

STUDIES OF BORATE MINERALS (V): REINVESTIGATION
OF THE X-RAY CRYSTALLOGRAPHY OF ULEXITE
AND PROBERTITE*

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ABSTRACT

Ulexite and probertite crystals have been examined by *x*-ray precession methods and earlier findings confirmed. Revised data for the crystallographic elements are as follows: ulexite, $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$, triclinic $P\bar{1}-C_1^1$, $a=8.80_9 \pm 0.02$, $b=12.86 \pm 0.04$, $c=6.67_8 \pm 0.02$ Å, $\alpha=90^\circ 15'$, $\beta=109^\circ 07'$, $\gamma=105^\circ 06'$ (all $\pm 05'$); probertite, $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$, monoclinic $P2_1/a-C_{2h}^5$, $a=13.43 \pm 0.04$, $b=12.57 \pm 0.04$, $c=6.58_9 \pm 0.02$ Å, $\beta=100^\circ 15' \pm 05'$. *X*-ray powder patterns of both minerals have been indexed, and all calculated interplanar spacings are given for $d \geq 2.5$ Å.

INTRODUCTION, EXPERIMENTAL TECHNIQUES, AND ACKNOWLEDGMENTS

In connection with current crystal structure studies of sodium calcium borates, the *x*-ray crystallography of ulexite and probertite have been re-examined and *x*-ray powder patterns of these minerals have been indexed.

Single crystal studies were made on a quartz-calibrated precession camera with both Mo/Zr and Cu/Ni radiations. Film measurements were corrected for horizontal and vertical film shrinkage. A 114.59 mm. diameter powder camera was used with Cu/Ni radiation for the powder films and the measurements were corrected for film shrinkage.

We are grateful to several colleagues at the U. S. Geological Survey for their collaboration during these studies: W. T. Schaller supplied crystals of ulexite and probertite, Mary E. Mrose prepared the *x*-ray powder patterns, H. T. Evans, Jr. contributed helpful discussion, and D. E. Appleman carried out the calculations for *d*-spacings.

SINGLE CRYSTAL STUDY OF ULEXITE

The crystallography of ulexite, $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$, was the subject of a comprehensive study by Murdoch (1940), who summarized earlier findings and compiled crystallographic data based on his own goniometric measurements of terminated crystals and on his measurements from *x*-ray oscillation photographs. Ulexite crystals used in the present study originated at the Baker mine, Boron, California. *X*-ray examination of these crystals shows that ulexite is triclinic and the space group is therefore either $P1$ or $P\bar{1}$. Piezoelectric tests were made of the crystals, using an apparatus of the Giebe-Scheibe type. The negative results of these

* Publication authorized by the Director, U. S. Geological Survey.

tests, considered together with the crystal morphology found by Murdoch (1940), confirm his selection of space group $P\bar{1}$ with cell contents $2[\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}]$. Values of the direct crystallographic elements obtained in the present study are compared in Table 1 with those found by Murdoch (1940); the agreement is excellent.

Table 2 contains a complete set of data for direct and reciprocal cell elements of ulexite, including the direct and reciprocal Cartesian matrices together with the components v_1 and v_2 of the b -axis on the x - and y -axes, respectively, of Cartesian coordinates (Evans, 1948). The six reciprocal cell elements listed in Table 2 were chosen from among all available data as the best measurements, the three reciprocal lengths being those obtained from the present precession x -ray studies and the three reciprocal angles, those found by Murdoch (1940) from goniometric measurements. The six direct cell elements in Table 2 were calculated from the given six reciprocal cell elements. The present calculated density is in much better agreement with the observed density of Murdoch (1940) than was the earlier calculated value.

SINGLE CRYSTAL STUDY OF PROBERTITE

Barnes (1949) examined probertite crystals with precession x -ray techniques using Cu/Ni radiation. He makes no statement regarding

TABLE 1. COMPARISON OF DIRECT CELL ELEMENTS FOR ULEXITE

Triclinic, space group $P\bar{1} - C_i^1, Z = 2[\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}]$		
	Present Study*	Murdoch (1940)†
a	$8.80_9 \pm 0.02 \text{ \AA}$	8.73 \AA
b	12.86 ± 0.04	12.75
c	$6.67_8 \pm 0.02$	6.70
α	$90^\circ 15' \pm 05'$	$90^\circ 16'$
β	$109^\circ 10' \pm 05'$	$109^\circ 08'$
γ	$105^\circ 05' \pm 05'$	$105^\circ 07'$
$a:b:c$	$0.685_0:1:0.519_3$	$0.6855:1:0.5191$
Cell Volume	687.0 \AA^3	676.9 \AA^3
Density (calc.)	1.959 g.cm.^{-3}	1.988 g.cm.^{-3}

* Values of a , b , c , and α were calculated from the reciprocal elements given in Table 2; values for β and γ are readings obtained from the precession camera dial settings.

† Values of a , b , and c were calculated by Murdoch "from the x -ray data using the morphologic axial angles." The axial ratio $a:b:c$ is from goniometric measurements, not from the given axial lengths. Conversion from kX to Ångstrom units has been carried out by the present authors.

calibration of camera or correction for film shrinkage. The direct cell elements which he found are listed in Table 3, column 1; these elements define a direct cell corresponding to the crystal description given by Schaller (1930) as modified by Palache, Berman, and Frondel (1951). The space group assigned by Barnes (1949) is $P2_1/n-C_{2h}^5$. Standard settings for C_{2h}^5 are given in International Tables (1952) as $P2_1/c$ or $P2_1/a$. If the crystal form taken by Schaller (1930) as $\{101\}$ is trans-

TABLE 2. DIRECT AND RECIPROCAL CRYSTALLOGRAPHIC DATA FOR ULEXITE

Triclinic, space group $P\bar{1}-C_i^1, Z=2[\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}]$	
Direct Cell Elements:†	
$a = 8.80_9 \pm 0.02 \text{ \AA}$	$\alpha = 90^\circ 15' \pm 05'$
$b = 12.86 \pm 0.04$	$\beta = 109^\circ 07' \pm 05'$
$c = 6.67_8 \pm 0.02$	$\gamma = 105^\circ 06' \pm 05'$
$a:b:c = 0.685_0:1:0.519_3$	
Volume = 687.0 \AA^3	Density (g.cm. ⁻³), calc. 1.959
	obs. (Murdoch, 1940) 1.955 ± 0.001
Reciprocal Cell Elements:‡	
$a^* = 0.1250_8 \text{ \AA}^{-1}$	$\alpha^* = 84^\circ 20.5'$
$b^* = 0.0809_1$	$\beta^* = 70^\circ 05.5'$
$c^* = 0.1592_6$	$\gamma^* = 73^\circ 53.5'$
$p_0:q_0:r_0 = 0.785_3:0.508_0:1$	
Projection Elements:§	
$x_0' = 0.3467$	$p_0' = 0.8352$
$y_0' = 0.1049$	$q_0' = 0.5403$
$\nu = 73^\circ 53.5'$	
Cartesian Matrices:§	
$v_1 = -0.2774_5$	$v_2 = 0.9607_3$
Direct Matrix:	$\begin{vmatrix} 8.323 & -3.569 & 0 \\ 0 & 12.360 & 0 \\ -2.886 & -0.059 & 6.678 \end{vmatrix}$ (in \AA)
Reciprocal Matrix:	$\begin{vmatrix} 0.12015 & 0 & 0.05192 \\ 0.03470 & 0.08091 & 0.01570 \\ 0 & 0 & 0.14974 \end{vmatrix}$ (in \AA^{-1})

† Direct cell elements were calculated from the six reciprocal cell elements.

‡ Values for a^* , b^* , and c^* are from precession x -ray measurements; values for α^* , β^* , and γ^* are from goniometric measurements by Murdoch (1940). Reciprocal angles obtained from precession film measurements were within $\pm 2.5'$ of Murdoch's values.

§ Values calculated from direct and reciprocal cell elements using equations given by Evans (1948). Projection element values listed by Murdoch (1940) agree with these to ± 0.0001 .

formed to $\{001\}$, the transformation matrix being $\overline{101}/010/001$, the direct cell thus obtained is in the $P2_1/a$ orientation. In both descriptions of the cell the cleavage plane is (110). Table 3, column 2, gives the measurements of Barnes (1949) as transformed to the $P2_1/a$ setting. In the present study probertite crystals from the California mine, Boron, California, were examined and the values of the crystallographic elements found are given in Table 3, column 3, for the $P2_1/a$ setting. A slight improvement in the agreement of calculated with observed density has resulted.

TABLE 3. CRYSTALLOGRAPHIC DATA FOR PROBERTITE
Monoclinic, space group $P2_1/a-C_{2h}^5$, $Z=4[\text{NaCaB}_6\text{O}_9 \cdot 5\text{H}_2\text{O}]$

	Barnes (1949)		Present Study
	(1) $P2_1/n$	(2)* $P2_1/a$	(3) $P2_1/a$
a	13.88 Å	13.44	13.43 ± 0.04 Å
b	12.56	12.56	12.57 ± 0.04
c	6.609	6.609	$6.58_9 \pm 0.02$
β	$107^\circ 40'$	$100^\circ 17'$	$100^\circ 15' \pm 05'$
$a:b:c$ †	1.1053:1:0.5263	1.070:1:0.526	1.068:1:0.524
Volume	1097.2 \AA^3		1095 \AA^3
Density (calc.)	2.126 g.cm.^{-3}		2.131 g.cm.^{-3}
(obs.)	2.141 (Schaller, 1930)		

* Transformed from original values in column (1) with the matrix $\overline{101}/010/001$.

† Schaller (1930) from morphologic measurements found 1.1051:1:0.5237; for the transformed cell, using his average of $99^\circ 53'$ for β , the ratio becomes 1.0683:1:0.5237.

POWDER DIFFRACTION STUDY

A pattern of ulexite was prepared from crystals originating at the Jenifer shaft, Boron, California; a probertite pattern, from type locality crystals found at the Baker mine, Boron, California. A complete set of interplanar spacings for each mineral was calculated down to values of 1.5 \AA on the Datatron computer using a program developed by D. E. Appleman. For ulexite, the reciprocal matrix given in Table 2 was used for the calculations, and for probertite, a reciprocal matrix prepared from the data in Table 3, column 3, was used. Table 4 lists observed and calculated interplanar spacings for ulexite and Table 5, those for probertite. Indexing for probertite is given for both the original cell ($P2_1/n$) and the transformed cell ($P2_1/a$). Observed spacings found in the present

TABLE 4. X-RAY POWDER DATA FOR ULEXITE, NaCaB₅O₉ · 8H₂OTriclinic *PI*: $a = 8.80_9 \pm 0.02$, $b = 12.86 \pm 0.04$, $c = 6.67_3 \pm 0.02$ Å;
 $\alpha = 90^\circ 15'$, $\beta = 109^\circ 07'$, $\gamma = 105^\circ 06'$ (all $\pm 05'$)

Measured*		Calculated†		Measured*		Calculated†			
I	d_{hkl}	d_{hkl}	hkl	I	d_{hkl}	d_{hkl}	hkl		
100	12.2	12.36	010	15	2.914	2.918	022		
15	8.03	8.00	100			2.915	311		
80	7.75	7.77	110			2.888	141		
		6.28	001			2.887	041		
		6.18	020			2.859	240		
30	6.00	6.04	101			2.858	212		
		6.00	110			2.851	321		
7	5.83	5.835	011			15	2.844	2.844	222
6	5.66	5.717	120					2.824	301
		5.688	111					2.809	141
4	5.42	5.388	011	10	2.767	2.769	310		
4	5.19	5.195	111			2.765	241		
		4.639	021			2.746	231		
7	4.60	4.590	121			2.739	320		
15	4.33	4.345	111	15	2.692	2.718	211		
		4.341	120			2.694	022		
		4.281	101			2.692	131		
		4.202	021						
30	4.16	4.163	130			2.672	112		
		4.157	210			2.670	041		
		4.129	211	15	2.661	2.665	300		
		4.120	030			2.659	331		
		4.090	121			2.646	140		
		4.056	201			2.633	102		
3.998	200	2.631	141						
3.939	121	2.625	032						
3	3.89	3.884	220			2.619	231		
		3.799	111			2.615	311		
3	3.79	3.791	221	10	2.597	2.606	132		
		3.627	211			2.597	222		
7b	3.59	3.612	031			2.590	122		
		3.601	131			2.589	330		
		3.528	210	2.580	232				
		3.375	230	2.578	132				
		3.352	131	2.572	150				
		3.334	102	2.539	230				
6	3.29	3.308	130	2.535	312				
		3.299	031						
		3.268	231	5d	2.415				
		3.235	131	3	2.381				
		3.228	112	3	2.350				
		3.210	121, 112	3	2.313				
10b	3.20	3.196	140	3	2.282				
		3.140	002	7	2.232				
		3.117	012	6	2.198				
		3.096	221	6	2.173				
15b	3.10	3.090	040	3	2.129				
		3.045	211	4	2.090				
		3.019	202	3	2.063				
15	3.01	3.013	212	4b	2.023				
		2.999	220	15	1.933				
		2.974	012						
		2.966	221						
		2.948	201, 122						
		2.921	122						

* Corrected for shrinkage; b=broad, d=diffuse. Radiation: Cu/Ni, $\lambda\text{CuK}\alpha = 1.5418$ Å. Lower limit of 2θ measurable: approximately 7° (13 Å).† All calculated lines listed for $d_{hkl} \geq 2.5$ Å.

TABLE 5. X-RAY POWDER DATA FOR PROBERTITE, $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$
 Monoclinic $P2_1/a$; $a = 13.43 \pm 0.04$, $b = 12.57 \pm 0.04$, $c = 6.58_9 \pm 0.02$ Å; $\beta = 100^\circ 15' \pm 05'$

Measured*		Calculated†		
Present Study		Present Study		For $P2_1/n$ (Barnes, 1949)
I	d_{hkl}	d_{hkl}	hkl	hkl
100	9.1 ₂	9.108	110	110
20	6.62	6.608	200	200
		6.484	001	101
		6.285	020	020
		5.849	210	210
10	5.74	5.762	011	111
		5.676	120	120
		5.618	111	011
		5.104	201	101
9	5.02	5.000	111	211
9	4.73	4.729	211	111
10	4.53	{4.554	220	220
		{4.513	021	121
10	4.44	4.442	121	021
		4.264	201	301
2	4.16	4.157	310	310
		4.118	121	221
10	4.05	4.038	211	311
10	4.00	3.994	130	130
		3.962	221	121
6	3.80	3.802	311	211
		3.607	320	320
		{3.539	230	230
20	3.52	{3.529	221	321
		{3.519	031	131
		3.485	131	031
2	3.37	3.368	321	221
3	3.31	{3.322	131	231
		{3.304	400	400
		3.260	311	411
9	3.24	{3.242	002	202
		{3.239	231	131
		3.195	410	410
2	3.18	3.182	401	301
		3.180	112	112
		{3.143	040	040
2	3.14	3.140	202	002
		3.139	012	212
		3.084	411	311
10b	3.08 to 3.04	3.057	140	140
		{3.046	212	012
		3.036	330	330
		2.989	231	331
		2.974	321	421
20	2.935	{2.942	112	312
		{2.924	420	420
		2.913	122	122
20	2.884	{2.889	331	231
		{2.881	022	222
		{2.839	421	321
4	2.837	{2.838	240	240
		2.828	041	141
		{2.810	141	041
35	2.807	2.809	222	022
		2.794	312	112

(continued on next page)

TABLE 5.—(continued)

Measured*		Calculated†		
Present Study		Present Study		For $P2_1/n$ (Barnes, 1949)
I	d_{hkl}	d_{hkl}	hkl	hkl
		2.752	401	501
		(2.727	122	322
6	2.731	2.725	202	402
		2.722	141	241
2	2.697	2.689	411	511
		(2.676	241	141
2	2.666	2.663	212	412
		2.628	331	431
		2.608	322	122
		(2.594	430	430
9	2.591	2.586	132, 510	132, 510
		(2.564	032	232
		2.561	511	411
6	2.558	2.558	340	340
		(2.552	402	202
		2.534	431	331
		2.530	241	341
		2.521	421	521
		2.513	232	032
		2.501	412	212
		2.500	222	422
4	2.473			
7b	2.378 to 2.327			
1	2.241			
1	2.217			
20	2.172			
6	2.138			
6	2.120			
9	2.080			
9	2.020			
20	1.993			
1	1.938			
6	1.860			
6	1.824			
10	1.805			
6	1.777			

* Corrected for shrinkage; b=broad. Radiation: Cu/Ni, $\lambda_{CuK\alpha} = 1.5418 \text{ \AA}$. Lower limit of 2θ measurable: approximately 7° (13 \AA).

† All calculated lines listed for $d_{hkl} \geq 2.5 \text{ \AA}$.

study are in good agreement with those given in previously published powder data. Observed spacings for ulexite are given on ASTM card 2-0914 and in a paper by Baur and Sand (1957). Powder data for prober-tite are listed on ASTM card 4-0107. No indexed patterns for these minerals have previously been available.

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Manuscript received October 16, 1958.