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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, $NaCaB_5O_9 \cdot 8H_2O$, triclinic $P\bar{1}-C_i^1$, $a=8.80_9\pm0.02$, $b=12.86\pm0.04$, $c=6.67_8 \pm0.02$ Å, $\alpha=90°15'$, $\beta=109°07'$, $\gamma=105°06'$ (all $\pm05'$); probertite, $NaCaB_5O_9\cdot 5H_2O$, monoclinic $P2_1/a-C_{2h}^5$, $a=13.43\pm0.04$, $b=12.57\pm0.04$, $c=6.58_9\pm0.02$ Å, $\beta=100°15' \pm05'$. X-ray powder patterns of both minerals have been indexed, and all calculated interplanar spacings are given for $d\geq2.5$ 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, $NaCaB_5O_9 \cdot 8H_2O$, 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

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tests, considered together with the crystal morphology found by Murdoch (1940), confirm his selection of space group $P\bar{1}$ with cell contents $2[NaCaB_5O_9 \cdot 8H_2O]$. 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 $P\bar{1}-C_i^1$, $Z=2[NaCaB_5O_9 \cdot 8H_2O]$		
	Present Study*	Murdoch (1940)†
a	$8.80_9 \pm 0.02$ Å	8.73 Å
b	12.86 ± 0.04	12.75
c	$6.67_8 \pm 0.02$	6.70
α	$90°15' \pm 05'$	90°16′
β	$109°10' \pm 05'$	109°08′
γ	$105°05 \pm 05'$	105°07′
$a:b:c$	$0.685_0:1:0.519_3$	0.6855:1:0.5191
Cell Volume	687.0 $Å^3$	676.9 $Å^3$
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 $\{\bar{1}01\}$ is trans-

TABLE 2. DIRECT AND RECIPROCAL CRYSTALLOGRAPHIC DATA FOR ULEXITE

Triclinic, space group $P\bar{1}-C_i^1$, Z=2[$NaCaB_5O_9 \cdot 8H_2O$]

Direct Cell Elements:†

$a=8.80_9\pm0.02$ Å	$\alpha=90°15'\pm05'$
$b=12.86\pm0.04$	$\beta=109°07'\pm05'$
$c=6.67_8\pm0.02$	$\gamma=105°06'\pm05'$

$a:b:c=0.685_0:1:0.519_3$

Volume = 687.0 Å^3 — Density (g.cm.$^{-3}$), calc. 1.959; obs. (Murdoch, 1940) 1.955±0.001

Reciprocal Cell Elements:‡

$a^*=0.1250_6$ Å^{-1}	$\alpha^*=84°20.5'$
$b^*=0.0809_1$	$\beta^*=70°05.5'$
$c^*=0.1592_6$	$\gamma^*=73°53.5'$

$p_0:q_0:r_0=0.785_3:0.508_0:1$

Projection Elements:§

$x_0'=0.3467$	$p_0'=0.8352$
$y_0'=0.1049$	$q_0'=0.5403$

$\nu=73°53.5'$

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 Å)

Reciprocal Matrix: $\begin{Vmatrix} 0.12015 & 0 & 0.05192 \\ 0.03470 & 0.08091 & 0.01570 \\ 0 & 0 & 0.14974 \end{Vmatrix}$ (in Å^{-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 ±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 $\bar{1}0\bar{1}/010/001$, 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 $P2_1/a-C_{2h}^5$, $Z=4[NaCaB_5O_9\cdot 5H_2O]$

	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±0.02
β	107°40′	100°17′	100°15′±05′
$a:b:c$†	1.1053:1:0.5263	1.070:1:0.526	1.068:1:0.524
Volume	1097.2 Å^3		1095 Å^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 $\bar{1}0\bar{1}/010/001$.

† Schaller (1930) from morphologic measurements found 1.1051:1:0.5237; for the transformed cell, using his average of 99°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 Å 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, $NaCaB_5O_9 \cdot 8H_2O$

Triclinic $P\bar{1}$: $a = 8.80_9 \pm 0.02$, $b = 12.86 \pm 0.04$, $c = 6.67_8 \pm 0.02$ Å; $\alpha = 90°15'$, $\beta = 109°07'$, $\gamma = 105°06'$ (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	$0\bar{2}2$
15	8.03	8.00	100			2.915	$\bar{3}11$
80	7.75	7.77	$\bar{1}10$			2.888	$\bar{1}41$
		6.28	001			2.887	$0\bar{4}1$
		6.18	020			2.859	$\bar{2}40$
30	6.00	6.04	$\bar{1}01$			2.858	$\bar{2}\bar{1}2$
		6.00	110			2.851	$\bar{3}21$
7	5.83	5.835	$0\bar{1}1$	15	2.844	2.844	$\bar{2}22$
		5.717	$\bar{1}20$			2.824	$\bar{3}01$
6	5.66	5.688	$\bar{1}11$			2.809	$1\bar{4}1$
4	5.42	5.388	011	10	2.767	2.769	$\bar{3}10$
4	5.19	5.195	$\bar{1}\bar{1}1$			2.765	$\bar{2}41$
		4.639	$0\bar{2}1$			2.746	$2\bar{3}1$
7	4.60	4.590	$\bar{1}21$			2.739	$\bar{3}20$
15	4.33	4.345	$1\bar{1}1$			2.718	211
		4.341	120	15	2.692	2.694	022
		4.281	101			2.692	131
		4.202	021				
30	4.16	4.163	$\bar{1}30$			2.672	$1\bar{1}2$
		4.157	$\bar{2}10$			2.670	041
		4.129	$\bar{2}11$	15	2.661	2.665	300
		4.120	030			2.659	$\bar{3}31$
		4.090	$\bar{1}\bar{2}1$			2.646	140
		4.056	$\bar{2}01$			2.633	102
4	3.98	3.998	200			2.631	$\bar{1}\bar{4}1$
		3.939	$1\bar{2}1$			2.625	$0\bar{3}2$
3	3.89	3.884	$\bar{2}20$			2.619	$\bar{2}\bar{3}1$
3	3.79	3.799	111			2.615	$\bar{3}\bar{1}1$
		3.791	$\bar{2}21$	10	2.597	2.606	$\bar{1}32$
		3.627	$\bar{2}\bar{1}1$			2.597	$\bar{2}\bar{2}2$
7b	3.59	3.612	$0\bar{3}1$			2.590	$1\bar{2}2$
		3.601	$\bar{1}31$			2.589	$\bar{3}30$
		3.528	210			2.580	$\bar{2}32$
		3.375	$\bar{2}30$			2.578	$\bar{1}\bar{3}2$
		3.352	$1\bar{3}1$	10	2.572	2.572	$\bar{1}50$
		3.334	$\bar{1}02$			2.539	230
6	3.29	3.308	130			2.535	$\bar{3}12$
		3.299	031	5d	2.415		
		3.268	$\bar{2}31$	3	2.381		
		3.235	$\bar{1}\bar{3}1$	3	2.350		
		3.228	$\bar{1}12$	3	2.313		
10b	3.20	3.210	121, $\bar{1}\bar{1}2$	3	2.282		
		3.196	$\bar{1}40$	7	2.232		
		3.140	002	6	2.198		
		3.117	$0\bar{1}2$	6	2.173		
15b	3.10	3.096	$\bar{2}\bar{2}1$	3	2.129		
		3.090	040	4	2.090		
		3.045	$2\bar{1}1$	3	2.063		
		3.019	$\bar{2}02$	4b	2.023		
15	3.01	3.013	$\bar{2}12$	15	1.933		
		2.999	220				
		2.974	012	plus additional lines,			
		2.966	$2\bar{2}1$	all with I$\leq$7			
		2.948	201, $\bar{1}22$				
		2.921	$\bar{1}\bar{2}2$				

* Corrected for shrinkage; b = broad, d = diffuse. Radiation: Cu/Ni, $\lambda CuK\alpha = 1.5418$ 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, $NaCaB_5O_9 \cdot 5H_2O$

Monoclinic $P2_1/a$; $a = 13.43 \pm 0.04$, $b = 12.57 \pm 0.04$, $c = 6.58_9 \pm 0.02$ Å; $\beta = 100°15' \pm 05'$

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	$\bar{1}01$
		6.285	020	020
		5.849	210	210
10	5.74	5.762	011	$\bar{1}11$
		5.676	120	120
		5.618	$\bar{1}11$	011
		5.104	$\bar{2}01$	101
9	5.02	5.000	111	$\bar{2}11$
9	4.73	4.729	$\bar{2}11$	111
10	4.53	4.554	220	220
		4.513	021	$\bar{1}21$
10	4.44	4.442	$\bar{1}21$	021
		4.264	201	$\bar{3}01$
2	4.16	4.157	310	310
		4.118	121	$\bar{2}21$
10	4.05	4.038	211	$\bar{3}11$
10	4.00	3.994	130	130
		3.962	$\bar{2}21$	121
6	3.80	3.802	$\bar{3}11$	211
		3.607	320	320
20	3.52	3.539	230	230
		3.529	221	$\bar{3}21$
		3.519	031	$\bar{1}31$
		3.485	$\bar{1}31$	031
2	3.37	3.368	$\bar{3}21$	221
3	3.31	3.322	131	$\bar{2}31$
		3.304	400	400
		3.260	311	$\bar{4}11$
9	3.24	3.242	002	$\bar{2}02$
		3.239	$\bar{2}31$	131
2	3.18	3.195	410	410
		3.182	$\bar{4}01$	301
		3.180	$\bar{1}12$	$\bar{1}12$
2	3.14	3.143	040	040
		3.140	$\bar{2}02$	002
		3.139	012	$\bar{2}12$
10b	3.08 to 3.04	3.084	$\bar{4}11$	311
		3.057	140	140
		3.046	$\bar{2}12$	012
		3.036	330	330
		2.989	231	$\bar{3}31$
		2.974	321	$\bar{4}21$
20	2.935	2.942	112	$\bar{3}12$
		2.924	420	420
		2.913	$\bar{1}22$	$\bar{1}22$
20	2.884	2.889	$\bar{3}31$	231
		2.881	022	$\bar{2}22$
4	2.837	2.839	$\bar{4}21$	321
		2.838	240	240
		2.828	041	$\bar{1}41$
35	2.807	2.810	$\bar{1}41$	041
		2.809	$\bar{2}22$	022
		2.794	$\bar{3}12$	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	$\bar{5}01$
		2.727	122	$\bar{3}22$
6	2.731	2.725	202	$\bar{4}02$
		2.722	141	$\bar{2}41$
2	2.697	2.689	411	$\bar{5}11$
2	2.666	2.676	$\bar{2}41$	141
		2.663	212	$\bar{4}12$
		2.628	331	$\bar{4}31$
		2.608	$\bar{3}22$	122
9	2.591	2.594	430	430
		2.586	$\bar{1}32$, 510	$\bar{1}32$, 510
		2.564	032	$\bar{2}32$
		2.561	$\bar{5}11$	411
6	2.558	2.558	340	340
		2.552	$\bar{4}02$	202
		2.534	$\bar{4}31$	331
		2.530	241	$\bar{3}41$
		2.521	421	$\bar{5}21$
		2.513	$\bar{2}32$	032
		2.501	$\bar{4}12$	212
		2.500	222	$\bar{4}22$
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			
plus additional lines, all with $I \leq 4$				

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

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

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 probertite are listed on ASTM card 4-0107. No indexed patterns for these minerals have previously been available.

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