THE UNIT CELL OF DICKINSONITE

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The crystallography of dickinsonite has been described by G. J. Brush and E. S. Dana (1878) and (1890). The material examined by them was unsatisfactory for an accurate determination of the elements. In the course of my investigation of the minerals of the chemical type $A_3(XO_4)_2 \cdot nH_2O$, dickinsonite from Poland, Maine, was studied by x-ray diffraction methods to see whether it properly belonged in the type. The conclusion is that it does not, and for that reason the data obtained are given here.

The type Branchville material in the Harvard collection was not suitable for accurate work. A powder picture of the type material, however, proved to be identical with one of dickinsonite from Poland, Maine, which had been described by Berman and Gonyer (1930). Two crystals of the Poland material were studied morphologically, and x-ray diffraction pictures were obtained from one of them. Both lines of study gave concurrent results.

The zone [010] was well developed on the crystals, making orientation about the b-axis simple and accurate. Rotation, 0-layer-line, and 1-layer-line pictures were taken about this axis, and rotation and 0-layer-line pictures were taken about the [001] axis. The following constants were derived from these pictures.

$$a_0 = 16.70 \text{ Å}$$
$$b_0 = 9.95 \text{ Å} \quad a_0 : b_0 : c_0 = 1.695 : 1 : 2.507$$
$$c_0 = 24.69 \text{ Å}$$
$$\beta = 104°41'$$

The reflections observed on the Weissenberg pictures are:

hkl with $h+k$, even
$h0l$ with h, even and l, even
$h00$ with h, even
$0k0$ with k, even
$00l$ with l, even

The crystals are holohedral, and the space group is $C_{2h}^6 - C2/c$.

The elements given by Brush and Dana are:

$$a:b:c = 1.73205:1:1.19806; \ \beta = 118°30'.$$

The correlation between these elements and the elements determined in this study is only approximate, due to the poor character of the crystals measured by Brush and Dana. The basal and side pinacoids, and correspondingly, the a and b axes are identical in the two orientations. Their

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$a(100)$ probably corresponds to my $(\bar{1}01)$, although there is a difference of five degrees between their measured angle to the basal pinacoid and that obtained from my elements. Their $s(\bar{2}21)$ is (110) in the structural lattice. The transformation formula from Brush and Dana to the orientation adopted here is:

$$\bar{1}00/010/102$$

The approximate nature of this transformation is shown by the following tabulation of calculated angles for equivalent faces in the two orientations.

Brush and Dana			Wolfe	
(110) to $(\bar{1}10)$,	113°24′	=	$(\bar{1}11)$ to $(\bar{1}\bar{1}1)$,	113°56′
(001) to $(\bar{2}21)$,	82 02	=	(001) to (110),	82 21½
(001) to $(\bar{1}11)$,	61 08	=	(001) to (111),	61 48
(001) to (100),	61 30	=	(001) to $(\bar{1}01)$,	66 23
$(\bar{1}00)$ to $(\bar{2}21)$,	68 22	=	(101) to (110),	66 00

To check the foregoing work, type Branchville specimens were obtained from the Yale Brush collection through the courtesy of Mr. George Switzer. The measurement of four crystals gave concurrent results with those obtained on the Poland material. One additional form, $p\{111\}$, which is $\{\bar{1}11\}$ of Brush and Dana, was observed in good position and is included in the angle table. The transformed form list of Brush and Dana has not been included in the angle table given below except where the forms have also been observed by me.

Table 1. Dickinsonite-Measured and Calculated Angles

Forms	Size	Quality	No.	Measured		Calculated	
				ϕ_2	ρ_2	ϕ_2	ρ_2
001	L	B	4	75°19′	90°00′	75°19′	90°00′
110	S	E	1	0 16	32 40	0 00	31 38
102	M	D	1	44 08	90 00	44 15½	90 00
302	S	D	1	21 50	90 00	21 22½	90 00
401	S	C	1	8 19	90 00	8 55	90 00
$\bar{1}02$	M	C	1	116 53	90 00	116 40	90 00
$\bar{3}04$	S	C	1	132 22	90 00	131 29	90 00
$\bar{1}01$	M	B	1	141 48	90 00	141 42	90 00
$\bar{2}01$	S	D	1	161 19	90 00	160 18½	90 00
111	S	C	3	— —	38 32	33 12	39 34½
$\bar{1}11$	S	C	1	138 51	33 29	141 42	33 02

$b(010)$ was observed on three Branchville crystals.

The two Poland crystals measured in this study were not completely developed. Consequently, positive orthodomes were found on one crystal, while negative orthodomes appeared on the other. All of the faces could be easily and accurately indexed. The check between measured and calculated values is fairly good, as is shown in Table 1. The x-ray elements were used as a basis for calculation.

The face $(\bar{1}11)$ was small, but definite. The deviation of its measured and calculated ϕ_2 values is probably due to a distortion of the crystal, as it is practically impossible to obtain a crystal which has not been somewhat bent. No evidence of such distortion could be observed on the x-ray pictures, however. Figure 1 is a composite picture of the two Poland crystals.

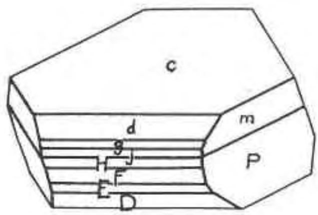

FIG. 1. Dickinsonite from Poland, Maine.

Table 2 gives the angle table for dickinsonite.

TABLE 2. DICKINSONITE—ANGLE TABLE

Dickinsonite—$H_2Na_6Mn_{14}(PO_4)_{12} \cdot H_2O$

Monoclinic: Prismatic—$2/m$

$a:b:c = 1.6784:1:2.4814$; $\beta = 104°41'$; $p_0:q_0:r_0 = 1.4784:2.4004:1$

$r_2:p_2:q_2 = 0.4166:0.6159:1$; $\mu = 75°19'$; $p_0' = 1.5284$, $q_0' = 2.4814$, $x_0' = 0.2620$

Forms		ϕ	ρ	ϕ_2	ρ_2	C	A
c	001	90°00′	14°41′	75°19′	90°00′	—	75°19′
b	010	0 00	90 00	—	0 00	90°00′	90 00
m	110	31 28	90 00	0 00	31 38	82 21½	58 32
d	102	90 00	45 44½	44 15½	90 00	31 03½	44 15½
g	302	90 00	68 37½	21 22½	90 00	53 56½	21 22½
j	401	90 00	81 05	8 55	90 00	66 24	8 55
D	$\bar{1}02$	−90 00	26 40	116 40	90 00	41 21	116 40
E	$\bar{3}04$	−90 00	41 29	131 29	90 00	56 10	131 29
F	$\bar{1}01$	−90 00	51 42	141 42	90 00	66 23	141 42
H	$\bar{2}01$	−90 00	60 49	150 49	90 00	75 30	150 49
p	111	35 48½	71 54	33 12	39 34½	61 48	56 12½
P	$\bar{1}11$	−27 02½	70 15½	141 42	33 02	77 23	115 20

Chemistry. Three reliable analyses of dickinsonite have been made: two by H. L. Wells on material from Branchville, Connecticut, and one by F. A. Gonyer on a sample from Poland, Maine. The specific gravity values given for the Branchville dickinsonite are 3.143, 3.338, and 3.343. That given for dickinsonite from Poland is 3.266. All of the various impurities listed in the several analyses possess a specific gravity lower than that of dickinsonite. Their effect, therefore, would be to lower the determined value. On three separate mineral fragments of undoubted purity from Poland, I obtained a value of 3.38, 14.2 milligrams of selected material from Branchville gave 3.41, which is probably the best value. Using the value of 3.38 in conjunction with a cell volume of 3968.46 Å^3 obtained from the Weissenberg pictures, we obtain $4[H_2Na\ Mn_{14}(PO_4)_{12}\cdot H_2O]$ as the approximate contents of the unit cell. The calculated specific gravity is 3.42. Table 3 gives the derivation of this formula.

TABLE 3. CHEMISTRY OF DICKINSONITE

	1	2	3	4	5	6
FeO	12.36%	13.61%		13.99	15.40	
MnO	31.91	32.44		36.58	37.19	
CaO	2.01	2.21		2.91	3.20	
MgO	1.67			3.37		
ΣA″	47.95	48.26	48.57%	56.85	55.79	56.00
Na_2O	7.42	7.66		19.46	20.10	
K_2O	1.73	1.56		2.99	2.70	
Li_2O	0.20	0.18		1.09	0.95	
ΣA′	9.35	9.40	8.26	23.54	23.75	24.00
P_2O_5	40.88	40.65	41.42	23.40	23.27	24.00
H_2O	1.82	1.69	1.75	8.22	7.65	8.00
Total	100.00	100.00	100.00			

1. Weight percentages—Poland dickinsonite—analyst Gonyer.
2. Weight percentages—Branchville dickinsonite—analyst Wells.
3. Weight percentages—theoretical formula $H_2Na\ Mn_{14}(PO_4)_{12}\cdot H_2O$.
4. No. of molecules in unit cell of "1." $M_0=8130.7$. Sp. Gr. = 3.38.
5. No. of molecules in unit cell of "2."
6. No. of molecules in unit cell of "3." $M_0=8230.6$. Sp. Gr. = 3.42.

The formula given for dickinsonite by Brush and Dana conforms to $A_3(PO_4)_2 \cdot \frac{1}{3}H_2O$, which differs, principally, from the one given in this paper in that the H_2O is distributed between acid water and water of crystallization here, while the earlier authors make it entirely water of crystallization. The necessity for this change is indicated by the valence requirements which may be determined from columns "4" and "5."

References

Berman, H., and Gonyer, F. A. *Am. Mineral.*, **15**, 375 (1930).
Brush, G. J., and Dana, E. S., *Am. Jour. Sci.* **16**, 114 (1878); *Am. Jour. Sci.*, **39**, 213 (1890).