

## The Crystal Structure of Ameghinite

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### Abstract

Ameghinite is a hydrous sodium borate with oxide formula  $\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . The cell constants are:  $a = 18.428(3)$ ,  $b = 9.882(2)$ ,  $c = 6.326(2)$  Å,  $\beta = 104^\circ 23'(6')$ ;  $V = 1116$  Å<sup>3</sup>, space group  $C2/c$  and  $Z = 4$ . The structural formula is  $\text{Na}[\text{B}_3\text{O}_3(\text{OH})_4]$ . Three dimensional X-ray data have been collected by a Philips PW1100 diffractometer using  $\text{MoK}\alpha$  monochromatized by a flat graphite crystal. The crystal structure has been solved by direct methods and refined by least-squares procedures to  $R = 0.038$  for 1024 independent reflections. All the hydrogen atoms have been located in the difference Fourier maps. The crystal structure consists of isolated units  $[\text{B}_3\text{O}_3(\text{OH})_4]^-$  formed by one tetrahedron and two triangles. Hydrogen bonds and sodium atoms link these polyanions to form a three dimensional framework.

### Introduction

As a part of a systematic study of borate minerals, we have continued our investigations of the crystal structures of minerals that occur in the system  $\text{MO}-3\text{B}_2\text{O}_3-\text{H}_2\text{O}$ , where  $M$  represents, in this case, a monovalent cation. In the present paper we describe the crystal structure of the mineral ameghinite  $\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ .

Ameghinite from the Tincalayu borax deposit in the province of Salta (Argentina) was first described by Aristarain and Hurlbut (1967), who presented its chemical and physical properties. The manner of occurrence of ameghinite is identical with that of ezcurrite and rivadavite with which it is closely associated.

### Experimental

The lattice parameters were redetermined with a Philips PW1100 single crystal automatic diffractometer and are given in Table 1, along with other relevant crystallographic data.

The X-ray diffraction data were collected from a crystal fragment whose dimensions were  $0.15 \times 0.10 \times 0.12$  mm. using  $\text{MoK}\alpha$  radiation monochromatized by a flat graphite crystal. The intensities of the reflections within two octants of the reciprocal sphere were measured up to  $2\theta = 60^\circ$ , by the  $\theta - 2\theta$  scan mode with a symmetrical scan range of  $1.2^\circ$ . The scan rate was  $0.03^\circ/\text{sec}$ . Three standard reflections,

monitored at three-hour intervals, showed no variation in intensity greater than 3 percent.

Processing of the data was carried out in the manner described by Davies and Gatehouse (1973) to yield values of  $F_o$  and  $\sigma(F_o)$ . Of the 1636 reflections collected, the 1024 with  $F_o \geq \sigma(F_o)$  were employed in the refinement. No correction for absorption was made because of the low value of the linear absorption coefficient ( $\mu = 2.76 \text{ cm}^{-1}$ ) and the small size of the crystal.

### Structure Analysis

The structure was solved by the use of direct methods utilizing the symbolic addition procedure for centrosymmetric structures (LSAM program) developed by Germain and Woolfson (1968). The statistical averages for the data indicated the presence of a center of symmetry and therefore the space group chosen was  $C2/c$ .

A total of 360 normalized structure factors with  $|E| \geq 1.0$  were calculated, and the phases given by the set with the high consistency were used in calculation of an  $E$  map. This map clearly indicated the position of the sodium atom and most of the oxygen atoms. Successive three-dimensional Fourier syntheses, computed on the basis of these coordinates, yielded the coordinates of all non-hydrogen atoms.

The initial  $R$  factor of 0.38 was reduced to 0.072 after two least-squares cycles carried out with the Busing, Martin, and Levy (1962) modified computer program ORFLS. Scattering factor curves for neutral

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TABLE 1. Unit Cell Parameters and Other Relevant Crystallographic Data

Space group	<i>C2/c</i>
<i>a</i>	18.428 (3) Å
<i>b</i>	9.882 (2)
<i>c</i>	6.326 (2)
$\beta$	104°23' (6')
<i>V</i>	1116 Å <sup>3</sup>
Cell content	8 Na[B <sub>3</sub> O <sub>3</sub> (OH) <sub>4</sub> ]
Specific gravity meas*	2.030 gr.cm <sup>-3</sup> *
calc	2.037 gr.cm <sup>-3</sup>

\* (Aristarain et al., 1967).

Na, O, and B atoms, as given by Hanson *et al* (1964) were utilized.

At this stage isotropic convergence was attained, and anisotropic thermal parameters were introduced. After two cycles the *R* factor was reduced to 0.048. A final difference Fourier revealed the locations of the hydrogen atoms. A further least-squares cycle was undertaken using anisotropic thermal parameters for all non-hydrogen atoms; hydrogens were included in the structure factor calculation with isotropic temperature factors equal to 3.0 Å<sup>2</sup>. The *R* decreased to 0.038 for all the 1024 reflections with  $F_o \geq \sigma(F_o)$ . All the observed structure factors were weighted equally during the refinement.

The final positional and isotropic temperature factors are given in Table 2, and the observed and cal-

TABLE 2. Atomic Parameters and Equivalent Isotropic Temperature Factors after Hamilton (1959)†

Atom	$x/a$	$y/b$	$z/c$	$B_H(\text{Å}^2)$
Na	0.1730(1)	0.2380(1)	0.1032(2)	1.64
O(1)*	0.5494(1)	0.1575(2)	0.4964(3)	1.62
O(2)*	0.3011(1)	0.1606(2)	0.2150(3)	1.29
O(3)*	0.3058(1)	0.1016(2)	0.5929(3)	1.35
O(4)*	0.3986(1)	0.5352(2)	0.5164(3)	1.61
O(5)	0.4701(1)	0.3401(2)	0.4812(3)	1.48
O(6)	0.3437(1)	0.3196(2)	0.4990(3)	1.50
O(7)	0.4194(1)	0.1177(2)	0.4800(3)	1.26
B(1)	0.3412(2)	0.1716(3)	0.4414(5)	1.07
B(2)	0.4028(2)	0.3987(3)	0.4959(5)	1.14
B(3)	0.4778(2)	0.1994(3)	0.4828(5)	1.12
H(1)	0.561	0.059	0.505	3.00
H(2)	0.303	0.065	0.171	3.00
H(3)	0.252	0.130	0.560	3.00
H(4)	0.447	0.581	0.517	3.00

†Standard deviations in parentheses.

\*Marks oxygen atoms belonging to hydroxyls.

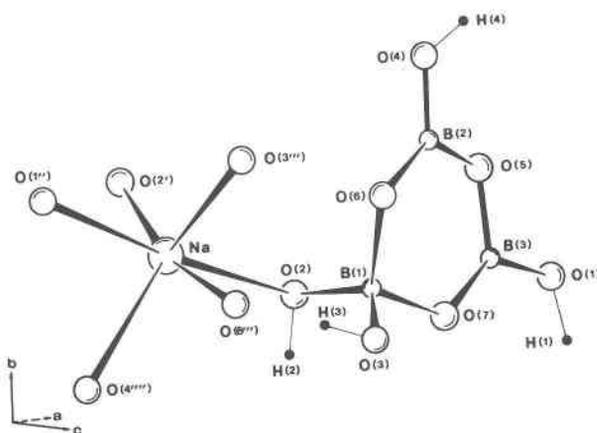


FIG. 1. Clinographic projection of the  $[\text{B}_3\text{O}_3(\text{OH})_4]^{1-}$  polyanion and the coordination around the sodium atom. The primes refer to the symmetry operations listed in Table 7.

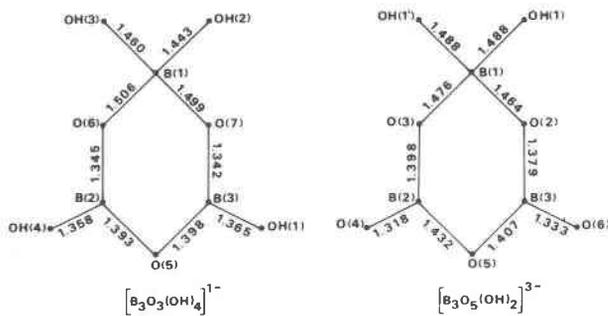


FIG. 2. Schematic illustration of the  $[\text{B}_3\text{O}_3(\text{OH})_4]^{1-}$  unit in ameghinite and the  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$  unit in synthetic  $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$ .

culated structure factors are compared in Table 3<sup>2</sup>.

### Description of the Structure

The ameghinite structure is characterized by monomeric units of composition  $[\text{B}_3\text{O}_3(\text{OH})_4]^{-}$  found for the first time in this structure. The polyanion consists of a six-membered ring composed of two  $\text{BO}_2(\text{OH})$  triangles and a  $\text{BO}_3(\text{OH})$  tetrahedron (Fig. 1).

The unit is similar to the triborate ring formed by corner-sharing among one tetrahedron and two triangles described by Krogh-Moe (1960) in the anhydrous compound  $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ ; but in this case the B-O polyanion shares those four oxygens which are bonded to only one boron with four identical B-O polyanions, thus forming a three-dimensional network.

<sup>2</sup> To obtain a copy of Table 3, order Document AM-75-007 from The Mineralogical Society of America, Business Office, 1909 K St. N.W., Washington, D.C. 20006. Please remit in advance \$1.00 for a copy of the microfiche.

TABLE 4. Ring Angles, Plane, Deviations from Planarity and B-B Distances

Equation* of plane through three oxygens in the form $Ax + By + Cz = D$				
Ring	A	B	C	D
O(5)-O(6)-O(7)	0.8891	-0.2353	6.0429	3.2458
Atom Deviation from plane (Å)				
B(1)	-0.315(3)			
B(2)	0.015(3)			
B(3)	0.050(3)			
Angles O-B-O and B-O-B internal to the ring				
B(1)-O(6)-B(2)	122.53°(22)	O(5)-B(2)-O(6)	119.80°(25)	
B(1)-O(7)-B(3)	121.66°(21)	O(5)-B(3)-O(7)	121.20°(24)	
B(2)-O(5)-B(3)	120.29°(21)	O(6)-B(1)-O(7)	109.58°(21)	
	Mean value	119.18°		
B(1)-B(2)	2.501(4) Å			
B(1)-B(3)	2.482(4)			
B(2)-B(3)	2.420(4)			
Average	2.468			

\* $x, y, z$  are the atomic coordinates (Å) referred to the crystallographic axes and  $D$  is the distance of the plane from the origin (Å).

TABLE 5. Boron-Oxygen, Oxygen-Oxygen Distances and Oxygen-Boron-Oxygen Angles\*

B(1)-O(2)	1.443(4) Å	B(2)-O(4)	1.359(3) Å
B(1)-O(3)	1.460(3)	B(2)-O(5)	1.393(3)
B(1)-O(6)	1.506(3)	B(2)-O(6)	1.345(3)
B(1)-O(7)	1.499(3)	Average	1.366
Average	1.477	B(3)-O(1)	1.365(3) Å
		B(3)-O(5)	1.398(3)
		B(3)-O(7)	1.342(3)
		Average	1.368
O(2)-O(3)	2.441(3) Å	O(4)-O(5)	2.376(2) Å
O(2)-O(6)	2.369(3)	O(4)-O(6)	2.350(2)
O(2)-O(7)	2.434(4)	O(5)-O(6)	2.369(2)
O(3)-O(6)	2.385(2)	Average	2.365
O(3)-O(7)	2.379(3)	O(1)-O(5)	2.310(2) Å
O(6)-O(7)	2.455(2)	O(1)-O(7)	2.404(2)
Average	2.410	O(5)-O(7)	2.387(2)
		Average	2.367
O(2)-B(1)-O(3)	114.44°(22)	O(4)-B(2)-O(5)	119.43°(24)
O(2)-B(1)-O(6)	106.88°(22)	O(4)-B(2)-O(6)	120.71°(26)
O(2)-B(1)-O(7)	111.67°(24)	O(5)-B(2)-O(6)	119.80°(25)
O(3)-B(1)-O(6)	107.07°(23)	O(1)-B(3)-O(5)	113.42°(23)
O(3)-B(1)-O(7)	107.04°(22)	O(1)-B(3)-O(7)	125.32°(26)
O(6)-B(1)-O(7)	109.58°(21)	O(5)-B(3)-O(7)	121.20°(24)

\*Standard deviations in parentheses.

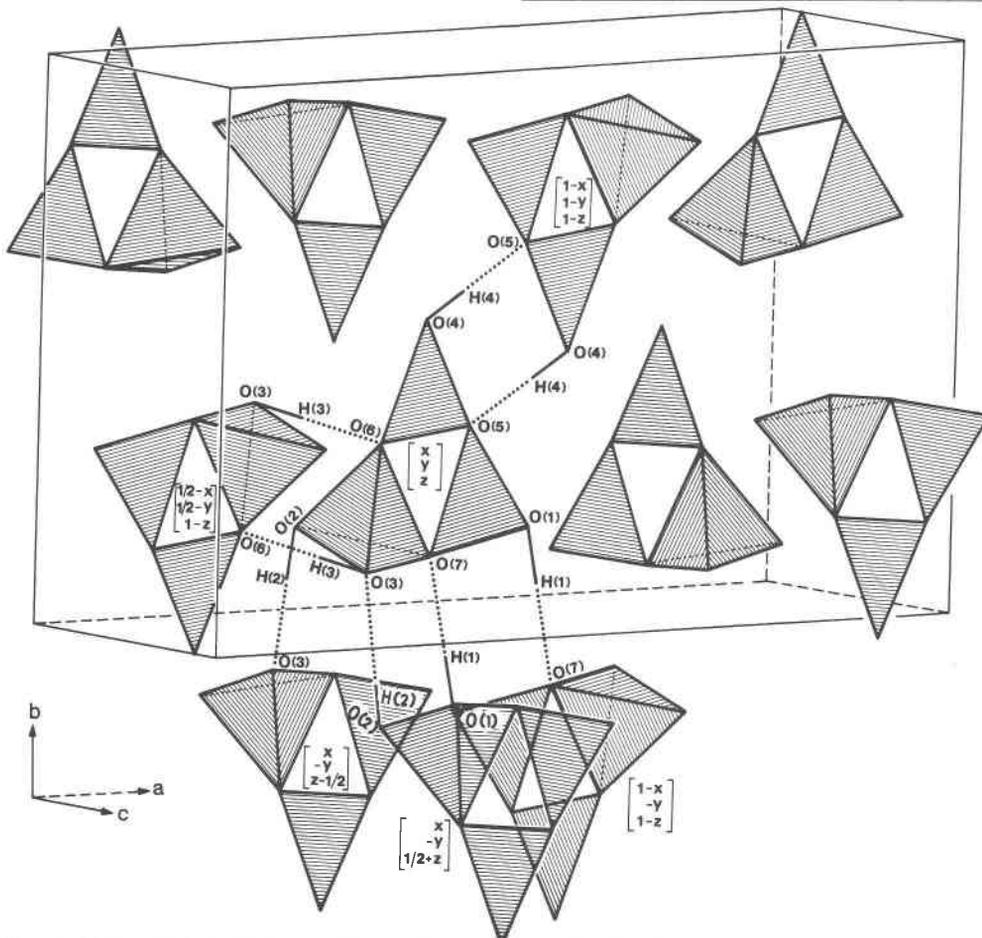


FIG. 3. Clinographic projection of the crystal structure of ameghinite showing the hydrogen bonds among the polyanions (Na atoms omitted).

TABLE 6. Distances Related to the Hydrogen Bonds

Donor *	Hydrogen	Receptor	Receptor at	O-H distance	O-O distance
O(1)	H(1)	O(7)	1 - x; -y; 1 - z;	0.99 Å	2.776(2) Å
O(2)	H(2)	O(3)	x; -y; z-1/2;	0.99	2.711(3)
O(3)	H(3)	O(6)	1/2-x; 1/2-y; 1 - z;	0.99	2.782(3)
O(4)	H(4)	O(5)	1 - x; 1 - y; 1 - z;	1.00	2.711(2)

\* Donor atoms at  $\underline{x}, \underline{y}, \underline{z}$  in Table 2.

Recently, Corazza *et al* (1975) discovered an isolated unit,  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$ , which is intermediate between the anhydrous and the hydrated form of the triborate ring.

In ameghinite, according to Christ's (1960) third rule, the oxygens linked to only one boron have an attached proton. However this is not the case for synthetic  $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$ , which evidently formed under conditions of less than full hydration.

In Figure 2 the  $[\text{B}_3\text{O}_5(\text{OH})_4]^-$  and  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$  units are compared. Clearly, the ameghinite unit is the more regular because all the oxygens linked to only one boron have an attached proton; in this way the polyanion reaches an internal equilibrium with regular bond-lengths. In contrast, the  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$  unit exhibits two short bond-lengths between the triangularly coordinated boron atoms and the oxygens which are not protonated. This effect, due to the increased attraction between oxygen and boron atoms, produces increased distortion of the six-membered ring with respect to that of ameghinite and a resultant increase in the internal B-B separations. Within the six-membered ring of ameghinite, the mean internal B-B distance is 2.468 Å while in the  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$  polyanion it is 2.528 Å and in the  $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$  ring it is 2.50 Å. Therefore the ameghinite polyanion is the smallest and is quite similar in dimensions to the rings of the ezcurrite unit

(Cannillo *et al*, 1973) in which the mean B-B value is 2.472 Å for both rings. The ameghinite ring is practically planar with a mean value for the internal angles of 119.2°, the greatest distance from the mean plane being -0.31 Å (Table 4).

The interatomic distances and bond angles related to the boron atoms are given in Table 5. The tetrahedral B-O and O-O average distances of 1.477

TABLE 8. Analysis of the Anisotropic Thermal Parameters\*

Atom	r.m.s.	$U_{1a}$	$U_{1b}$	$U_{1c}$
Na	0.128(2)	169	100	91
	0.149(2)	87	94	175
	0.155(2)	85	5	94
O(1)	0.103(4)	153	64	83
	0.120(4)	64	26	89
	0.191(3)	83	93	172
O(2)	0.113(4)	114	108	148
	0.125(4)	75	31	116
	0.143(3)	138	62	61
O(3)	0.108(4)	164	105	92
	0.123(4)	102	32	120
	0.157(4)	66	113	146
O(4)	0.099(5)	112	22	91
	0.118(4)	157	112	85
	0.193(3)	88	106	164
O(5)	0.099(4)	147	57	91
	0.107(4)	122	147	93
	0.187(3)	75	96	164
O(6)	0.103(4)	168	78	89
	0.107(4)	78	16	80
	0.187(3)	74	83	163
O(7)	0.099(4)	129	39	87
	0.107(4)	40	50	95
	0.163(3)	87	102	167
B(1)	0.091(7)	174	84	88
	0.098(7)	85	5	91
	0.151(6)	77	92	167
B(2)	0.112(7)	148	60	99
	0.123(6)	61	30	83
	0.125(7)	66	96	155
B(3)	0.115(6)	144	66	115
	0.118(7)	69	105	154
	0.124(6)	104	162	80

\*Root mean square thermal vibrations along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and the principal axes ( $U_i$ ) of the vibration ellipsoid.

TABLE 7. Sodium-Oxygen Distances\*

Oxygen atom	Oxygen atom at**	Na-O distance
O(1''')	$x - \frac{1}{2}$ ; $\frac{1}{2} - y$ ; $z - \frac{1}{2}$	2.438(2) Å
O(2)	$x$ ; $y$ ; $z$	2.414(2)
O(2')	$\frac{1}{2} - x$ ; $\frac{1}{2} - y$ ; $-z$	2.401(2)
O(3''''')	$\frac{1}{2} - x$ ; $\frac{1}{2} - y$ ; $1 - z$	2.447(2)
O(4''''''')	$\frac{1}{2} - x$ ; $y - \frac{1}{2}$ ; $\frac{1}{2} - z$	2.416(2)
O(6''''')	$\frac{1}{2} - x$ ; $\frac{1}{2} - y$ ; $1 - z$	2.671(2)

\*Standard deviations in parentheses.

\*\*Sodium atom at  $x, y, z$  in Table 2.

TABLE 9. Charge Balance

	B(1)	B(2)	B(3)	Na	H(1)	H(2)	H(3)	H(4)	$\Sigma$
O(1)			1.01	0.17	0.79				1.97
O(2)	0.82			{0.18 0.18		0.75			1.93
O(3)	0.78			0.17		0.25	0.79		1.99
O(4)		1.01		0.18				0.75	1.94
O(5)		0.94	0.94					0.25	2.13
O(6)	0.69	1.04		0.11			0.21		2.05
O(7)	0.71		1.05		0.21				1.97
$\Sigma$	3.00	2.99	3.00	0.99	1.00	1.00	1.00	1.00	13.98

Å and 2.410 Å are consistent with those found in the literature, as are the triangular B-O and O-O distances of 1.367 Å and 2.366 Å, respectively. The tetrahedron and one of the triangles are quite regular, as shown by the O-B-O angles listed in Table 5. However, the second triangle is rather distorted with O-B-O angles ranging from 113.4° to 125.3°.

In ameghinite (Fig. 3) each polyanion is linked to five others through hydrogen bonds to form a three-dimensional framework; three of these are centrosymmetrically related to the basic unit at atomic coordinates  $x, y, z$  (Table 2) and linked to it through pairs of centrosymmetric hydrogen bonds involving the hydroxyls O(1), O(3), and O(4). The two other polyanions, related to each other by a  $c$  translation, are linked to the basic unit in this way: the O(2) hydroxyl gives its hydrogen H(2) to the oxygen O(3) belonging to the polyanion at  $x, -y, z - \frac{1}{2}$ , and O(3) acts as acceptor of the hydrogen H(2) of the polyanion at  $x, -y, \frac{1}{2} + z$ . The O-O distances involved in hydrogen-bonding and the O-H bond-lengths are listed in Table 6.

Further inter-connection among the polyanions is provided by the sodium atoms. In ameghinite the sodium is six-fold coordinated by five hydroxyls and one oxygen, forming a rather distorted octahedron. Each Na atom links five polyanions, insuring in this way a three dimensional linkage. Moreover each Na-polyhedron shares an edge [O(2)-O(2')] with another Na-polyhedron forming centrosymmetric pairs isolated in the structure. Five of the six Na-O bond lengths range from 2.401 Å to 2.447 Å, the sixth being 2.671 Å (Table 7). As can be seen in Table 8, the thermal anisotropy of the ameghinite atoms is not large.

On the basis of the method proposed by Donnay and Allman (1970), a curve for bond lengths *versus* bond strengths was computed for the cations Na and B. For the hydrogen-oxygen bonds the correlations given by Zachariassen (1963) were used. As shown in Table 9, the range in valence units for the oxygen atoms is 1.93 to 2.13, and the summation of 13.98 for anions and cations is within the validity conditions generally accepted.

Even though many resemblances exist between ameghinite and ezcurrite (occurrence, unit cell parameters, and chemical composition) the crystal structures of the two minerals are quite different.

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