}$	0.0	0
136	0.0	0
$13\bar{7}$	9.8	*m*
137	5.0	*m*
$13\bar{8}$	0.0	0
138	0.0	0
$13\bar{9}$	1.5	*w*
139	10.2	*m*−
330	0.0	0
$33\bar{1}$	11.0	*s*
331	2.5	*s*−
$33\bar{2}$	0.0	0
332	0.0	0
$33\bar{3}$	2.2	*m*
333	0.9	*w*
$33\bar{4}$	0.0	0
$33\bar{5}$	1.7	*m*
$33\bar{6}$	0.0	0