

THE CRYSTAL STRUCTURE OF TUNELLITE,
 $\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}^1$

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ABSTRACT

Tunellite is a member of the borate series $M^{2+}\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, with $M^{2+} = \text{Sr}$ and $x = 4$. The mineral is monoclinic, $P2_1/a$, $a = 14.390 \pm 0.003$, $b = 8.213 \pm 0.002$, $c = 9.934 \pm 0.002$ Å, $\beta = 114^\circ 02' \pm 1'$, and is isostructural with the Ca analogue, nobleite. The crystal structure contains infinite sheets composed of polymerized borate polyanions, with Sr^{2+} cations and water molecules filling available spaces in and near the sheets. Each Sr^{2+} is coordinated by ten oxygens at an average distance of 2.74 Å. Adjacent sheets are held together solely by bonds to water molecules. The polymerized borate polyanions are composed of individual borate groups, each group containing three B-O tetrahedra and three B-O triangles. These polyhedra link at corners so that one oxygen is shared by all three tetrahedra, and three six-membered B-O rings result, each made up of two tetrahedra and one triangle. This is the first occurrence in any hydrated borate structure of one oxygen linked to three borons. The structural formula for tunellite is $\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. With one minor modification, Christ's rules for formation of hydrated borate polyanions are confirmed by the tunellite structure, whereas the first Edwards and Ross postulate is invalidated by linkage of three borons to one oxygen.

INTRODUCTION

Of the numerous known members in the borate series $M^{2+}\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (Table 1), only seven are minerals; all are rare, and all were found within the last 30 years. The first mineral of the series to be described was veatchite with $x = 2$ (Switzer, 1938), initially considered a Ca borate, but later found to be a Sr borate (Switzer and Brannock, 1950). The correct formula for veatchite remained in doubt for some years (Clark *et al.*, 1956), and as recently as 1963 Jäger and Lehmann proposed a formula which would remove veatchite from the $1 \cdot 3 \cdot x$ series. Their proposed formula, however, is incompatible with the veatchite crystallography (Clark, 1964), and Parkerson (1963a) has described the preparation of both synthetic veatchite and a synthetic Ca isomorph. There seems little doubt that veatchite correctly belongs in the $1 \cdot 3 \cdot x$ series. A dimorph of veatchite, called *p*-veatchite, was described by Braitsch (1959), and its relationship to veatchite was discussed by Clark and Mrose (1960).

The other minerals in the $1 \cdot 3 \cdot x$ series are higher hydrates, and the list includes two Mg borates, two Ca borates, and the Sr borate tunellite (Table 1). A synthetic dimorph of tunellite has been reported by Parkerson (1963b). Most of the minerals were known as synthetic compounds before their discovery in nature.

¹ Studies of Borate Minerals (XII). Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. KNOWN MEMBERS OF THE SERIES $M^{2+}O \cdot 3B_2O_3 \cdot xH_2O$

Mineral	M^{2+}	x	Reference
(synthetic) veatchite	Ca	2	Parkerson (1963a)
	Sr	2	Switzer (1938); Switzer and Brannock (1950)
<i>p</i> -veatchite	Sr	2	Braitsch (1959)
nobleite	Ca	4	Erd, McAllister and Vlisidis (1961)
tunellite	Sr	4	Erd, Morgan and Clark (1961)
(synthetic) ¹	Sr	4	Parkerson (1963b)
(synthetic)	Ba	4	Gode and Kešāns (1953)
aksaite	Mg	5	Blazko, <i>et al.</i> (1962); Clark and Erd (1963)
gowerite	Ca	5	Erd, <i>et al.</i> (1959)
(synthetic)	Sr	5	Gode and Kešāns (1953)
(synthetic)	Ba	5	Kešāns and Kupaks (1950)
(synthetic)	Ba	7	Sborgi (1914)
(synthetic) ²	Mg	7.5	Kešāns (1955); Kešāns, Švarcs and Vimba (1955)
(synthetic) ³	Ca	8	Meyerhoffer and van't Hoff (1907)
(synthetic)	Co, Mn, Ni	8	Kešāns (1955); Kešāns and Krymova (1956); Kešāns Vimba and Švarcs (1955)
(synthetic)	Ni	10	Krymova (1955)
(synthetic) ³	Ca	12	Meyerhoffer and van't Hoff (1907); Sborgi (1913)

¹ Dimorph of tunellite.

² Has been found in nature recently (oral communication, W. T. Schaller, M. E. Mrose and A. C. Vlisidis, 1963).

³ Needs verification; has been reported only by reference given.

The rarity of these $1 \cdot 3 \cdot x$ borates as minerals despite the large number of known synthetic compounds, and the presence of two known pairs of dimorphs in the series suggested study of the series in order to determine the nature of the borate polyanions. The formation of borate polyanions in hydrated borates has been discussed in recent years by Ingri *et al.* (1957) and Ingri (1963), by Edwards and Ross (1960) and by Christ (1960). The latter proposed four simple rules governing the formation of borate polyanions in hydrated borate minerals. Using these rules, Christ (1960) predicted the polyanions that might be found in crystals of as yet unknown structure. His prediction that inderite, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$, would prove to have the same $[B_3O_3(OH)_5]^{2-}$ polyanion as the higher

hydrates of the $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ series (summary, Clark, Appleman, and Christ, 1964) was confirmed by Ashirov, Rumanova, and Belov (1962). The prediction (Christ, 1960) that hydroboracite, $\text{MgO} \cdot \text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, would contain the same $[\text{B}_3\text{O}_4(\text{OH})_3]_n^{-2n}$ chains as colemanite was verified by Rumanova and Ashirov (1963). Finally, the prediction (Christ, 1960) that probertite, $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$, would contain a polyanion formed by replacing two borate triangles of the pentaborate polyion (Zachariasen, 1937; Zachariasen and Plettinger, 1963) by two tetrahedra was confirmed by Kurbanov *et al.* (1963).

For members of the $1 \cdot 3 \cdot x$ series Christ (1960), and also Edwards and Ross (1960), predicted a polyanion formed by joining one borate tetrahedron and two borate triangles at corners to make a six-membered boron-oxygen ring. A few months later, Krogh-Moe (1960) reported the presence of such a polyanion in the structure of anhydrous cesium triborate, $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$. In hydrated borates, the polyanion would have the formula $[\text{B}_3\text{O}_3(\text{OH})_4]^{1-}$ if isolated in the structure. The possibility of the polyanions forming dimers, chains, or sheets by combining and splitting out water was also discussed by Christ (1960).

Crystal-structure studies for the various members of the series were started by examination of the isostructural pair, tunellite (Sr, $x=4$) and nobleite (Ca, $x=4$). The present paper describes the results for the tunellite structure. A preliminary account of the structure (Clark, 1963*a*) and a note on the nature of the polyanion (Clark, 1963*b*) have already appeared.

EXPERIMENTAL WORK

Crystal description, cell dimensions and space group. The crystals of tunellite used in the present study were supplied by Richard C. Erd, U. S. Geological Survey, from among those found in the Jenifer mine, Kramer borate district, California. The crystallography of tunellite, including both single-crystal and powder x -ray diffraction data, optics and other physical properties, description of locality, and preparation of synthetic $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ are all given by Erd, Morgan, and Clark (1961). Similar data for nobleite are given by Erd, *et al.* (1961).

The cell constants initially obtained for tunellite have been refined by least-squares treatment of the x -ray diffractometer powder data using a program written for the Burroughs 220 digital computer by Evans, *et al.* (1963). The refined constants and other crystallographic data pertinent to the present work are given in Table 2.

Intensity measurements. X -ray equi-inclination Weissenberg photographs of tunellite were taken for the $h0l$, $h1l$, $h2l$, $hk0$, $hk1$, and $hk2$ levels with Ni-filtered Cu radiation. An $0kl$ photograph was taken on the precession

camera with Zr-filtered Mo radiation. Intensities were estimated visually and are greater than zero for 1206 out of 1315 independent observations. For nobleite, a complete set of pictures about rotation axis [010] were taken with Zr-filtered Mo radiation, but intensities were read only for the $h0l$ level. The resulting data were used chiefly to confirm the isostructural relationship. The x and z parameters obtained for Ca and some of the other atoms have not been refined and are therefore not reported here.

TABLE 2. CRYSTALLOGRAPHIC DATA FOR TUNELLITE AND NOBLEITE

	Tunellite ¹ SrO·3B ₂ O ₃ ·4H ₂ O	Nobleite ² CaO·3B ₂ O ₃ ·4H ₂ O
symmetry	monoclinic	monoclinic
a	14.390 ± 0.003 Å	14.56 ± 0.05 Å
b	8.213 ± 0.002	8.01 ₆ ± 0.02
c	9.934 ± 0.002	9.83 ₃ ± 0.02
β	114°02' ± 1'	110°45' ± 10'
cell volume	1072 Å ³	1066 Å ³
space group	$P2_1/a$	$P2_1/a$
cell contents	4[SrO·3B ₂ O ₃ ·4H ₂ O]	4[CaO·3B ₂ O ₃ ·4H ₂ O]
density, g cm ⁻³ , calc.	2.381	2.09 ₃
obs.	2.40 ± 0.01	2.09 ± 0.01
cleavages	(100) perfect (001) distinct	(100) perfect (001) indistinct

¹ Cell constants, volume, and calculated density from present study; other data from Erd, Morgan, and Clark (1961).

² Data from Erd, McAllister, and Vlisidis (1961).

The intensities were corrected for Lorentz and polarization factors to obtain the observed structure amplitudes. No corrections for absorption or extinction were made.

Refinement procedures. The following atomic scattering factors were used: for boron, the zero-valence values of Ibers (1957); for all oxygen atoms, the zero-valence values of Berghuis *et al.* (1955); and for strontium, the doubly ionized values of Thomas and Umeda (1957).

Least-squares refinement of the data was carried out on a Burroughs 220 digital computer, using a program written by J. Marshek and Daniel E. Appleman, U.S. Geological Survey. The program uses the full matrix of the normal equations and permits refinement of atomic coordinates, temperature factors B (overall isotropic, individual isotropic or anisotropic), and scaling constants relating calculated and observed structure factors.

TABLE 3. FINAL ATOMIC PARAMETERS AND ASSOCIATED STANDARD ERRORS FOR TUNELLITE, $\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$

Atom	Coordinates and standard errors (cycles)			Isotropic temperature factors B and standard errors (\AA^2)
	x	y	z	
B ₁	0.1941 ± 0.0013	0.1509 ± 0.0031	0.8490 ± 0.0020	1.31 ± 0.30
B ₂	0.1940 ± 0.0012	0.1561 ± 0.0029	0.5854 ± 0.0019	0.88 ± 0.27
B ₃	0.0429 ± 0.0013	0.2475 ± 0.0030	0.6248 ± 0.0020	1.24 ± 0.29
B ₄	0.1867 ± 0.0011	0.4550 ± 0.0026	0.2202 ± 0.0018	0.75 ± 0.26
B ₅	0.2534 ± 0.0014	0.3889 ± 0.0029	0.4865 ± 0.0022	1.27 ± 0.30
B ₆	0.2513 ± 0.0014	0.3883 ± 0.0029	0.0221 ± 0.0020	1.20 ± 0.30
O ₁	0.1944 ± 0.0009	0.0254 ± 0.0019	0.9525 ± 0.0013	1.67 ± 0.22
O ₂	0.2028 ± 0.0009	0.0376 ± 0.0019	0.4823 ± 0.0013	1.83 ± 0.22
O ₃ ¹	0.0501 ± 0.0009	0.6806 ± 0.0019	0.4257 ± 0.0014	1.99 ± 0.23
O ₄ ²	0.9982 ± 0.0010	0.1682 ± 0.0021	0.2383 ± 0.0015	2.44 ± 0.25
O ₅ ¹	0.0905 ± 0.0009	0.5360 ± 0.0019	0.1721 ± 0.0014	2.10 ± 0.24
O ₆	0.2417 ± 0.0008	0.7988 ± 0.0018	0.3989 ± 0.0013	1.46 ± 0.21
O ₇	0.2079 ± 0.0008	0.3413 ± 0.0019	0.3396 ± 0.0013	1.56 ± 0.21
O ₈	0.2382 ± 0.0008	0.7853 ± 0.0018	0.0815 ± 0.0013	1.53 ± 0.21
O ₉	0.1941 ± 0.0008	0.3498 ± 0.0018	0.1011 ± 0.0013	1.47 ± 0.21
O ₁₀	0.0889 ± 0.0008	0.2117 ± 0.0017	0.7728 ± 0.0012	1.28 ± 0.20
O ₁₁	0.0871 ± 0.0008	0.2102 ± 0.0017	0.5344 ± 0.0012	1.23 ± 0.20
O ₁₂ ²	0.0208 ± 0.0008	0.8401 ± 0.0019	0.0676 ± 0.0013	1.59 ± 0.21
O ₁₃ ²	0.1392 ± 0.0009	0.5802 ± 0.0019	0.7117 ± 0.0014	2.01 ± 0.23
O ₁₄ ³	0.2272 ± 0.0008	0.0828 ± 0.0017	0.7338 ± 0.0012	1.06 ± 0.19
Sr	0.1621 ± 0.0001	0.0562 ± 0.0002	0.1949 ± 0.0002	1.23 ± 0.04

¹ Hydroxyl oxygen.

² Water oxygen.

³ Oxygen linked to three borons.

A program for calculation of all possible bond distances less than a pre-assigned value, written by David S. Handwerker, U. S. Geological Survey, was helpful in verifying the proposed structure as well as insuring that no pertinent bonds were overlooked. Final calculations of bond distances and angles were made from the atomic coordinates in Table 3. The standard errors were determined from the complete inverse matrix of the normal equations, using a program written by David S. Handwerker in which the procedure is similar to that described by Busing and Levy (1959).

STRUCTURE DETERMINATION

Tunellite has one strontium, fourteen oxygen, and six boron atoms located in the general fourfold positions $4e$ of space group $P2_1/a$. Ini-

tially, an effort was made to solve the structure using $hk0$ and $h0l$ projection data only. The x , y , z coordinates of Sr were determined from the two respective Patterson maps, and refinement by successive electron-density calculations permitted gradual assignment of x and z coordinates for fourteen oxygens. The $h0l$ residual, $R = \frac{\sum | | F_o | - | F_c | |}{\sum | F_o |}$, dropped to 0.19 during this refinement. However, assignment of y coordinates was hampered by considerable overlap and ambiguity in the $hk0$ projection, and the residual for the $hk0$ data could not be lowered below 0.29. A satisfactory structure could not be evolved, therefore, and recourse to three-dimensional data was required.

The coordinates for Sr were confirmed from a three-dimensional Patterson map. Signs were then obtained from a set of structure factors based on the strontium coordinates and fourteen "best"-atom coordinates (three-dimensional data, R for Sr alone 0.37; R for Sr plus 14 "best" atoms, 0.29), and a three-dimensional electron-density map was calculated. From this map the y coordinates of 14 atoms were confirmed or corrected, and positions of the remaining six atoms were added to produce a satisfactory structure. Six cycles of least-squares refinement were then carried out, the first four with an overall isotropic B and the last two with individual isotropic B_i . Computer capacity was insufficient for refinement of individual anisotropic temperature factors. After only two cycles of refinement the residual dropped to 0.17 and a final R of 0.11 for the 1206 structure factors observed greater than zero was achieved. The final set of atomic parameters is given in Table 3, and the observed and calculated structure factors are compared in Table 4.¹ Standard errors in the bond distances and angles are listed in Tables 5-11.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Tunellite has a sheet structure, in accordance with its common platy habit and direction of perfect cleavage. The infinite sheets contain polymerized borate polyanions, Sr^{2+} cations, and water molecules. Adjacent sheets are linked *via* bonds to water molecules. Details of the structure are considered in the following sequence: first, the borate polyanions; second, the $\text{SrB}_6\text{O}_9(\text{OH})_2$ -water sheets; and third, the intersheet linkage and hydrogen bonding.

Borate polyanion in tunellite. The polyanion in tunellite is not the one

¹ Table 4 has been deposited as Document No. 8113 with the ADI Auxiliary Publications Project, Photopublication Service, Library of Congress, Washington, D. C., 20540. A copy may be secured by citing the Document number and by remitting \$5.00 for photoprints or \$2.25 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE 5. OXYGEN-BORON-OXYGEN ANGLES¹ IN TUNELLITE

(see Fig. 1)

	Atoms	Angle (°)
Tetrahedron around B ₁	O ₁ -B ₁ -O ₈ ''	113
	O ₁ -B ₁ -O ₁₀	108
	O ₁ -B ₁ -O ₁₄	111
	O ₈ ''-B ₁ -O ₁₀	110
	O ₈ ''-B ₁ -O ₁₄	107
	O ₁₀ -B ₁ -O ₁₄	108
Tetrahedron around B ₂	O ₂ -B ₂ -O ₆ ''	112
	O ₂ -B ₂ -O ₁₁	110
	O ₂ -B ₂ -O ₁₄	110
	O ₆ ''-B ₂ -O ₁₁	109
	O ₆ ''-B ₂ -O ₁₄	107
	O ₁₁ -B ₂ -O ₁₄	109
Tetrahedron around B ₄ '' (O ₈ '' is OH ⁻)	O ₅ ''-B ₄ ''-O ₇ ''	115
	O ₅ ''-B ₄ ''-O ₉ ''	112
	O ₅ ''-B ₄ ''-O ₁₄	109
	O ₇ ''-B ₄ ''-O ₉ ''	102
	O ₇ ''-B ₄ ''-O ₁₄	109
	O ₉ ''-B ₄ ''-O ₁₄	109
	average of 18,	109°
Triangle around B ₃ (O ₈ ' is OH ⁻)	O ₃ '-B ₃ -O ₁₀	117
	O ₃ '-B ₃ -O ₁₁	121
	O ₁₀ -B ₃ -O ₁₁	121
Triangle around B ₅ ''	O ₂ -B ₅ ''-O ₆	117
	O ₂ -B ₅ ''-O ₇ ''	118
	O ₆ -B ₅ ''-O ₇ ''	125
Triangle around B ₆ ''	O ₁ -B ₆ ''-O ₈	115
	O ₁ -B ₆ ''-O ₉ ''	122
	O ₈ -B ₆ ''-O ₉ ''	123
	average of 9	120°

¹ All angles ±1.5°.

that was predicted for members of the 1·3·x series (Christ, 1960; Edwards and Ross, 1960). The actual polyanion is formed of three boron-oxygen triangles and three tetrahedra. These polyhedra are linked at corners so that one oxygen is in common with all three tetrahedra and is the central point of three six-membered boron-oxygen rings, each ring

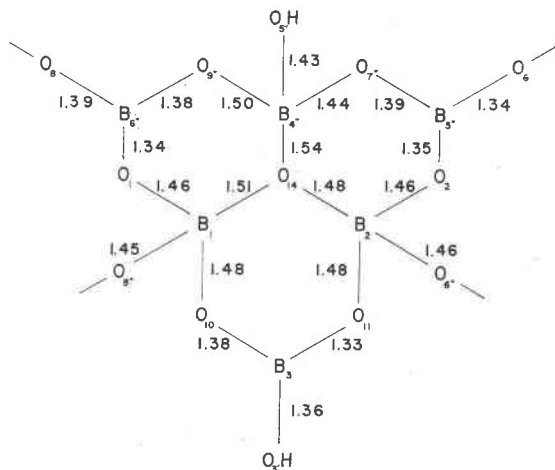


FIG. 1. Schematic view of $[B_6O_9(OH)_2]^{2-}$ polyanion in tunellite showing B-O distances (in Å, all ± 0.03 Å). Average values, for 12 tetrahedral B-O 1.47 Å, for 9 triangular B-O 1.36 Å. Identification of atoms as in Table 3; atoms with doubly primed numbers are at $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$ (or $1-z$).

formed by corner-sharing among two tetrahedra and one triangle. A schematic view of this polyanion is given in Fig. 1, on which B-O bond lengths are indicated. The polyanion provides the first example in any hydrated borate crystal structure of three borons linked to one oxygen. Berger (1953) proposed a structure for anhydrous B_2O_3 in which such coordination occurs, but that structure was determined from x -ray powder diffraction data only and has not been refined by modern techniques. Comparison is therefore meaningless at present.

In tunellite the B-O distances (Figure 1) and the O-B-O angles (Table 5), both triangular and tetrahedral, are within the expected ranges found in other borates (Zachariassen, 1963; Clark *et al.*, 1964). For the triply linked oxygen O_{14} , the three tetrahedral B-O distances are 1.48, 1.51, and 1.54 Å (all ± 0.03 Å). The average of 1.51 Å is slightly higher than the usual 1.47 Å, an increase that would be expected from bonding considerations, and a value identical to that suggested by Zachariassen (1963) for oxygen bonded to three borons. The three B-O-B angles about this oxygen (Table 6) are 118° , 119° , and 122° (all $\pm 2^\circ$). The B-O-B ring angles previously noted (Clark *et al.*, 1964) average 121.9° .

The six-membered B-O ring formed by corner-sharing of two tetrahedra and a triangle was first described in the structure of colemanite (Christ, Clark, and Evans, 1958) and is present in all members of the $2M^{2+}O \cdot 3B_2O_3 \cdot xH_2O$ series (Clark *et al.*, 1964) and in hydroboracite

TABLE 6. RING ANGLES, PLANES AND DEVIATIONS FROM PLANEARITY IN TUNELLITE

(See Figs. 1 and 2)

Ring no.	Ring atoms	B-O-B angles ¹	
		Atoms	Angle (°)
1	B ₁ -O ₁ -B ₆ ''-O ₉ ''-B ₄ ''-O ₁₄	B ₁ -O ₁ -B ₆ ''	124
		B ₁ -O ₁₄ -B ₄ ''	119
		B ₄ ''-O ₉ ''-B ₆ ''	124
		B ₂ -O ₂ -B ₅ ''	128
2	B ₂ -O ₂ -B ₅ ''-O ₇ ''-B ₄ ''-O ₁₁	B ₂ -O ₁₄ -B ₄ ''	119
		B ₄ ''-O ₇ ''-B ₅ ''	122
		B ₁ -O ₁₀ -B ₃	125
3	B ₁ -O ₁₀ -B ₃ -O ₁₁ -B ₂ -O ₁₄ Linking adjacent polyanions	B ₁ -O ₁₄ -B ₂	122
		B ₂ -O ₁₁ -B ₅	124
		B ₁ -O ₈ ''-B ₆	124
		B ₂ -O ₆ ''-B ₅	123
		average of 11	123°

Equation², $lx + mY + nZ = p$, of plane through three oxygens

Ring no.	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>	Nearest crystallographic plane
1	0.605	0.576	0.549	4.23	421
2	0.862	0.476	0.174	1.74	72 $\bar{1}$
3	0.459	0.867	0.194	2.02	340

Ring no.	Atom	Perpendicular distance ³ from plane of ring oxygens (Å)
1	B ₁	-0.33
	B ₄ ''	-0.26
	B ₆ ''	+0.11
	O ₃	+0.43
2	O ₃ ''	-1.73
	B ₂	-0.16
	B ₄ ''	-0.48
	B ₅ ''	+0.10
	O ₆	+0.29
3	O ₆ ''	-1.48
	B ₁	-0.25
	B ₂	-0.32
	B ₃	+0.03
	O ₃ ' (OH)	+0.13

Angles between planes of ring oxygens

1,2	153°
1,3	152°
2,3	147°

¹ All angles $\pm 1.5^\circ$ ² Perpendicular form of equation referred to orthogonal axes; $X = ax + c \cos \beta z$, $Y = by$, $Z = cz (1 - \cos^2 \beta)^{1/2}$.³ All distances ± 0.03 Å.

(Rumanova and Ashirov, 1963). It also occurs in the probertite structure (Kurbanov *et al.*, 1963). At present no description of the ring has been given for probertite or for hydroboracite, but in the $2 \cdot 3 \cdot x$ series members the ring is nearly planar when the polyanions are isolated units (monomers) in the crystal structure (Clark, 1959; Clark and Christ, 1959; Christ and Clark, 1960*a*). Distortions from the planar ring configuration are found in colemanite which contains polyanion chains (Christ *et al.*, 1958) and in a synthetic compound which contains polyanion sheets (Clark, *et al.*, 1962).

These previous results suggest that the three six-membered B-O rings in the polymerized polyanion of tunellite will not be planar rings, and they are not (Table 6). Within the limits of error, the triply linked oxygen and its three borons are planar, but the constraints thus imposed on the remaining ring atoms lead to some distortion in each ring. All

TABLE 7. OXYGEN-OXYGEN DISTANCES¹ WITHIN THE BORON-OXYGEN POLYHEDRA OF TUNELLITE

(See Fig. 1)

Tetrahedron around B ₁		Tetrahedron around B ₂	
O ₁ -O ₁₄	2.45 Å	O ₂ -O ₁₄	2.41 Å
O ₁₀ -O ₁₄	2.42	O ₁₁ -O ₁₄	2.41
O ₈ ''-O ₁₄	2.37	O ₆ ''-O ₁₄	2.36
O ₁ -O ₈ ''	2.42	O ₂ -O ₆ ''	2.42
O ₁ -O ₁₀	2.37	O ₂ -O ₁₁	2.40
O ₈ ''-O ₁₀	2.39	O ₆ ''-O ₁₁	2.39
Average	2.40 Å	Average	2.40 Å
Tetrahedron around B ₄ ''		Triangle around B ₃	
O ₇ ''-O ₁₄	2.43 Å	O ₁₀ -O ₁₁	2.36 Å
O ₉ ''-O ₁₄	2.47	O ₁₀ -O ₈ ' (OH)	2.34
O ₁₄ -O ₅ '' (OH)	2.43	O ₁₁ -O ₈ ' (OH)	2.34
O ₇ ''-O ₅ '' (OH)	2.43		
O ₇ ''-O ₉ ''	2.30		
O ₉ ''-O ₅ '' (OH)	2.43		
Average	2.42 Å		
Triangle around B ₅ ''		Triangle around B ₆ ''	
O ₂ -O ₆	2.29 Å	O ₁ -O ₉ ''	2.37 Å
O ₂ -O ₇ ''	2.35	O ₁ -O ₈	2.30
O ₆ -O ₇ ''	2.42	O ₈ -O ₉ ''	2.44
Average of 9 triangular O-O distances			2.36 Å
Average of 18 tetrahedral O-O distances			2.41 Å

¹ All O-O distances, ± 0.02 Å.

TABLE 8. BORON-BORON DISTANCES¹ IN TUNELLITE

Within the polyanion			
B ₁ -B ₄ ''	2.64 Å	B ₂ -B ₅ ''	2.52 Å
B ₁ -B ₂	2.62	B ₄ ''-B ₅ ''	2.48
B ₂ -B ₄ ''	2.59	B ₂ -B ₃	2.48
B ₄ ''-B ₆ ''	2.56	B ₁ -B ₃	2.52
B ₁ -B ₆ ''	2.47	Average of nine,	2.54 Å
Cross-linking polyanions			
B ₁ -B ₆	2.51 Å	B ₂ -B ₅	2.46 Å

¹ All B-B distances, ± 0.03 Å.

three rings have one triangular boron within ± 0.1 Å of the plane defined by the three ring oxygens, but in two rings the other two borons are each approximately -0.3 Å off the plane, and in the third ring one boron is off by -0.5 Å. The angles between the planes average 151° .

Other distances of interest within the polyanion are those between oxygens linked to the same boron (Table 7), and those between borons (Table 8). These distances are all within the expected ranges of values (Clark *et al.*, 1964). The average B-B distance of 2.54 Å is slightly longer than the 2.50_5 Å average found in the $2 \cdot 3 \cdot x$ borates. The difference arises from the three longer B-B separations (2.64 , 2.62 , and 2.59 Å) around the triply linked oxygen in tunellite.

The polyanions in tunellite are not monomers, and further structural studies of $1 \cdot 3 \cdot x$ borates will be required to show whether any do contain monomers of the present polyanion. Such monomers, according to Christ's third rule (Christ, 1960) would have protons on those oxygens linked to only one boron and hence would have the chemical formula¹ $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$. However, in tunellite the polyanions are linked according to Christ's fourth rule (Christ, 1960) to form infinite sheets of composition $n[\text{B}_6\text{O}_9(\text{OH})_2]^{2-}$.

The SrB₆O₉(OH)₂-water sheets. The strontium cations and the water molecules fit into the spaces left by the polyanion linkage (Fig. 2). The strontium cations are an integral part of the sheet structure in tunellite, and the Sr-O bonding is probably of major importance to the stability of the sheet structure. Two of the three water molecules (O₄, O₁₂) must also be considered a part of the sheet structure, since they form hydrogen

¹ Christ (1960) gives this chemical formula in connection with a dimer form of the predicted $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ polyanion. The configuration of such a dimer would be completely different from the monomer form of the tunellite polyanion despite the identity of formula.

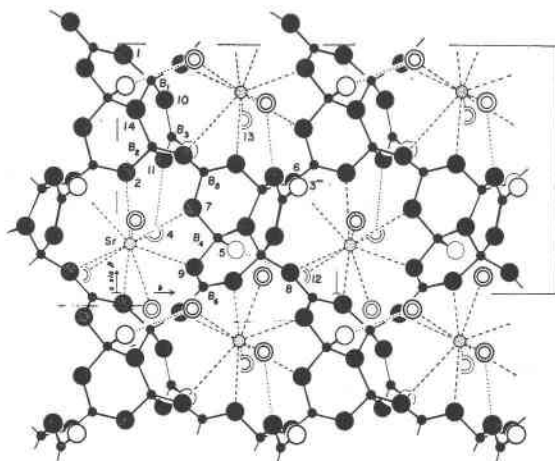


FIG. 2. View along a of one $\text{SrB}_6\text{O}_9(\text{OH})_2$ -water sheet in tunellite; the sheet related by the a glide plane has been omitted. Dashed lines indicate Sr-O bonds (Table 10); dotted lines, H-bonds within the sheet (Table 9). Labelled atoms are at y, z of Table 3 except for O_3'' , at $\frac{1}{2} + y, z$, and O_6 , which has been shifted slightly upward along z to avoid confusion in the drawing. Key for atoms is same as on Figure 3.

bonds within the sheets (Table 9). The $\text{Sr}[\text{B}_6\text{O}_9(\text{OH})_2]$ -water sheets are about 3.6 \AA thick and are oriented approximately parallel to (100).

Strontium is coordinated by an irregular array of six oxygens plus four water molecules, all within 2.61 to 2.98 \AA (Table 10). There are no Sr-O distances of the present accuracy ($\pm 0.015 \text{ \AA}$) in the literature, and few have ever been determined at all. The present structure is the first reported example of tenfold oxygen coordination for strontium. Eight symmetry-equivalent Sr-O distances of $2.60 \pm 0.03 \text{ \AA}$ were found by Smith

TABLE 9. POSTULATED HYDROGEN BONDS IN TUNELLITE

(See Figs. 2 and 3)

Bond	Atoms ¹	Distance ² (Å)
A ₁	$\text{O}_4(\text{H}_2\text{O})$ at $x-1, y, z$ to O_{11} (ring O^{2-})	2.71
A ₂	$\text{O}_{12}(\text{H}_2\text{O})$ to $\text{O}_5(\text{OH}^-)$	2.73
A _n bonds within the $\text{SrB}_6\text{O}_9(\text{OH})_2$ -water sheets		
R _n bonds across adjacent $\text{SrB}_6\text{O}_9(\text{OH})_2$ -water sheets		
R ₁	$\text{O}_{12}(\text{H}_2\text{O})$ to O_{10}' (ring O^{2-}) at $\bar{x}, 1-y, 1-z$	2.69
R ₂	$\text{O}_{13}(\text{H}_2\text{O})$ to $\text{O}_3(\text{OH}^-)$	2.73

¹ Atoms at x, y, z of Table 3 unless otherwise noted.

² Distances $\pm 0.02 \text{ \AA}$.

(1953) in strontium hydroxide octahydrate, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. A similar set of eight at 2.64 Å was found by Vannerberg (1959) in strontium peroxide octahydrate, $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$. Furberg and Helland (1962) reported eight-coordinated Sr with four pairs of symmetry-equivalent Sr-O distances, 2.58, 2.59, 2.60, and 2.68 Å, in strontium arabonate pentahydrate, $\text{Sr}(\text{C}_5\text{O}_6\text{H}_9)_2 \cdot 5\text{H}_2\text{O}$. Twelve-coordinated Sr(Sr-O, 2.76 Å) occurs in the

TABLE 10. STRONTIUM-OXYGEN DISTANCES¹ IN TUNELLITE
(See Fig. 2)

Oxygen	Sr-O distance (Å)	Location of oxygen ²
O ₁₂ (H ₂ O)	2.606	$x, y-1, z$
O ₁₃ (H ₂ O)	2.630	$\frac{1}{2}-x, y-\frac{1}{2}, 1-z$
O ₁	2.644	$x, y, z-1$
O ₂	2.675	x, y, z
O ₇	2.685	x, y, z
O ₉	2.691	x, y, z
O ₄ (H ₂ O)	2.724	$x-1, y, z$
O ₆	2.828	$x, y-1, z$
O ₈	2.902	$x, y-1, z$
O _{12'} (H ₂ O)	2.977	$\bar{x}, 1-y, \bar{z}$
Average of 10,	2.736	

¹ All Sr-O distances, ± 0.015 Å.

² x, y, z as in Table 3; Sr taken at x, y, z .

perovskite-like structure of strontium titanate, SrTiO_3 (Donnay *et al.*, 1963). The present average Sr-O value of 2.74 Å may be compared to average Ca-O values of from 2.46 to 2.48 Å in the $2 \cdot 3 \cdot x$ series for eight-coordinated Ca (Clark *et al.*, 1964). The closest Sr-Sr approach in tunellite is 4.79 Å.

Linkage of sheets and hydrogen bonding. The $\text{Sr}[\text{B}_6\text{O}_9(\text{OH})_2]$ -water sheets are joined solely through water molecules (Fig. 3). There are no direct contacts between polyanions in adjacent sheets. One long Sr-water bond links across the sheets (Sr-O_{12'}, 2.98 Å), in addition to two hydrogen bonds (Table 9). A 3.04 Å approach of two water molecules (Table 11) is probably not a hydrogen bond, for reasons discussed below. The perfect cleavage parallel to (100), as well as the common habit of the crystals, platy with large {100}, are satisfactorily explained by the structure. As Fig. 3 shows, the water molecules and hydroxyls are on the surfaces of the sheets. These same atoms, with the exception of water O₁₂ which coordinates two Sr cations, appropriately have the highest isotropic temperature factors observed in the structure (Table 3).

Four of the eight protons associated with the asymmetric unit probably are not participating in hydrogen-bond formation. This at first surprising observation is explained when the overall charge balance in the structure is considered according to correlations given by Zachariasen (1963) for bond strength vs. bond length in borates (Table 12). In com-

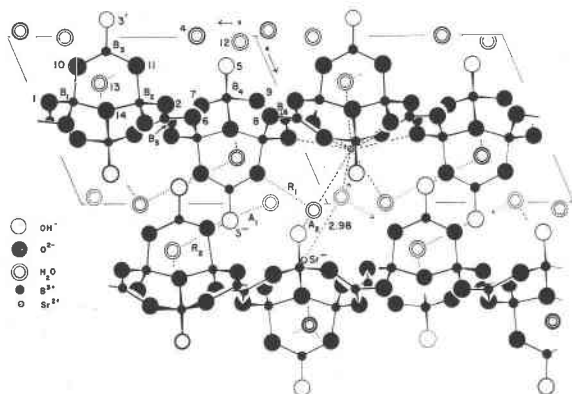


FIG. 3. View along b in tunellite, showing the $\text{SrB}_6\text{O}_9(\text{OH})_2$ -water sheets on edge and the intersheet linkages. Numbered atoms are those at x, z of Table 3, except for O_3' ($\bar{x}, 1-z$) and O_3''' , Sr''' ($\frac{1}{2}+x, z$). The solid lines enclose $\frac{1}{2}a, 1c$. Sr-O bonds (Table 10) are shown for Sr at $\frac{1}{2}-x, \bar{z}$ by dashed lines; one intersheet Sr- O_{12}' bond is labelled. Dotted lines show H-bonds (Table 9); A_n bonds are intrasheet and R_n bonds are intersheet.

piling the present table, Zachariasen's values for B-O and O-H \cdots O bonds were used, and a 0.2 value was assigned to each Sr-O bond regardless of length. (The summations are not improved by taking the Sr-O lengths into account.) The summations of 28.14 for anions and for cations are satisfactory in view of the standard errors associated with the bonds. The analysis shows that the hydroxyls are almost certainly accepting rather than donating protons in their hydrogen bonds with water molecules. The analysis also suggests that the 3.04 Å approach of two water molecules (Table 11) is unlikely to be a hydrogen bond, as retention of one proton by water molecule O_4 and O_{13} would best maintain the local charge balance.

The environment of the water molecules is detailed in Table 11. Water O_{12} makes two donor hydrogen bonds and two Sr contacts, one short and one long (in violation of a common assumption that a water molecule will have only one *divalent* cation neighbor—see *e.g.* Wells, 1962, p. 576). A 2.90 Å distance to its centrosymmetric equivalent O_{12}' at $\bar{x}, 1-y, \bar{z}$ is the shortest edge of the Sr coordination polyhedron. The other two water molecules each make one Sr contact and one donor hydrogen bond.

TABLE 11. WATER MOLECULE ENVIRONMENT IN TUNELLITE
(See Fig. 3)

Neighbor ¹	Distance (Å)
Around O ₄ at $x-1, y, z$	
O ₁₁ (ring O ²⁻) ³	2.71 ± 0.02
Sr ²⁺	2.724 ± 0.015
O ₁₃ ' (H ₂ O) at $\bar{x}, 1-y, 1-z$ angles: Sr-O ₄ -O ₁₁ , 99° 07' ± 28' O ₁₁ -O ₄ -O ₁₃ ', 77° 42' ± 31'	3.04 ± 0.02
Around O ₁₂ at x, y, z	
O ₁₀ ' (ring O ²⁻) ³ at $\bar{x}, 1-y, 1-z$	2.69 ± 0.02
O ₅ (OH ⁻) ²	2.73 ± 0.02
Sr ²⁺ at $x, 1+y, z$	2.606 ± 0.015
Sr ²⁺ at $\bar{x}, 1-y, \bar{z}$	2.977 ± 0.015
Angles O ₅ -O ₁₂ -O ₁₀ ', 81° 02' ± 32' Sr-O ₁₂ -Sr' 117° 51' ± 32' Sr-O ₁₂ -O ₅ 110° 10' ± 29' Sr'-O ₁₂ -O ₅ 130° 36' ± 34' Sr-O ₁₂ -O ₁₀ ' 110° 33' ± 31' Sr'-O ₁₂ -O ₁₀ ' 92° 17' ± 24'	
Around O ₁₃ at x, y, z	
O ₃ (OH ⁻) ³	2.73 ± 0.02
Sr ²⁺ at $\frac{1}{2}x, \frac{1}{2}+y, 1-z$	2.630 ± 0.015
O ₄ '(H ₂ O) at $1-x, 1-y, 1-z$	3.04 ± 0.02
angles: Sr''-O ₁₃ -O ₃ , 111° 54' ± 31' O ₃ -O ₁₃ -O ₄ ', 84° 28' ± 34'	

¹ All atoms at x, y, z of Table 3 unless otherwise noted.

² Donor H-bond within SrB₆O₉(OH)₂-water sheet.

³ Donor H-bond across SrB₆O₉(OH)₂-water sheet.

CRYSTAL CHEMICAL CONSIDERATIONS

Rules for formation of hydrated borates. Among those authors who have discussed formation of hydrated borate polyanions, only Ingri *et al.* (1957) specifically considered the possibility that one oxygen might link to more than two borons. Ingri *et al.* concluded that such linkage was unlikely in the aqueous solutions which were their particular concern. Although Christ (1960) did not discuss the possibility, it can readily be included in his rules with the addition of only two words to his third rule. The revised third rule, with the added words in italics, is as follows: In

the polyions of hydrated borates those oxygens not shared by two *or more* borons always attach a proton and exist as hydroxyl groups. With this slight revision, all four of Christ's rules remain valid.

Of the five postulates proposed by Edwards and Ross (1960), the first states that the ratio of tetrahedral boron to total boron is equivalent to the ratio of cation charge to total boron. Similar considerations have been advanced by Krogh-Moe (1960, 1962). This postulate depends on the tacit assumption that one oxygen is shared by no more than two borons. The postulate is therefore invalidated by the existence of the tunellite

TABLE 12. CHARGE BALANCE¹ IN TUNELLITE

Cation Anion	T	T	Δ	T	T	Δ		H		
	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	Sr ²⁺	bond	H ⁺	Σ
O ₁	0.78					1.07	0.20			2.05
O ₂		0.78			1.04		0.20			2.02
O ₃ (OH)			1.01					0.24	1.00	2.25
O ₅ (OH)				0.85				0.24	1.00	2.09
O ₆		0.78			1.10		0.20			2.08
O ₇				0.83	0.94		0.20			1.97
O ₈	0.80					0.94	0.20			1.94
O ₉				0.69		0.97	0.20			1.86
O ₁₀	0.74		0.97					0.26		1.97
O ₁₁		0.74	1.10					0.24		2.08
O ₁₄	0.67	0.74		0.60						2.01
O ₄ (H ₂ O)							0.20	0.76	1.00	1.96
O ₁₂ (H ₂ O)							0.40	1.50		1.90
O ₁₃ (H ₂ O)							0.20	0.76	1.00	1.96
Σ	2.99	3.04	3.08	2.97	3.08	2.98	2.00	4.00	4.00	28.14
										28.14

¹ Values for B-O and H-bonds taken from Zachariassen (1963); Sr-O assumed 0.20.

² T means tetrahedral B; Δ, triangular B.

polyanion. The present results emphasize the importance of experimental crystal-structure determination, since the tunellite polyanion was not predicted despite excellent knowledge about the principles of formation for hydrated borates. The four rules established by Christ are the best available statement of these principles.

Unanswered questions about the 1·3·x borates. Earlier speculations concerning the probable structures of veatchite and *p*-veatchite (Clark and Mrose, 1960), gowerite (Christ and Clark, 1960*b*), and aksaite (Clark and Erd, 1963) must be revised in view of the tunellite structure results. The tunellite polyanion, possibly modified according to Christ's rules, almost certainly is present in other 1·3·x borates. In particular, the occurrence of sizeable amounts of Ba in some tunellite crystals suggests that syn-

thetic $\text{BaO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ may have the same structure as tunellite (Erd Morgan and Clark, 1961).

A number of problems concerning these $1 \cdot 3 \cdot x$ borates still remain, however. For instance, is the monomeric form $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$ of the tunellite polyanion actually stable? If it is, it should be found in crystal structures of other members of this series. Can such a polyanion also be stable in solution or does it form only in the crystallization process? Why should the polyanions link to form the tunellite sheet structure and leave three water molecules rather than hydrate to form monomers, leaving only one water molecule? The very existence of the sheet structure in the presence of three water molecules raises some doubts about the stability of the monomer. Theoretically, the polyanions might also link to form dimers or chains. Do any of the $1 \cdot 3 \cdot x$ compounds actually realize this possibility?

Finally, the existence of two pairs of known dimorphs in this series poses the interesting query as to whether the dimorphs merely reflect a different kind of linkage among the same basic polyanions or whether there exist two distinct polyanions each associated with one of the two dimorphs. One dimorph might contain the tunellite polyanion whereas its related compound might contain the $[\text{B}_3\text{O}_3(\text{OH})_4]^{1-}$ polyanion originally proposed. Structural studies of gowerite, veatchite, and *p*-veatchite, among others, are in progress to investigate these problems.

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