THE AMERICAN MINERALOGIST, VOL. 56, SEPTEMBER-OCTOBER, 1971

THE CRYSTAL STRUCTURE OF AKSAITE

A. DAL NEGRO AND L. UNGARETTI, *Centro di studio del C.N.R. per la cristallografia strutturale, Istituto di Mineralogia della Università di Pavia, Italy* AND C. SABELLI, *Centro di studio del C.N.R. per la geochimica e la cristallochimica, Istituto di Mineralogia della Università di Firenze, Italy.*

ABSTRACT

Aksaite is a hydrous magnesium borate with chemical formula $MgO \cdot 3B_2O_3 \cdot 5H_2O$. The lattice parameters are: $a=12.540(6)$, $b=24.327(11)$, and $c=7.480(3)$ Å. Space group $Pbca$, $Z=8$. Integrated Weissenberg photographs were taken by using Cu Kα radiation and multiple-film packs. The crystal structure has been solved by means of a three-dimensional Patterson synthesis and some consecutive three-dimensional Fourier syntheses. The least-squares refinement, performed in the last cycle with anisotropic thermal parameters, was stopped at a final R value of 0.039 for the observed reflexions. The crystal structure of aksaite contains monomeric polyanions $[B_6O_7(OH)_6]^{2-}$ formed by three six-membered boron oxygen rings, each ring consisting of two tetrahedra and one triangle. Therefore the structural formula of aksaite is $Mg[B_6O_7(OH)_6] \cdot 2H_2O$. The monomeric units are linked together, along the z direction, by MgO_6 octahedra; other linkages are formed by a thick network of hydrogen bonds.

INTRODUCTION

Aksaite, a hydrated magnesium borate, has been described as a new mineral by Blazko *et al.* (1962). These authors suggested two chemical formulas as most probable: $2MgO \cdot 5B_2O_3 \cdot 8H_2O$ and $3MgO \cdot 7B_2O_3 \cdot 10H_2O$. Clark and Erd (1963), while working on $MgO \cdot 3B_2O_3 \cdot 5H_2O$ synthetized by Lehmann and Papenfuss (1959), discovered that this synthetic magnesium borate was identical with aksaite. Therefore aksaite should belong to the family of $1{:}3x$ borates. This series includes many members both mineral and synthetic; nevertheless, only a few of them have been examined from a structural point of view. Furthermore, it was interesting to investigate whether some structural features found in macallisterite (Dal Negro *et al.*, 1969), the other Mg-member of the $1{:}3x$ series, were present also in aksaite.

The sample used in this investigation was prepared by Lehmann and Papenfuss and was supplied to us by Clark.

EXPERIMENTAL

The specimen used in this investigation is a colorless prismatic fragment. The unit-cell parameters have been redetermined by extrapolating the values deduced from measurements with a single-crystal diffractometer. The new unit-cell parameters, obtained in this way, are reported below together with other relevant crystallographic data:

Space group	*Pbca*
a	12.540(6) Å
b	24.327(11) Å
c	7.480(3) Å
Cell volume	2282 Å^3
Cell contents	8 $Mg[B_6O_7(OH)_6]\cdot 2H_2O$
Specific gravity calc.	1.975
Specific gravity obs.	1.99(1) (Clark and Erd, 1963).

The crystal was rotated about the *c* axis and integrated Weissenberg photographs were taken by using Cu Kα radiation and multiple-film packs. Lorentz-polarization and $\alpha_1-\alpha_2$ spot-doubling corrections were applied to the photometrically measured intensities. No correction for absorption was made because of the low value of the linear absorption coefficient and the smallness of the sample ($\mu R=1.5$). A total of 1884 independent reflexions out of the 2610 possible with Cu Kα radiation (about 72 percent) were inspected; 486 spots were too weak to be accurately measured and were considered as unobserved.

STRUCTURE ANALYSIS

A three-dimensional Patterson synthesis was first computed and the solution of the crystal structure was attempted at the same time by means of direct methods. From the Patterson synthesis it was possible to obtain the coordinates of the Mg atom and of the six octahedrally coordinated oxygen atoms, in complete agreement with the hypothesis suggested by the direct methods. By using such coordinates and by some consecutive three-dimensional Fourier synthesis it has been possible to establish the position of all the atoms present in the asymmetric unit, with the obvious exclusion of hydrogens.

A structure-factor calculation with the coordinates so obtained yielded an overall disagreement index $R=\Sigma|\Delta F|/\Sigma|F_0|=0.10$. The *f*-curves for neutral atoms of Mg, O, and B given by Hanson *et al.* (1964) were used.

After two least-squares cycles performed with the Busing, Martin, and Levy (1962) computer program ORFLS, with isotropic thermal parameters, the *R* index lowered to 0.065. At this stage a comparison between the observed and calculated structure-factors suggested that many of the strongest reflexions might be suffering from secondary extinction effects. The correction proposed by Zachariasen (1963a) was applied (final value $g=1.5\ 10^{-5}$), and it was decided to use anisotropic thermal parameters.

Convergence was attained after one cycle and the *R* index was reduced to 0.045. A three-dimensional difference Fourier synthesis was carried out in order to locate the hydrogen atoms. On the basis of the difference map and of the O-O distances, it was possible to determine the coordinates of nine out of the ten hydrogen atoms contained in the asymmetric unit. The nine hydrogen atoms were included in the structure-factor calculation with isotropic temperature factors fixed at 2.5 Å^2. The reliability index decreased to a final value $R=0.39$ after one least-squares cycle in which the parameters of the hydrogen atoms were not refined. All the observed structure-factors were weighted equally.

The observed and calculated structure-factors are listed in Table 1.[1] The positional and thermal parameters with their standard deviations are listed in Table 2.

---

[1] To obtain a copy of Table 1, listing observed and calculated structure-factors of aksaite, order NAPS Document 01518 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N.Y. 10022; remitting in advance $2.00 for microfiche or $5.00 for photocopies, payable to CCMIC-NAPS.

Table 2. Fractional Atomic Coordinates with their Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors after Hamilton (1959)

Atom	x/a	y/b	z/c	B_H(Å^2)
Mg	0.4316(1)	0.1279(1)	0.0542(2)	0.67
B(1)	.6592(3)	.3673(1)	.3902(6)	0.82
B(2)	.5015(3)	.3358(1)	.1876(6)	0.86
B(3)	.5303(3)	.4387(1)	.2506(7)	0.79
B(4)	.6577(3)	.2761(1)	.2450(6)	0.85
B(5)	.4553(3)	.4053(1)	−.0318(6)	0.83
B(6)	.7130(3)	.4635(1)	.3434(6)	0.82
O(1)	.7141(2)	.3181(1)	.3330(3)	0.93
O(2)*	.5967(2)	.3586(1)	.5529(4)	1.08
O(3)	.5767(2)	.3814(1)	.2491(3)	0.64
O(4)	.7338(2)	.4125(1)	.4020(3)	0.95
O(5)	.5593(2)	.2842(1)	.1821(3)	0.95
O(6)*	.4143(2)	.3331(1)	.3133(3)	1.00
O(7)	.4669(2)	.3509(1)	.0081(3)	1.04
O(8)	.4743(2)	.4465(1)	.0835(4)	0.92
O(9)*	.4606(2)	.4438(1)	.4074(4)	1.07
O(10)	.6178(2)	.4777(1)	.2659(4)	1.07
O(11)*	.6977(2)	.2244(1)	.2442(4)	1.78
O(12)*	.4273(2)	.4178(1)	−.2081(4)	1.02
O(13)*	.7878(2)	.5048(1)	.3526(4)	1.66
O(14)**	.2659(2)	.1127(1)	.0541(4)	1.92
O(15)**	.4140(2)	.1996(1)	.2065(3)	0.96

The sign (*) marks the oxygen atoms belonging to hydroxyls. The sign (**) marks those belonging to water molecules.

Discussion

The aksaite structure is characterized by monomeric polyanions $[B_6O_7(OH)_6]^{2-}$ similar to those found for the first time in macallisterite. They consist of three $BO_2(OH)$ triangles and of three $BO_3(OH)$ tetrahedra sharing one vertex (see Fig. 1). A complex of three six-membered boron oxygen rings is originated, each ring being formed by two tetrahedra and one triangle. Therefore, each polyanion consists of 13 oxygens, one of them being central and common to three B atoms, six shared between a triangular boron and a tetrahedral one, and six linked to a single boron. The latter oxygens belong to hydroxyls, in complete agreement with the third Christ's rule (Christ, 1960).

The three rings of the polyanions are not coplanar; in particular the planes formed by the oxygens of each ring intersect each other with angles of 156°, 166°, and 158° (see Table 3), with a mean value of 160° somewhat larger than that, (151°), found in tunnellite (Clark, 1964)

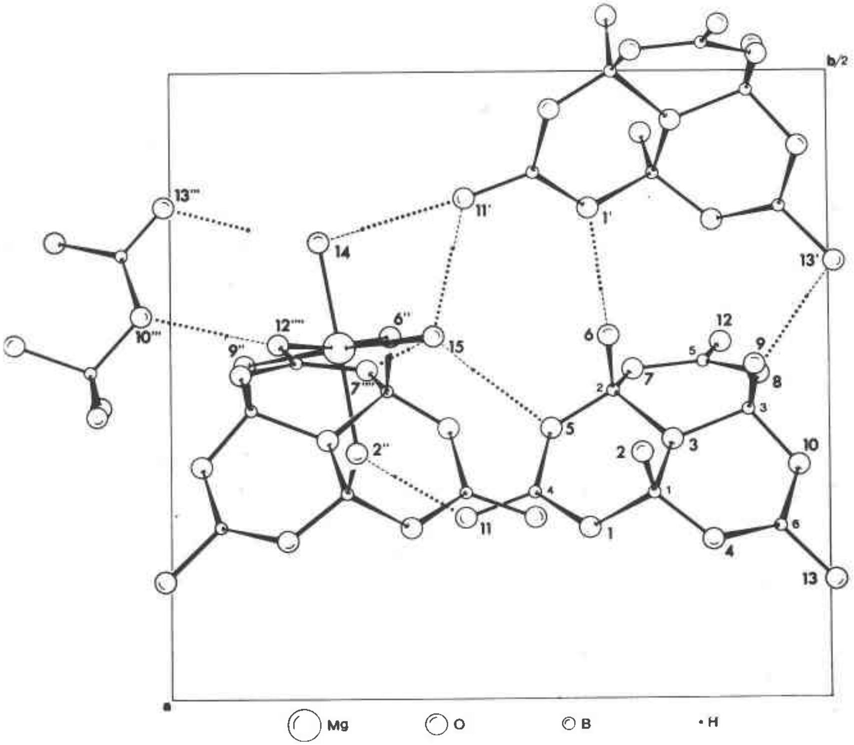

FIG. 1. Details of the projection on the *xy* plane showing some $[B_6O_7(OH)_6]^{2-}$ polyanions and one MgO_6 octahedron involved in hydrogen bonds. Origin at upper left with $+c$ up; the polyanion shown from 0 to $b/4$ is at $1/2+z$ with respect to its counterpart in the region $b/4$ to $b/2$. Unconnected bonds are to atoms related by $+1$ in z to those shown.

Atoms marked with (′) are at $x-1/2$, y, $1/2-z$
Atoms marked with (″) are at x, $1/2-y$, $z-1/2$
Atoms marked with (‴) are at $1-x$, $y-1/2$, $1/2-z$
Atoms marked with (⁗) are at x, $1/2-y$, $1/2+z$

TABLE 3. RING ANGLES, PLANES AND DEVIATIONS FROM PLANARITY

Ring	Ring atoms	B-O-B angles[1]	
1	B(1)-O(1)-B(4)-O(5)-B(2)-O(3)	B(1)-O(1)-B(4)	119° 46′
		B(4)-O(5)-B(2)	124° 31′
		B(2)-O(3)-B(1)	117° 46′
2	B(2)-O(7)-B(5)-O(8)-B(3)-O(3)	B(2)-O(7)-B(5)	118° 31′
		B(5)-O(8)-B(3)	122° 53′
		B(3)-O(3)-B(2)	115° 41′

[1] All angles ±20′.

TABLE 3 (*Continued*)

Ring	Ring atoms	R-O-B angles	
3	B(1)-O(3)-B(3)-O(10)-B(6)-O(4)	B(3)-O(10)-B(6)	121° 40′
		B(6)-O(4)-B(1)	123° 54′
		B(1)-O(3)-B(3)	117° 49′
		average of 9	120° 16′

Equation[2] of plane through three oxygens in the form $Ax+By+Cz=D$

Ring	A	B	C	D
1	−0.4488	−0.1445	0.8774	−2.9518
2	−0.7635	−0.1233	0.6339	−5.4842
3	−0.5205	0.0689	0.8511	−1.5396

Angles between planes of ring oxygens

1,2	156°
1,3	166°
2,3	158°

Ring	Atom	Deviation from plane of ring oxygens (Å)
1	B(1)	+0.513
	B(2)	+0.181
	B(4)	−0.113
	O(11)	−0.162
	O(2)	+1.969
	O(6)	+1.511
2	B(2)	+0.565
	B(3)	+0.279
	B(5)	−0.241
	O(12)	−0.846
	O(6)	+2.004
	O(9)	+1.675
3	B(1)	+0.336
	B(3)	+0.408
	B(6)	−0.152
	O(13)	−0.512
	O(2)	+1.765
	O(9)	+1.870

---

[2] x, y, z are the atomic coordinates in Å units referred to the crystallographic axes and D is the distance of the planes from the origin in Å units.

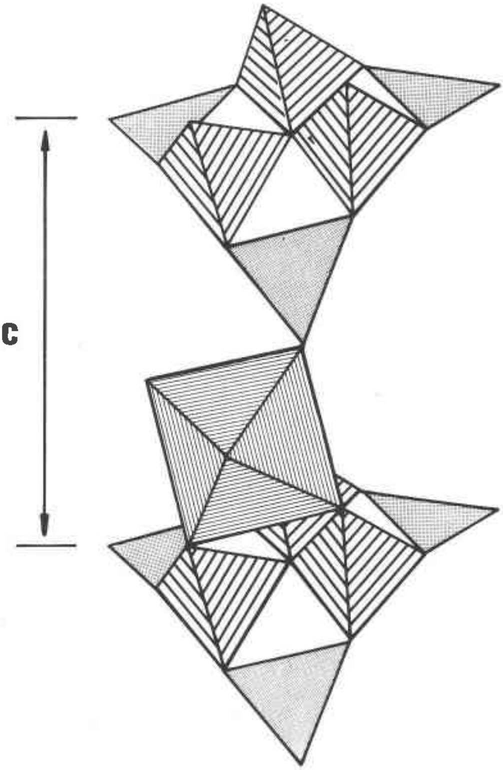

FIG. 2. Clinographic projection of the $[B_6O_7(OH)_6]^{2-}$ polyanion and MgO_6 octahedron, linked together to form a chain along the *c* axis.

where the deviation from 180° was considered dependent on polymerization of the polyanions to form sheets.

The B-O bonds involving the three tetrahedral hydroxyls of the polyanions are all almost exactly perpendicular to the planes of the rings, the hydroxyls standing out on the same side. Such hydroxyls [O(2″), O(6″), O(9″)], the two water molecules [O(14), O(15)] and the triangular hydroxyl O(12⁗) which belongs to another polyanion at the distance of one *c*-period, give rise to an almost regular octahedron around the Mg atom (mean distance Mg-O = 2.090 Å).

Each $Mg\text{-}O_6$ octahedron connects two adjacent polyanions; in this way infinite chains along the *z*-axis are generated (see Fig. 2). This structural feature is the basic difference between aksaite and macallisterite, where the polyanion-octahedron complex is isolated.

The hydroxyl O(12) connecting the octahedra with the polyanions is the furthest from the plane of the oxygens belonging to the ring 2 (see Table 3).

TABLE 4. DISTANCES RELATED TO THE HYDROGEN BONDS

Atoms	Bond Lengths	Atoms	Bond Lengths
O(2″) –O(11)	2.780(3) Å	O(2″)——H	0.997 Å
O(6) –O(1′)	2.763(3)	O(6)——H	0.998
O(11′) –O(15)	2.803(3)	O(11′)——H	1.000
O(12⁗)–O(10‴)	2.641(3)	O(12⁗)——H	0.992
O(13′) –O(8)	2.777(3)	O(13′)——H	0.998
O(14) –(O(13‴)	2.800(4)	O(14)——H	0.992
O(15) –O(5)	2.754(3)	O(14)——H	1.003
O(15) –O(7⁗)	2.653(4)	O(15)——H	0.995
		O(15)——H	0.996

Besides the connections between octahedra and polyanions along the *z* direction, a thick network of hydrogen bonds is present which insures the connections among the polyanions either directly or through the water molecules.

Only nine, out of the ten hydrogen atoms contained in the asymmetric unit, have been located. Eight of them connect oxygen atoms with distances smaller than 3.0 Å by means of hydrogen bonds.

A three-dimensional difference Fourier, computed at $R=0.045$, showed a number of small peaks. The number of these peaks was greater than the number of hydrogen atoms present in the unit-cell, indicating that some peaks were spurious. The positions for eight hydrogen atoms were chosen by taking into account eight peaks which were along the O-O directions listed in Table 4. A ninth peak was located along the direction of the oxygens O(14) and O(11′), whose distance is 3.22 Å. Thus it has been possible to single out the hydrogens belonging to the two water molecules and to five oxygens connected to a single boron. However, there was a sixth oxygen atom, O(9), connected to a single boron and which had to be a hydroxyl; around this atom the difference

TABLE 5. FRACTIONAL COORDINATES OF HYDROGEN ATOMS

Atom	*x/a*	*y/b*	*z/c*
$H_{2''-11}$	0.633	0.171	0.122
$H_{6-1'}$	0.342	0.328	0.260
$H_{11'-15}$	0.275	0.216	0.238
$H_{12''''-10'''}$	0.410	0.043	0.270
$H_{13'-8}$	0.355	0.484	0.124
$H_{14-13'''}$	0.247	0.074	0.087
H_{14}	0.245	0.147	0.117
$H_{15-7''''}$	0.434	0.181	0.320
H_{15-5}	0.467	0.230	0.198

TABLE 6. MAGNESIUM-OXYGEN AND BORON-OXYGEN DISTANCES AND THEIR STANDARD DEVIATIONS IN PARENTHESES

Mg–O(2'')	2.095(3) Å	Mg–O(6'')	2.048(3) Å
Mg–O(9'')	2.093(3)	Mg–O(12'''')	2.098(3)
Mg–O(14)	2.111(3)	Mg–O(15)	2.094(3)
B(1)–O(1)	1.445(4) Å	B(2)–O(3)	1.527(4) Å
B(1)–O(2)	1.463(5)	B(2)–O(5)	1.450(4)
B(1)–O(3)	1.517(4)	B(2)–O(6)	1.444(4)
B(1)–O(4)	1.446(4)	B(2)–O(7)	1.458(5)
Average	1.468	Average	1.470
	B(3)–O(3)	1.510(4) Å	
	B(3)–O(8)	1.446(5)	
	B(3)–O(9)	1.468(5)	
	B(3)–O(10)	1.455(4)	
	Average	1.470	
B(4)–O(1)	1.372(4) Å	B(5)–O(7)	1.363(4) Å
B(4)–O(5)	1.363(4)	B(5)–O(8)	1.344(5)
B(4)–O(11)	1.357(4)	B(5)–O(12)	1.399(5)
Average	1.364	Average	1.369
	B(6)–O(4)	1.342(4) Å	
	B(6)–O(10)	1.371(4)	
	B(6)–O(13)	1.376(4)	
	Average	1.363	

Average of 12 tetrahedral B-O distances 1.469
Average of 9 triangular B-O distances 1.365

map showed a smearing of the electron density and furthermore the oxygen closest to it, O(13'), was at a distance of 3.27 Å. Therefore it has not been possible to establish the position of the tenth hydrogen which does not seem to belong to a hydrogen bond.

The fractional coordinates of the nine hydrogen atoms are listed in Table 5.

All interatomic distances and angles with their standard deviations were calculated by using Busing, Martin, and Levy's (1964) ORFFE program.

The B-O distances both in the triangles and in the tetrahedra (see Table 6) and the O-B-O angles (see Table 7) are within the range of the values found in other borates.

As it was predicted by Zachariasen (1963b) and actually found in

TABLE 7. OXYGEN-BORON-OXYGEN ANGLES AND THEIR STANDARD DEVIATIONS IN PARENTHESES

	Atoms	Angles
Tetrahedron around B(1)	O(1)–B(1)–O(2)	113°55′(18′)
	O(1)–B(1)–O(3)	107°50′(17′)
	O(1)–B(1)–O(4)	109°48′(16′)
	O(2)–B(1)–O(3)	104°16′(15′)
	O(2)–B(1)–O(4)	113°55′(18′)
	O(3)–B(1)–O(4)	108° 7′(16′)
Tetrahedron around B(2)	O(3)–B(2)–O(5)	109°12′(15′)
	O(3)–B(2)–O(6)	107°47′(18′)
	O(3)–B(2)–O(7)	106°12′(16′)
	O(5)–B(2)–O(6)	110°52′(17′)
	O(5)–B(2)–O(7)	109°53′(18′)
	O(6)–B(2)–O(7)	112°42′(16′)
Tetrahedron around B(3)	O(3)–B(3)–O(8)	107°34′(17′)
	O(3)–B(3)–O(9)	108°16′(17′)
	O(3)–B(3)–O(10)	108° 7′(16′)
	O(8)–B(3)–O(9)	112°59′(16′)
	O(8)–B(3)–O(10)	110°23′(18′)
	O(9)–B(3)–O(10)	109°20′(18′)
Triangle around B(4)	O(1)–B(4)–O(5)	121°57′(18′)
	O(1)–B(4)–O(11)	121°38′(19′)
	O(5)–B(4)–O(11)	116°24′(18′)
Triangle around B(5)	O(7)–B(5)–O(8)	124°25′(21′)
	O(7)–B(5)–O(12)	116°22′(20′)
	O(8)–B(5)–O(12)	119° 7′(18′)
Triangle around B(6)	O(4)–B(6)–O(10)	122°44′(19′)
	O(4)–B(6)–O(13)	121°44′(19′)
	O(10)–B(6)–O(13)	115°31′(17′)

TABLE 8. BORON-BORON DISTANCES WITHIN THE POLYANION WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

B(1)–B(2)	2.606(6) Å
B(1)–B(3)	2.592(5)
B(1)–B(4)	2.437(5)
B(1)–B(6)	2.461(5)
B(2)–B(3)	2.571(5)
B(2)–B(4)	2.490(5)
B(2)–B(5)	2.425(6)
B(3)–B(5)	2.451(6)
B(3)–B(6)	2.468(5)
Average	2.500

TABLE 9. OXYGEN-OXYGEN DISTANCES WITHIN THE BORON-OXYGEN POLYHEDRA

Tetrahedron around B(1)		Tetrahedron around B(2)	
O(1)–O(2)	2.418(3) Å	O(3)–O(6)	2.401(3) Å
O(1)–O(3)	2.394(3)	O(3)–O(5)	2.427(3)
O(1)–O(4)	2.366(3)	O(3)–O(7)	2.388(3)
O(2)–O(3)	2.353(4)	O(5)–O(6)	2.384(3)
O(2)–O(4)	2.439(3)	O(5)–O(7)	2.381(3)
O(3)–O(4)	2.399(3)	O(6)–O(7)	2.416(4)
Average	2.395	Average	2.399
Tetrahedron around B(3)			
O(3)–O(8)	2.385(3) Å		
O(3)–O(9)	2.413(3)		
O(3)–O(10)	2.400(3)		
O(8)–O(9)	2.430(4)		
O(8)–O(10)	2.382(3)		
O(9)–O(10)	2.385(3)		
Average	2.399		
Triangle around B(4)		Triangle around B(5)	
O(1)–O(5)	2.392(3) Å	O(7)–O(8)	2.395(3)
O(1)–O(11)	2.383(3)	O(7)–O(12)	2.347(3)
O(5)–O(11)	2.312(3)	O(8)–O(12)	2.365(4)
Average	2.362	Average	2.369
Triangle around B(6)			
O(4) –O(10)	2.381(3) Å		
O(4) –O(13)	2.374(3)		
O(10)–O(13)	2.323(3)		
Average	2.359		

Average of 18 tetrahedral O–O distances 2.398 Å
Average of 9 triangular O–O distances 2.363

tunellite, in strontium and lead tetraborates (Perloff 1966), and in macallisterite, the three B-O lengths for the oxygen bonded to three boron atoms, are slightly larger (mean value 1.518 Å) than the usual value 1.470 Å; such an increase is to be expected from bonding considerations and coincides with that suggested by Zachariasen.

TABLE 10. CHARGE BALANCE[1]

	Te B(1)	Te (B2)	Te B(3)	Tr B(4)	Tr B(5)	Tr B(6)	Mg^{++}	H bond	H^+	Σ
O(1)	0.82			0.98				0.22		2.02
O(2)	0.77						0.33	0.79		1.89
O(3)	0.65	0.63	0.69							1.97
O(4)	0.81					1.06				1.87
O(5)		0.80		1.00				0.28		2.08
O(6)		0.82					0.33	0.78		1.93
O(7)		0.78			1.00			0.23		2.01
O(8)			0.81		1.06			0.21		2.08
O(9)			0.76				0.33		1.00	2.09
O(10)			0.79			0.98		0.28		2.05
O(11)				1.02				1.01		2.03
O(12)					0.92		0.33	0.72		1.97
O(13)						0.97		1.00		1.97
O(14)							0.33	0.79	1.00	2.12
O(15)							0.33	1.69		2.02
Σ	3.05	3.03	3.05	3.00	2.98	3.01	1.98	8.00	2.00	30.10

[1] Values for B-O and H-bonds taken from Zachariasen (1963b). Te means tetrahedral B and Tr triangular B.

The mean B-B distance in Table 8 is 2.500 Å, smaller than that found both in tunellite and in macallisterite (2.54 Å), but close to that found in the 2:3x borates (Clark *et al.*, 1964). However even in aksaite three larger B-B separations are present (2.606, 2.592, and 2.571 Å) around the triply linked oxygen. Basically the three rings of the polyanion $[B_6O_7(OH)_6]^{2-}$ are smaller than those found in tunellite and in macallisterite. In particular the ring 2, connected to the Mg-octahedron through the O(12), is the smallest, having a mean B-B separation of

Table 11. Analysis of the Anisotropic Thermal Parameters[1]

Atom	r.m.s.	$U_{i}a$	$U_{i}b$	$U_{i}c$	Atom	r.m.s.	$U_{i}a$	$U_{i}b$	$U_{i}c$
Mg	0.076(5)	88	96	173	O(5)	0.090(6)	68	158	86
	0.097(3)	60	30	94		0.106(6)	29	71	112
	0.106(3)	30	119	85		0.133(6)	109	101	157
B(1)	0.078(12)	56	142	105	O(6)	0.087(10)	99	89	163
	0.111(9)	34	55	86		0.113(5)	9	166	100
	0.122(13)	95	75	164		0.134(5)	87	92	76
B(2)	0.087(11)	90	150	119	O(7)	0.077(10)	113	116	143
	0.093(10)	16	82	104		0.108(6)	100	26	114
	0.134(11)	73	118	33		0.151(5)	154	89	64
B(3)	0.078(11)	146	121	93	O(8)	0.092(6)	74	164	90
	0.096(10)	118	34	107		0.102(8)	60	82	30
	0.121(12)	78	103	162		0.128(5)	145	104	59
B(4)	0.087(10)	126	137	145	O(9)	0.093(9)	65	79	152
	0.098(14)	101	57	117		0.103(6)	108	18	87
	0.125(9)	38	114	155		0.147(5)	148	105	117
B(5)	0.070(21)	76	111	154	O(10)	0.086(6)	111	158	88
	0.099(9)	27	63	87		0.104(6)	28	110	108
	0.132(8)	67	145	65		0.157(6)	107	84	161
B(6)	0.078(17)	77	117	30	O(11)	0.074(7)	70	160	85
	0.109(9)	133	56	62		0.133(5)	35	76	122
	0.115(8)	133	134	101		0.216(5)	118	104	147
O(1)	0.092(7)	108	142	59	O(12)	0.067(14)	102	92	167
	0.101(6)	27	116	97		0.108(5)	67	24	97
	0.132(6)	109	114	148		0.157(4)	153	66	79
O(2)	0.097(9)	78	110	23	O(13)	0.090(6)	109	160	91
	0.115(5)	22	67	93		0.126(5)	24	108	105
	0.140(5)	71	149	113		0.197(5)	103	84	165
O(3)	0.082(7)	63	143	113	O(14)	0.139(5)	142	123	74
	0.082(8)	62	54	131		0.151(5)	127	54	123
	0.114(6)	139	96	129		0.182(6)	81	127	142
O(4)	0.090(7)	149	94	59	O(15)	0.097(9)	80	84	169
	0.096(6)	84	18	72		0.119(5)	102	13	87
	0.148(6)	59	108	36		0.128(5)	164	101	100

[1] 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 ellipsoids.

2.482 Å, while the corresponding values for the other two rings are 2.511 and 2.507 Å.

The O-O distances between oxygens linked to the same boron (see Table 9) are all within the expected range of value.

As discussed above, two of the ten protons associated with the asymmetric unit are probably not participating in hydrogen bond formation. This can be understood when the overall charge balance in the structure is considered according to the correlations between bond length and bond strength in borates given by Zachariasen (1963b). In compiling Table 10, Zachariasen's values for B-O and O-H · · · O bonds were used, and a 0.33 value was assigned to the Mg-O distances.

The summation of 30.10 for anions and cations are within the validity conditions (±0.1 valence unit) found by Zachariasen. One proton of the O(14) water molecule and that of the O(9) hydroxyl were considered not participating in hydrogen bond formation and for this reason a 1.0 value was assigned to each of them.

As it can be seen in Table 11, aksaite does not present a large thermal anisotropy. According to the results of the structural analysis, the largest thermal motion is shown by the water molecule, O(14), which is only linked to the Mg atom and to O(13″) through a hydrogen bond. The thermal amplitude of two of the three triangular hydroxyls, O(11) and O(13), involved in a bond with boron as well as in two hydrogen bonds, is rather large. Much smaller is the displacement of the O(12) hydroxyl which is also participating to a bond with magnesium. It is also easy to understand the slight thermal motion of the water molecule O(15), which is involved in a bond with magnesium and in three hydrogen bonds as well. As expected the smallest thermal amplitude and the smallest thermal anisotropy is shown by the O(3) which is linked to three B atoms and which is the central point of the three six-membered rings.

ACKNOWLEDGEMENTS

We are much indebted to C. L. Christ and J. R. Clark who suggested the problem and made possible this investigation by sending some fine specimens.

REFERENCES

BLAZKO, L. N., V. V. KONDRAT'EVA, AND YA. YA. YARZHEMISKII (1962) Aksaite a new hydrous magnesium borate. *Zap. Vses. Mineral. Obshch.* **91,** 447–454 (in Russian).

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) *ORFLS, a Fortran crystallographic least-squares program. Oak Ridge National Laboratory* [U.S. Clearinghouse Fed. Sci. Tech. Info.] *Rep.* ORNL-TM-305.

———, ———, AND ——— (1964) *ORFFE, a Fortran crystallographic function and error program. Oak Ridge National Laboratory. [U.S. Clearinghouse Fed. Sci. Tech. Info.] Rep.* ORNL-TM-306.

CHRIST, C. L. (1960) Crystal chemistry and systematic classification of hydrated borate minerals. *Amer. Mineral.* **45,** 334–340.

CLARK, J. R. (1964) The crystal structure of tunellite, $SrB_6O_9(OH)_2 \cdot 3H_2O$. *Amer. Mineral.* **49,** 1549–1568.

———, AND R. C. ERD (1963) The probable chemical formula of aksaite, a new hydrated magnesium borate. *Amer. Mineral.* **48,** 930–935.

———, D. E. Appleman, and C. L. Christ (1964) Crystal chemistry and structure refinement of five hydrated calcium borates. *J. Inorg. Nucl. Chem.* **26,** 73–95.

Dal Negro, A., C. Sabelli, and L. Ungaretti (1969) The crystal structure of macallisterite $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$. *Acc. Naz. Lincei* **47,** 353–364.

Hamilton, W. C. (1959) On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.* **12,** 609–610.

Hanson, H. P., F. Herman, J. D. Lea, and S. Skilmann (1964) HFS atomic scattering factors. *Acta Crystallogr.* **17,** 1040–1044.

Lehmann, H. A., and H. J. Papenfuss (1959) Über ein wasserhaltiges Magnesiumhexaborat der Formel $MgB_6O_{10} \cdot 5H_2O$. *Z. Anorg. Allgemein. Chem.* **301,** 228–232.

Perloff, A., and S. Block (1966) The crystal structure of the strontium and lead tetraborates, $SrO \cdot 2B_2O_3$ and $PbO \cdot 2B_2O_3$. *Acta Crystallogr.* **20,** 274–279.

Zachariasen, W. H. (1963a) The secondary extinction correction. *Acta Crystallogr.* **16,** 1139–1144.

——— (1963b) The crystal structure of monoclinic metaboric acid. *Acta Crystallogr.* **16,** 385–389.

Manuscript received, January 18, 1971; accepted for publication, February 3, 1971.