

NOTES AND NEWS

X-RAY CRYSTALLOGRAPHY OF LARDERELLITE, $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4$ *

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Because of the minute size of all larderellite crystals available at the time a recent study of ammonium pentaborates was made (Clark and Christ, 1959), neither density nor single-crystal x -ray data could be obtained. Since that time, however, crystals of suitable size for such studies have been found on a specimen of larderellite from Larderello, Italy. The present note describes the results of examinations of these crystals.

The larderellite specimen was given to W. T. Schaller, U. S. Geological Survey, by Professor Stefano Bonatti, Director, Mineralogical Institute, University of Pisa, Italy. I am most grateful to Dr. Schaller for allowing the use of crystals from this specimen and for providing the prepublication results of chemical analyses carried out by himself and Angelina C. Vlisidis, U. S. Geological Survey, and of density determinations by M. K. Carron, U. S. Geological Survey. I am also indebted to my colleague, C. L. Christ, for numerous valuable suggestions.

Single-crystal x -ray data for larderellite, obtained by precession-camera techniques of the kind described in Clark and Christ (1959), are given in Table 1. Similar data found by Marinelli (1959) are also given in Table 1. His results became known to me only after completion of the present x -ray study, and the agreement is gratifying. The optical orientation given by Marinelli (1959), $Y=b$, and the perfect cleavage parallel to (100) as defined by the cell of Table 1, are both confirmed.

The density for larderellite was obtained with a pycnometer for a 1 g. sample, and the value is 1.905 ± 0.004 g. cm^{-3} (M. K. Carron, oral communication). The chemical formula usually ascribed to larderellite is $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 5\text{H}_2\text{O}$ (Palache, Berman and Frondel, 1951). For the experimentally determined cell volume of 830.9 \AA^3 (Table 1), with two of these formula units per cell, the calculated density is 1.959 g. cm^{-3} , so that the discrepancy between observed and calculated densities is sufficient to cast doubt on this chemical formula. New chemical analyses by Schaller and Vlisidis (oral communication) are compatible with assumption of either $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 4\text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 4\frac{1}{2}\text{H}_2\text{O}$. The calculated density based on two formula units per cell of the former is 1.887 g. cm^{-3} , of the latter, 1.923 g. cm^{-3} ; both these calculated values are in reasonable agreement with that of the observed density.

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

TABLE 1. CRYSTALLOGRAPHIC DATA FOR LARDERELLITE
 Symmetry: monoclinic

	Marinelli (1959)*	Present Study
<i>a</i>	11.65 ± 0.01 Å	11.63 ± 0.03 Å
<i>b</i>	7.63 ± 0.01	7.61 ₅ ± 0.02
<i>c</i>	9.47 ± 0.01	9.447 ± 0.03
β	97°05' ± 15'	96°45' ± 10'
Volume	835.4 Å ³	830.9 Å ³
Space Group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>
Cell Contents	2[(NH ₄) ₂ O · 5B ₂ O ₃ · 5H ₂ O]	2[(NH ₄) ₂ O · 5B ₂ O ₃ · 4H ₂ O]
Density (calc.)	1.95 g.cm. ⁻³	1.887 g.cm. ⁻³
(obs.)	—	1.905 ± 0.004

* Marinelli (1959) interchanged *a* and *c* and therefore assigned space group *P*2₁/*c*; transformation from his cell to the present one: 001/010/100.

Christ (1960) has pointed out that both ammonioborite and larderellite probably contain the pentaborate ion, [B₅O₆(OH)₄]⁻¹, known to exist in the two isostructural compounds, NH₄B₅O₆(OH)₄ · 2H₂O and KB₅O₆(OH)₄ · 2H₂O (Zachariasen, 1938). The structural formulas for larderellite corresponding to the two chemical formulas are, therefore, NH₄B₅O₆(OH)₄ and NH₄B₅O₆(OH)₄ · $\frac{1}{4}$ H₂O, respectively. Four such formula units per cell are required in each case to obtain the calcu-

 TABLE 2. COMPARISON OF SOME CHEMICAL AND PHYSICAL PROPERTIES
 OF THREE AMMONIUM PENTABORATES

	Synthetic ¹	Ammonioborite ²	Larderellite ³
Chemical composition			
Oxide form	(NH ₄) ₂ O · 5B ₂ O ₃ · 8H ₂ O	(NH ₄) ₂ O · 5B ₂ O ₃ · 5 $\frac{1}{2}$ H ₂ O	(NH ₄) ₂ O · 5B ₂ O ₃ · 4H ₂ O
Reduced form	NH ₄ B ₅ O ₆ · 4H ₂ O	NH ₄ B ₅ O ₆ · 2 $\frac{1}{2}$ H ₂ O	NH ₄ B ₅ O ₆ · 2H ₂ O
Structural form ⁴	NH ₄ B ₅ O ₆ (OH) ₄ · 2H ₂ O	NH ₄ B ₅ O ₆ (OH) ₄ · $\frac{3}{4}$ H ₂ O	NH ₄ B ₅ O ₆ (OH) ₄
Symmetry	Orthorhombic	Monoclinic	Monoclinic
<i>a</i>	11.324 ± 0.002 Å	25.27 ± 0.05 Å	11.63 ± 0.03 Å
<i>b</i>	11.029 ± 0.001	9.651 ± 0.03	7.61 ₅ ± 0.02
<i>c</i>	9.235 ± 0.004	11.56 ± 0.03	9.447 ± 0.03
β	—	94°17.5' ± 05'	96°45' ± 10'
Space Group	<i>A</i> ba2	<i>C</i> 2/ <i>c</i> (or <i>C</i> <i>c</i>)	<i>P</i> 2 ₁ / <i>a</i>
Cell Contents	4[NH ₄ B ₅ O ₆ (OH) ₄ · 2H ₂ O]	12[NH ₄ B ₅ O ₆ (OH) ₄ · $\frac{3}{4}$ H ₂ O]	4[NH ₄ B ₅ O ₆ (OH) ₄]
Volume	1153.4 Å ³	2811 Å ³	830.8 Å ³
Density (calc.)	1.567 g. cm. ⁻³	1.758 g. cm. ⁻³	1.887 g. cm. ⁻³
(obs.)	1.567 ± 0.005	1.765 ± 0.004	1.905 ± 0.004
Volume per oxygen atom	24.0 Å ³	22.0 Å ³	20.8 Å ³

¹ Data from Clark and Christ (1959) except cell constants; these from Cook and Jaffe (1957).

² Data from Clark and Christ (1959).

³ Data of present study.

⁴ Proposed by Christ (1960).

TABLE 3. X-RAY POWDER DATA FOR LARDERELLITE, $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4$
 Monoclinic $P2_1/a$: $a=11.63 \pm 0.03$, $b=7.61_6 \pm 0.02$, $c=9.44_7 \pm 0.03$ Å; $\beta=96^\circ 45' \pm 10'$

Measured				Calculated ¹	
Marinelli (1959) ²		Clark and Christ (1959) ³		Present Study	
I	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl
		50	9.4 ₆	9.38	001
				6.36	110
39	5.95 ⁴	18	5.91	5.913	011
17	5.83	25	5.79	5.775	200
48	5.61 ⁴				
49	5.45	71	5.44	5.429	$\bar{1}11$
				5.198	201
34	5.14	50	5.12	5.112	111
77	4.72	100	4.70	4.691	002
				4.679	201
		18	4.60	4.601	210
18	4.31	25	4.30	4.293	$\bar{2}11$
24	4.00	25	3.99	3.994	012
				3.986	211
				3.897	$\bar{1}12$
		4	3.88	3.871	202
15	3.82	18	3.81	3.808	020
24	3.68	18	3.66	3.663	112
				3.616	120
32	3.53 ⁴	4	3.53	3.528	021
15	3.47	12	3.45	3.450	$\bar{2}12$
				3.448	202
				3.436	310
		12	3.42	3.417	$\bar{1}21$
43	3.37 ⁴	12	3.34	3.341	$\bar{3}11$
15	3.30 ⁴			3.333	121
22	3.185 ⁵				
				3.179	220
				3.141	212
22	3.14	35	3.14	3.127	003
				3.122	311
				3.072	$\bar{2}21$

¹ All calculated spacings listed for $d \geq 2.300$ Å.

² X-ray diffractometer data, $\text{CuK}\alpha$ radiation.

³ Correction for film shrinkage negligible. Camera diameter, 114.59 mm; radiation, Cu/Ni , λ $\text{CuK}\alpha = 1.5418$ Å. Lower limit of 2θ measurable, approximately 7° (13 Å). Film no. 11101.

⁴ Corresponds to a strong or moderately strong line on the x-ray pattern for $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (Clark and Christ, 1959; see Table 4, this paper).

(Continued on next page)

TABLE 3 (continued)

Measured				Calculated ¹	
Marinelli (1959) ²		Clark and Christ (1959) ³		Present Study	
I	d_{hkl}	I	\bar{d}_{hkl}	d_{hkl}	hkl
69	2.97	71	2.960	2.956	022
				2.953	221
100	2.92	100	2.921	2.922	$\bar{3}12$
				2.916	$\bar{1}22$
		100	2.887	2.896	$\bar{2}03$
				2.893	013
				2.888	400
				2.881	$\bar{1}13$
24	2.822	25	2.816	2.856	$\bar{4}01$
13	2.780 ⁴			2.814	122
				2.737	113
21	2.723	35	2.713	2.714	222
				2.707	320, $\bar{2}13$
				2.700	400
				2.674	$\bar{4}11$
				2.673	401
10	2.675	12	2.663	2.660	$\bar{3}21$
				2.643	312
12	2.637	18	2.623	2.624	203
				2.599	$\bar{4}02$
				2.556	222
10	2.527 ⁴	6	2.545	2.546	321
				2.522	411
8	2.488	6	2.476	2.481	213
				2.479	130
				2.460	$\bar{4}12$
		6	2.444	2.450	031
				2.444	$\bar{3}13$
				2.433	$\bar{3}22$
				2.417	023
12	2.423	9	2.416	2.412	$\bar{1}31$
				2.410	$\bar{1}23$
10	2.383			2.382	131
21	2.372 ⁴			2.345	004
				2.339	402
		18	2.325	2.324	230
				2.323	123
				2.305	$\bar{2}23$
				2.301	420

TABLE 3 (continued)

Measured				Calculated ¹	
Marinelli (1959) ²		Clark and Christ (1959) ³		Present Study	
I	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl
12	2.270 ^{4,5}				
15	2.253	12	2.257		
		4	2.206		
15	2.186 ⁴				
29	2.159	25	2.156		
		4	2.138		
11	2.125 ⁵	4	2.124		
		6	2.094		
24	2.043	35	2.041		
18	2.016	12	2.013		
13	1.995	12	1.989		
6	1.967 ⁶				
8	1.947	8	1.937		
7	1.920	8	1.923		
16	1.890	25	1.887		
20	1.879	25	1.882		
11	1.854	4	1.855		
		4	1.818		
		2	1.790		
7	1.776	4	1.775		
		2	1.764		
		2	1.730		
6	1.711	4	1.710		
		4	1.683		
		4	1.669		
		4	1.623		
		4	1.615		
		4	1.578		
		4	1.561		
		4	1.536		
		4	1.501		
		4	1.482		
		plus additional weak lines			

⁵ Corresponds to a strong or moderately strong line on the X-ray pattern for sassolite.⁶ Indexes as larderellite I51; $d_{151} = 1.969 \text{ \AA}$ (calc.)

lated densities given above. Symmetry requirements of space group $P2_1/a$ can then be invoked to rule out the second formula, since for $4[\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4 \cdot \frac{1}{4}\text{H}_2\text{O}]$ per cell, the total number of oxygen atoms in the cell is 41, whereas the space group contains only general fourfold and special twofold positions, making mandatory an even number of each kind of atom in the cell. On the basis of all available evidence, therefore, the most probable chemical formula for larderellite is $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 4\text{H}_2\text{O}$, and the most probable structural formula, $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4$. A comparison of some of the chemical and physical properties of the three ammonium pentaborates, larderellite, ammonioborite, and synthetic $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, is given in Table 2.

The observed d -spacings given by Clark and Christ (1959) for the x -ray powder data of larderellite are in excellent agreement with the d -spacings calculated from the single-crystal cell constants as shown in Table 3. Intensities of single-crystal reflections conform qualitatively with intensities of corresponding powder lines. All calculated d -spacings greater than 2.300 Å are listed in Table 3, together with the observed data found by Clark and Christ (1959), and the diffractometer data reported by Marinelli (1959). Marinelli identifies two sassolite lines

TABLE 4. COMPARISON OF SOME OBSERVED X-RAY DIFFRACTOMETER DATA FOR IMPURE LARDERELLITE SAMPLE WITH OBSERVED X-RAY POWDER CAMERA DATA FOR $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$

Impure Larderellite Sample Marinelli (1959) ¹		$\text{KB}_5\text{O}_6 \cdot 4\text{H}_2\text{O}$ Clark and Christ (1959) ²	
I	d_{hkl} (Å)	d_{hkl} (Å)	I
39	5.95 ³	5.93	15
48	5.61	5.60	71
32	3.53 ³	3.52	84
43	3.37 ³	3.36	100
15	3.30	3.28	18
13	2.780	2.767	50
10	2.527	2.517	12
21	2.372	2.375	9
12	2.270 ⁴	2.290	9
15	2.186	2.181	21

¹ Selected portion of data (see Table 3 for complete listing); x -ray diffractometer, $\text{CuK}\alpha$ radiation.

² Selected portion of data, all observed lines with $I \geq 9$; camera diameter 114.59 mm., radiation Cu/Ni , $\lambda \text{CuK}\alpha = 1.5418$ Å, measurements not corrected for film shrinkage.

³ Larderellite observed line occurs here also.

⁴ Sassolite observed line occurs here also.

among his observed d -spacings. In addition he records appearance of a line at 5.61 Å which he cannot account for, suggesting that it may be a line due to ammonioborite, data for which were not then available to him. Comparison of his data with the calculated d -spacings for larderellite (Table 3) shows that the material in his sample gives additionally not only several sassolite lines and the unidentified 5.61 Å line, but also a series of lines clearly due neither to sassolite nor to ammonioborite. These observed lines are listed in Table 4 and compared with the observed d -spacings associated with lines of strong intensity of $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ($\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$, Clark and Christ, 1959). The matching of these two sets of observed d -spacings is preliminary evidence for the appearance of $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ in nature; confirming chemical tests would be of interest.

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THE CRYSTAL STRUCTURE OF POTARITE (PdHg) WITH
SOME COMMENTS ON ALLOPALLADIUM

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Potarite is a palladium amalgam which occurs in the Potaro river region of British Guiana (Palache, Berman, and Frondel 1944). It was first described by Harrison and Bourne (1924-5) and more fully characterized by Spencer (1928). Spencer further surveyed the known synthetic palladium amalgams and suggested that potarite might be identical with allopalladium. Cissarz (1930) reexamined simultaneously samples of potarite and allopalladium and found them to be different sub-