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CRYSTALLOGRAPHIC DATA FOR THE IRON BORATE MINERAL, HULSITE[1]

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The iron borate mineral, hulsite, from Brooks Mountain, Seward Peninsula, Alaska, was first described by Knopf and Schaller (1908). The chemical composition initially proposed for hulsite (Knopf and Schaller, 1908; Schaller, 1910) was later found to be incorrect (Schaller, written comm., 1955). The actual chemical composition is similar to that established for the ludwigite-vonsenite series of iron-magnesium-aluminum borates (Leonard and Vlisidis, 1960, 1961; Schaller and Vlisidis, 1961), *i.e.* $(Fe,Mg)_2^{2+}(Fe,Al)^{3+}BO_3O_2$. However, recent chemical studies by Schaller and Vlisidis (written comm., 1962) show that hulsite invariably contains tin (approximately 15 weight per cent SnO_2). Such sizeable amounts of tin have never been reported in analyses of members in the ludwigite-vonsenite series. Leonard, Hildebrand and Vlisidis (1962) state, "Tin is a minor constituent in quite a few members of the ludwigite-vonsenite series . . . and is a major constituent in the borate hulsite." Samples of hulsite from Brooks Mountain were kindly provided by W. T. Schaller for *x*-ray diffraction examinations, and the present note records the results.

The tiny hulsite cleavage fragments available (Schaller series no. H-5, least magnetic material, dimensions about $0.2\times0.2\times0.03$ mm) give excellent *x*-ray diffraction patterns. Single-crystal precession and Weissenberg techniques were used with Zr-filtered Mo radiation and Ni-filtered Cu radiation to obtain the diffraction data. Hulsite has monoclinic symmetry, and the diffraction data are compatible with space groups *P*2, *Pm*, and *P*2/*m*. Spatial considerations derived from accepted

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[1] Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. Crystallographic Data Compared for the Iron Borate Minerals, Hulsite, Vonsenite, and Ludwigite

	Hulsite	Vonsenite	Ludwigite
	Present Study	Takéuchi (1956)[1]	Carvalho da Silva *et al.* (1955)
Symmetry	Monoclinic	Orthorhombic	Orthorhombic
a (Å)	10.684 ± 0.003	9.37	9.25 ± 0.02
b (Å)	3.099 ± 0.001	12.35_7	12.21 ± 0.03
c (Å)	5.438 ± 0.002	3.05_5	2.988 ± 0.01
β	$94° 8.7' \pm 1.5'$	$(90°)$	$(90°)$
Cell Volume (Å³)	179.56 ± 0.07	354	338
Space Group	$P2$, probable; $P2/m$ possible; Pm unlikely	*Pbam*	*Pbam*
Cell Contents	$2[(Fe^{2+}, Mg^{2+}, Fe^{3+}, Sn^{4+})_3 BO_3O_2]$	$4[Fe_{1.25}, Mg_{0.75})^{2+} Fe^{3+}BO_3O_2]$	$4[(Fe_{0.15}, Mg_{1.85})^{2+} (Fe_{0.54}Al_{0.41})^{3+} Ti_{0.04}^{4+}BO_3O_2]$
Density, g cm⁻³			
calc.	—	4.41	3.60
obs.	4.5 to 4.6^2	4.21^3	3.64

[1] The values given by Takéuchi (1956) for a and for the calculated density were corrected by him (written communication, 1958), and the corrected values are given here. The chemical formula was assigned by Takéuchi on the basis of best agreement between observed and calculated structure factors.

[2] Observed density of impure samples, Schaller and Vlisidis (written comm., 1962).

[3] Observed density, Eakle (1920), for crystals of somewhat different composition than that assumed by Takéuchi (1956); observed specific gravity 4.75, for nearly pure vonsenite (Leonard and Vlisidis, 1960).

values for atomic separations suggest that $P2$ is the probable space-group assignment, $P2/m$ possible, and Pm unlikely.

Initial cell constants obtained from precession photograph measurements were refined on a digital computer by least-squares analyses of the x-ray diffraction powder data, using a program developed by Evans *et al.* (1963). The refined values and associated standard errors are compared in Table 1 with single-crystal data for the two iron borates, ludwigite and vonsenite. Clearly, the hulsite data are distinctive. The hulsite cleavage fragments are flattened on {100}, slightly elongated [010], and the flat plates are bound by {001} and unidentified {hk$l$} forms that give a diamond-shaped outline to the platelets.

Bulk samples of hulsite contain included iron oxides, principally mag-

netite (W. T. Schaller, written comm., 1955; Brian J. Skinner, oral comm., 1964), to such an extent that pure hulsite samples are most difficult to obtain. A small selection of hulsite crystals were therefore carefully hand-picked under the microscope for preparation of a powder spindle, and the observed and calculated x-ray diffraction powder data obtained from this spindle are presented in Table 2. All observed lines can be satisfactorily indexed from the single-crystal data for hulsite (Table 1), and the intensities of observed powder diffraction lines agree qualitatively with corresponding intensities of single-crystal diffraction spots. The calculated values (Table 2) are those resulting from the least-squares refinement procedure (Evans *et al.*, 1963).

The only other x-ray diffraction powder data (hereafter called T-G) that have been published for hulsite (Thompson and Gower, 1954) are given in Table 2 for comparison. The general agreement between both patterns is good, but it is not surprising to find that the T-G pattern contains some additional lines, undoubtedly due to the difficulty of obtaining pure hulsite samples. In fact, the strongest line (2.53 Å) of the T-G pattern is not a hulsite line at all, as comparison with the indexed hulsite pattern shows. The 2.53 Å line is actually the strongest line of magnetite (Basta, 1957), and other strong lines of magnetite can now be identified in the T-G listing (Table 2). One weak line (2.75 Å) probably corresponds to the strongest line of the associated mineral, vesuvianite (ASTM card 11-145). Comparison also shows that three other lines in the T-G pattern cannot be attributed to hulsite, magnetite or vesuvianite. These unidentified lines are marked X in Table 2.

Representative, indexed x-ray diffraction powder data for vonsenite (Leonard and Vlisidis, 1961) are also given in Table 2 to show that the hulsite and vonsenite patterns are distinctive, even though some lines do have similar d-spacing values. Patterns of ludwigite (Leonard *et al.*, 1962) show even fewer coincidences with the hulsite lines.

A preliminary examination of the crystal structure of hulsite reveals the presence in the structure of the same kind of layers, consisting of cations, $(BO_3)^{3-}$ triangles, and oxygen anions, that have been described for the known structures of vonsenite (Takéuchi, 1956), breislakite (=vonsenite, Federico, 1957, 1962), and ludwigite (Takéuchi *et al.* 1950; Carvalho da Silva *et al.* 1955). However, in hulsite these layers are oriented differently within the cell, a change that may be related to the change in symmetry from orthorhombic for members of the ludwigite-vonsenite series to monoclinic for hulsite.

TABLE 2. X-RAY DIFFRACTION POWDER DATA COMPARED FOR HULSITE AND VONSENITE

Hulsite: monoclinic, $P2$(or $P2/m$); $a=10.684\pm0.003$, $b=3.099\pm0.001$, $c=5.438\pm0.002$ Å $\beta=94°\ 8.7'\pm1.5'$

Vonsenite: orthorhombic, $Pbam$; $a=9.47\pm0.02$, $b=12.31\pm0.01$, $c=3.07\pm0.01$ Å (Leonard and Vlisidis, 1961)

Hulsite							Vonsenite			
Present Study				Thompson and Gower (1954)			Leonard and Vlisidis (1961)			
Calculated[1]		Observed[2]		Observed[3]			Calculated		Observed[4]	
hkl	d_{hkl}	d_{hkl}	I	Single crystal I	d_{hkl}	I	hkl	d_{hkl}	d_{hkl}	I
100	10.656	10.8	5	vw			110	7.51	7.52	3
001	5.424	—		m			020	6.16	6.16	2
200	5.328	5.35	70	m	H 5.37	5	120	5.16	5.16	50
$\bar{1}01$	4.981	4.99	35	s	H 4.99	1				
101	4.698	4.73	2	w			200	4.735	4.73	13
					X 4.49	4				
$\bar{2}01$	3.946	—		a			210	4.42	—	
					X 3.87	5				
201	3.671	3.68	10	m			—	—	4.13	0.3
300	3.552	3.55	10	m			130	3.77	3.77	4
010	3.099	3.10	15	s	H 3.09	½	220	3.75	—	
$\bar{3}01$	3.075	—		a			—	—	3.38	0.3
110	2.975	2.978	5	w	H, M 2.96	4			3.135	0.5
301	2.878	2.879	5	w			230	3.101	—	
					I 2.75	½				
002	2.712	2.709	5	s			040	3.078	—	
011	2.690	—		w			310	3.059	3.061 br	3
210	2.679	—		m			140	2.927	2.938	2
$\bar{1}02$	2.675	—		w			320	2.809	2.805	4
400	2.664	2.664	100	vs	H 2.67	5	021	2.746	2.753	9
$\bar{1}11$	2.631	—		w						
111	2.587 }			s						
102	2.584 }	2.585	70	w	I, H 2.59	2	240	2.580	2.580	100
					M 2.53	10				
$\bar{2}02$	2.491	2.491	35	s	H 2.49	½	330	2.502	2.494	0.5
$\bar{4}01$	2.463	—		w						
$\bar{2}11$	2.437	2.437	10	s						
							150	2.383 }	2.372 br	25
211	2.368	2.370	20	s	H 2.35	1	400	2.368 }		
202	2.349	2.348	20	s						
310	2.335	—		w						
401	2.326	—		a			410	2.325	2.331	0.5
$\bar{3}02$	2.235	—		w	X 2.24	½	250	2.184	—	
$\bar{3}11$	2.183	2.182	10	s	H 2.18	½	311	2.167	2.171 br	25
500	2.131	2.131	20	s	H 2.13	½				
311	2.109	2.109	5	w	H, M 2.09	½	321	2.072	2.074	18
302	2.084	—		vw			060	2.052	—	

[1] All possible calculated hkl listed for $d_{hkl}\geq1.490$ Å.

[2] Camera diameter, 114.59 mm. Mn-filtered Fe radiation, FeKα, $\lambda=1.9373$ Å. Lower limit of 2θ measurable, approximately 7° (16 Å); lines due to FeKβ radiation omitted from listing. Hulsite from Brooks Mountain, Seward Peninsula, Alaska; powder spindle no. 12498, film no. 16275, prepared by M. E. Mrose, U. S. Geological Survey. Film measurements corrected for film shrinkage. Single-crystal intensities estimated from precession patterns taken with various exposure times; vs =very strong, s =strong, m =medium, w =weak, vw =very weak, a =absent, — =no observation possible.

[3] Camera diameter not given. Manganese oxide filter with iron radiation ($\lambda=1.937$ Å). No cut-off value given. Hulsite from Brooks Mountain, Alaska. Identification of lines made by present author as follows: H =hulsite, M =magnetite (Basta, 1957), X =unidentified, 1 =idocrase (vesuvianite ASTM card 11-145).

[4] Camera diameter, 114.59 mm. Mn-filtered Fe radiation, FeKα, $\lambda=1.93728$ Å. Cut-off at $2\theta\sim5°$. Film measurements corrected for film shrinkage; br=broad. Vonsenite from analyzed sample (field no. J 2.21, Schaller series no. V-15), Jayville, New York. Film no. W-8495, prepared by F. A. Hildebrand, U. S. Geological Survey. Lines identified as due to FeKβ radiation or the presence of hypersthene have been omitted from this listing.

TABLE 2—(*continued*)

		Hulsite					Vonsenite			
		Present Study			Thompson and Gower (1954)		Leonard and Vlisidis (1961)			
	Calculated[1]		Observed[2]		Observed[3]		Calculated		Observed[4]	
hkl	d_{hkl}	d_{hkl}	I	Single crystal I	d_{hkl}	I	hkl	d_{hkl}	d_{hkl}	I
012	2.041	2.039	50	s	H 2.04	4	430	2.051	—	
$\bar{5}$01	2.034	—		m						
$\bar{1}$12	2.025	2.023	10	—						
410	2.020	—		w			160	2.005	2.001	4
112	1.984	—		—						
$\bar{4}$02	1.973	1.972	10	s	H 1.973	½	241	1.975	—	
$\bar{2}$12	1.941	1.942	5	—	H 1.937	½	350	1.941⎫	1.937	18
501	1.936	—		m			331	1.940⎭		
$\bar{4}$11	1.928	—		w			260	1.882	—	
212	1.872	—		—			440	1.876	1.875	3
411	1.860	1.861	10	s	H 1.859	½	510	1.872	—	
402	1.835	1.835	2	m						
$\bar{3}$12	1.813	—		—						
003	1.808	—		vw			520	1.810	1.810	2
$\bar{1}$03	1.804	—		vw			341	1.790	1.793	4
600	1.776	1.777	5	s	H 1.779	½	251	1.780	—	
103	1.762	—		m						
510	1.756	—		w						
$\bar{2}$03	1.751	—		m						
$\bar{5}$02	1.738	—		m	H? 1.732	1				
312	1.729	—		vw			170	1.729	1.728⎫	2
$\bar{6}$01	1.725	—		w			530, 360	1.720	1.719⎭	doublet
							450	1.707⎫	1.699 (or β)	1
$\bar{5}$11	1.701	—		w	M 1.702	½	431	1.705⎭		
203	1.676	—		a			161	1.679	1.678	1
$\bar{4}$12	1.664⎫	1.661	5	s						
$\bar{3}$03	1.660⎭			w			270	1.648	1.660 br (or β)	0.7
601	1.653	—		m			540	1.613		
511	1.642	1.641	10	vs	H 1.640	½	261	1.605⎫	1.602	13
502	1.620	—		m	M 1.610	1	511	1.598⎭		
412	1.579	1.579	10	vs	H 1.580	1	600	1.578	1.579	0.5
303	1.566	—		m						
013	1.562⎫	1.560	10	vs	H 1.559	½				
$\bar{1}$13	1.559⎭			m			521	1.559	1.558	3
020, $\bar{4}$03	1.549	1.549	20	vs, m	H 1.546	½				
610	1.541⎫	1.538	10	s			080	1.539⎫	1.538	18
$\bar{6}$02	1.538⎭			s			370	1.536⎭		
120	1.533	—		a						
113	1.531	—		vw						
$\bar{2}$13	1.524	—		vw						
700	1.522	—		w			180	1.519		
$\bar{5}$12	1.516	—		m			171	1.507⎫		
$\bar{6}$11	1.507	1.506	5	m	H 1.507	½	550	1.501⎬	1.499	13
$\bar{7}$01	1.494	—		w			531	1.500⎭		
021	1.490	—		w						
					M 1.479	4			1.472	1
		1.437	10		H 1.434	1			1.456	0.7
									1 426	0.7
									1.403	9
		plus additional lines, all with I ≤ 5			plus additional lines, all with I ≤ 1				plus additional lines all with I ≤ 9	

gave valuable information from his long experience with various iron borate minerals. He and A. C. Vlisidis made available the unpublished results of chemical analyses, F. A. Hildebrand and M. E. Mrose made x-ray diffraction powder patterns, D. E. Appleman carried out refinement of the powder data, and B. J. Skinner examined polished sections of hulsite samples. I am indebted to C. L. Christ, D. B. Stewart and B. J. Skinner for critical comments on the problems involved.

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