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The Crystal Structure of Teruggite

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Abstract

Teruggite has the chemical formula, $4CaO \cdot MgO \cdot 6B_2O_3 \cdot As_2O_5 \cdot 20H_2O$. The cell constants are: $a = 15.675(13)$, $b = 19.920(14)$, $c = 6.255(4)$ Å, $\beta = 99° 20'(5')$; $V = 1927$ Å^3, space group $P2_1/a$, density(calc) $= 2.192$, density(obs) $= 2.20$, structural formula $Ca_4Mg[AsB_6O_{11}(OH)_6]_2 \cdot 14H_2O$, $Z = 2$. The crystal structure has been solved by direct methods from three-dimensional X-ray diffractometer data and refined by least-squares methods to $R = 0.030$ for 2192 independent reflections. Nineteen out of twenty hydrogen atoms have been located. The crystal structure of teruggite contains monomeric polyanions $[AsB_6O_{11}(OH)_6]^{5-}$ formed by three six-membered boron-oxygen rings, two rings consisting of two tetrahedra and one triangle and the third ring being formed by three tetrahedra. The arsenic atom, which has tetrahedral coordination, is linked by sharing one oxygen to the ring of three B–O tetrahedra. The polyanions are connected by Ca atoms to form a three-dimensional framework which has cavities occupied by magnesium atoms. Magnesium atoms are octahedrally coordinated by water molecules which in turn are linked to the polyanions through hydrogen bonds. Several other hydrogen bonds consolidate the connection among the polyanions. One water molecule is not directly bonded to any cation; it is linked to the structure only through hydrogen bonds.

Introduction

Teruggite was first found in the Loma Blanca deposit, province of Jujuy, Argentina, and described by Aristarain and Hurlbut (1968). The sample used in this investigation was collected at the Hisarcik open pit mine of the Emet borate deposit in the province of Kütahya, Turkey (Özpeker, 1969). The most abundant mineral in the deposit is colemanite; the other minerals are ulexite, hydroboracite, teruggite, celestite, realgar, gypsum, and calcite. Teruggite is rare and occurs in cauliflower-shaped nodules containing countless minute white euhedral crystals.

Experimental Data

The crystal of teruggite used in this investigation was a colorless prismatic fragment elongated along the c axis and about $0.04 \times 0.07 \times 0.23$ mm in dimensions. The space group $P2_1/a$ reported by Aristarain and Hurlbut (1968) was confirmed. The cell parameters were redetermined and refined using the least-squares method applied to fifty high order reflections with $2\theta > 120°$. The cell constants so obtained are: $a = 15.675(13)$, $b = 19.920(14)$, $c = 6.255(4)$ Å and $\beta = 99°20'(5')$.

The powder X-ray diffraction data and the optical properties of teruggite are given by the authors mentioned above. No chemical analysis was made for the teruggite sample used in the present study. The crystal structure determination confirms the chemical composition reported by Aristarain and Hurlbut (1968) except for the water content which consists of twenty molecules instead of eighteen. The structural formula is $Ca_4Mg[AsB_6O_{11}(OH)_6]_2 \cdot 14H_2O$, $Z = 2$.

The intensities of 3901 reflections, out of the 4398 possible with Cu$K\alpha$ radiation, in the range $2\theta = 7° - 153°$, were measured with a four-circle Wooster diffractometer. The crystal was mounted with c parallel to the φ axis. Ni-filtered Cu radiation was used with a scintillator counter. The ω-scan technique with a scan angle of 1° and a scan speed of 2°/min was employed. Measurements of a reference reflection were repeated after every group of 100 reflections, but no significant difference was observed. Only 2192 reflections with a net intensity ranging from 500 to 240,000 counts were considered as observed. The data were corrected for Lorentz

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and polarization factors. No corrections were made for absorption ($\mu = 81.7$ cm^{-1}) or for extinction.

Determination of the Structure

Teruggite has two calcium, one arsenic, six boron, and twenty-four oxygen (including hydroxyl ions and water molecules) atoms in the general fourfold positions, 4*e*, and one magnesium atom in the twofold special position, 2*a*, of space group $P2_1/a$. The structure was solved by direct methods. The phase program applied (Long, 1965) is based on the Sayre relationship for centrosymmetric structures and uses normalized structure factors. For the sign determition 346 reflections with $|E| \geq 1.8$ were used. The statistical averages obtained with the data confirm a centrosymmetric space group. The positions of Mg, Ca(1), and twelve oxygen atoms were determined from the *E*-map. Starting from the structure factors calculated with the coordinates of these atoms, several three-dimensional Fourier syntheses were computed and the positions of As, Ca(2), boron atoms, and the remaining oxygen atoms were determined. At this stage the residual index $R = \Sigma |\Delta F|/\Sigma |F_o|$ was 0.14. The *f*-curves for neutral atoms of Mg, Ca, As, O, and B given by Hansen, Herman, Lea, and Skilman (1964) were used in structure factor calculations.

The parameters derived from the last Fourier synthesis were refined, using isotropic temperature factors, for three cycles of full matrix least-squares calculations, performed with the Busing, Martin, and Levy (1962) computer program ORFLS. The *R* value decreased to 0.049. At this stage it was decided to use anisotropic thermal parameters and to apply the correction proposed by Zachariasen (1963a) for the secondary extinction (final value $g = 7.2 \times 10^{-7}$). After one cycle of refinement using anisotropic temperature factors, and taking into account anomalous dispersion for As, the *R* value was 0.033.

The coordinates of nineteen out of twenty hydrogen atoms present in the asymmetric unit were

TABLE 1. Atomic Parameters (Standard Deviations in Parentheses) and Equivalent Isotropic Temperature Factors after Hamilton (1959)

Atom	x/a	y/b	z/c	B_H(Å^2)
Mg	0.0000	0.0000	0.0000	1.56
As	0.74892(3)	0.04890(2)	0.49105(8)	0.90
Ca(1)	0.73006(5)	0.21207(4)	0.21647(13)	1.14
Ca(2)	0.94886(5)	0.45050(4)	0.71508(12)	0.86
B(1)	0.2956(3)	0.1161(2)	0.0164(7)	1.06
B(2)	0.4502(3)	0.2778(2)	0.4384(8)	1.16
B(3)	0.4442(3)	0.0798(2)	0.1757(7)	0.86
B(4)	0.3641(3)	0.1729(2)	0.3541(7)	0.79
B(5)	0.5342(3)	0.1722(2)	0.4224(7)	0.77
B(6)	0.6067(3)	0.0981(2)	0.1774(7)	0.93
O(1)	0.2938(2)	0.1631(1)	0.1742(4)	1.30
O(2)	0.3699(2)	0.0810(1)	-0.0014(4)	0.91
O(3)	0.3720(2)	0.2458(1)	0.3859(5)	1.28
O(4)	0.4475(2)	0.1474(1)	0.2905(4)	0.80
O(5)	0.5220(2)	0.0697(1)	0.0849(4)	0.95
O(6)	0.5258(2)	0.2450(1)	0.4525(4)	1.06
O(7)	0.6007(2)	0.1590(1)	0.3014(4)	1.08
O(8)	0.6497(2)	0.0412(1)	0.3239(4)	1.19
O(9)	0.7296(2)	0.0296(1)	0.7376(4)	1.40
O(10)	0.8160(2)	-0.0062(1)	0.4011(5)	1.64
O(11)	0.7862(2)	0.1276(1)	0.4755(5)	1.75
O(12)*	0.2217(2)	0.1068(1)	-0.1286(5)	1.67
O(13)*	0.3508(2)	0.1371(1)	0.5472(4)	1.33
O(14)*	0.4323(2)	0.0254(1)	0.3271(4)	0.99
O(15)*	0.4507(2)	0.3463(1)	0.4772(5)	1.69
O(16)*	0.5396(2)	0.1365(1)	0.6299(5)	1.34
O(17)*	0.6599(2)	0.1164(1)	0.0177(4)	1.16
O(18)**	0.8020(2)	0.1999(2)	-0.0982(6)	3.32
O(19)**	0.6995(2)	0.2776(2)	0.5224(6)	3.33
O(20)**	0.6295(2)	0.2756(2)	-0.0216(7)	3.84
O(21)**	0.5477(2)	0.4551(2)	0.2934(5)	2.82
O(22)**	0.5307(2)	0.4116(2)	-0.1506(6)	3.35
O(23)**	0.3790(2)	0.4653(2)	0.0328(5)	2.18
O(24)**	0.4573(2)	0.2332(2)	-0.0926(5)	2.33

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

TABLE 3. Ring Angles, Planes, and Deviations from Plane of Ring Oxygens

Ring	Ring atoms	B-O-B angles	(± 20')
1	B(1)-O(1)-B(4)-O(4)-B(3)-O(2)	B(1)-O(1)-B(4)	123°18'
		B(4)-O(4)-B(3)	117° 7'
		B(3)-O(2)-B(1)	121°31'
2	B(6)-O(7)-B(5)-O(4)-B(3)-O(5)	B(6)-O(7)-B(5)	124° 6'
		B(5)-O(4)-B(3)	119°30'
		B(3)-O(5)-B(6)	123°58'
3	B(2)-O(3)-B(4)-O(4)-B(5)-O(6)	B(2)-O(3)-B(4)	122°58'
		B(4)-O(4)-B(5)	118° 8'
		B(5)-O(6)-B(2)	124°36'

Parameters of planes* defined by ring oxygens

Ring	A	B	C	D	angles between ring-planes
1	4.70921	13.71640	-4.37211	2.85912	1 ∧ 2 = 21°
2	-0.58240	12.23211	-4.83371	0.13820	2 ∧ 3 = 19°
3	2.54471	7.56190	-5.78581	0.57261	3 ∧ 1 = 24°

Deviations from ring-planes

Atom	Ring 1 Deviation(Å)	Atom	Ring 2 Deviation(Å)	Atom	Ring 3 Deviation(Å)
B(1)	+0.054	B(3)	-0.270	B(2)	+0.137
B(3)	-0.441	B(5)	-0.385	B(4)	-0.387
B(4)	-0.321	B(6)	-0.149	B(5)	-0.355
O(12)	+0.212	O(14)	-1.660	O(15)	+0.432
O(13)	-1.719	O(16)	-1.827	O(13)	-1.809
O(14)	-1.905	O(17)	+0.816	O(16)	-1.812
		O(8)	-1.578		

*The equations are of the form Ax + By + Cz = D where x, y, z are the atomic coordinates in Å units and D is the distance of the planes from the origin in Å units.

TABLE 4. Boron-Oxygen and Arsenic-Oxygen Distances *(Standard Deviations in Parentheses)*

B(1) - O(1)	1.364(5) Å	B(2) - O(3)	1.373(5) Å
B(1) - O(2)	1.379(5)	B(2) - O(6)	1.343(5)
B(1) - O(12)	1.364(5)	B(2) - O(15)	1.385(5)
Average	1.369	Average	1.367
B(3) - O(2)	1.471(5) Å	B(4) - O(1)	1.456(5) Å
B(3) - O(4)	1.523(5)	B(4) - O(3)	1.468(5)
B(3) - O(5)	1.440(5)	B(4) - O(4)	1.515(5)
B(3) - O(14)	1.470(5)	B(4) - O(13)	1.446(5)
Average	1.476	Average	1.471
B(5) - O(4)	1.551(5) Å	B(6) - O(5)	1.472(5) Å
B(5) - O(6)	1.470(5)	B(6) - O(7)	1.452(5)
B(5) - O(7)	1.409(5)	B(6) - O(8)	1.541(5)
B(5) - O(16)	1.471(5)	B(6) - O(17)	1.448(5)
Average	1.475	Average	1.478
As - O(8)	1.735(2) Å		
As - O(9)	1.664(3)		
As - O(10)	1.679(3)		
As - O(11)	1.683(3)		
Average	1.690		

Average of 6 triangular B-O distances 1.368 Å.

Average of 16 tetrahedral B-O distances 1.475 Å.

TABLE 5. Oxygen-Boron-Oxygen and Oxygen-Arsenic-Oxygen Angles *(Standard Deviations in Parentheses)*

Atoms	Angles	Atoms	Angles
O(1)-B(1)-O(2)	121°36'(21')	O(3)-B(2)-O(6)	122°11'(21')
O(1)-B(1)-O(12)	117°20'(21')	O(3)-B(2)-O(15)	118°37'(21')
O(2)-B(1)-O(12)	121° 2'(22')	O(6)-B(2)-O(15)	119°11'(21')
O(2)-B(3)-O(4)	107°39'(18')	O(1)-B(4)-O(3)	105°54'(18')
O(2)-B(3)-O(5)	108°49'(18')	O(1)-B(4)-O(4)	109°14'(18')
O(2)-B(3)-O(14)	109°13'(18')	O(1)-B(4)-O(13)	112°42'(19')
O(4)-B(3)-O(5)	110° 3'(18')	O(3)-B(4)-O(4)	108° 5'(18')
O(4)-B(3)-O(14)	110°12'(18')	O(3)-B(4)-O(13)	113°12'(19')
O(5)-B(3)-O(14)	110°48'(18')	O(4)-B(4)-O(13)	107°35'(18')
O(4)-B(5)-O(6)	107° 5'(16')	O(5)-B(6)-O(7)	113°27'(19')
O(4)-B(5)-O(7)	108°22'(18')	O(5)-B(6)-O(8)	103°27'(17')
O(4)-B(5)-O(16)	103°36'(18')	O(5)-B(6)-O(17)	114°10'(19')
O(6)-B(5)-O(7)	110° 1'(18')	O(7)-B(6)-O(8)	110°54'(18')
O(6)-B(5)-O(16)	110°59'(19')	O(7)-B(6)-O(17)	104°35'(18')
O(7)-B(5)-O(16)	116°11'(18')	O(8)-B(6)-O(17)	110°28'(18')
	O(8)-As-O(9)	104°57'(7')	
	O(8)-As-O(10)	106°52'(7')	
	O(8)-As-O(11)	109°27'(7')	
	O(9)-As-O(10)	112°10'(8')	
	O(9)-As-O(11)	112°42'(8')	
	O(10)-As-O(11)	110°19'(9')	

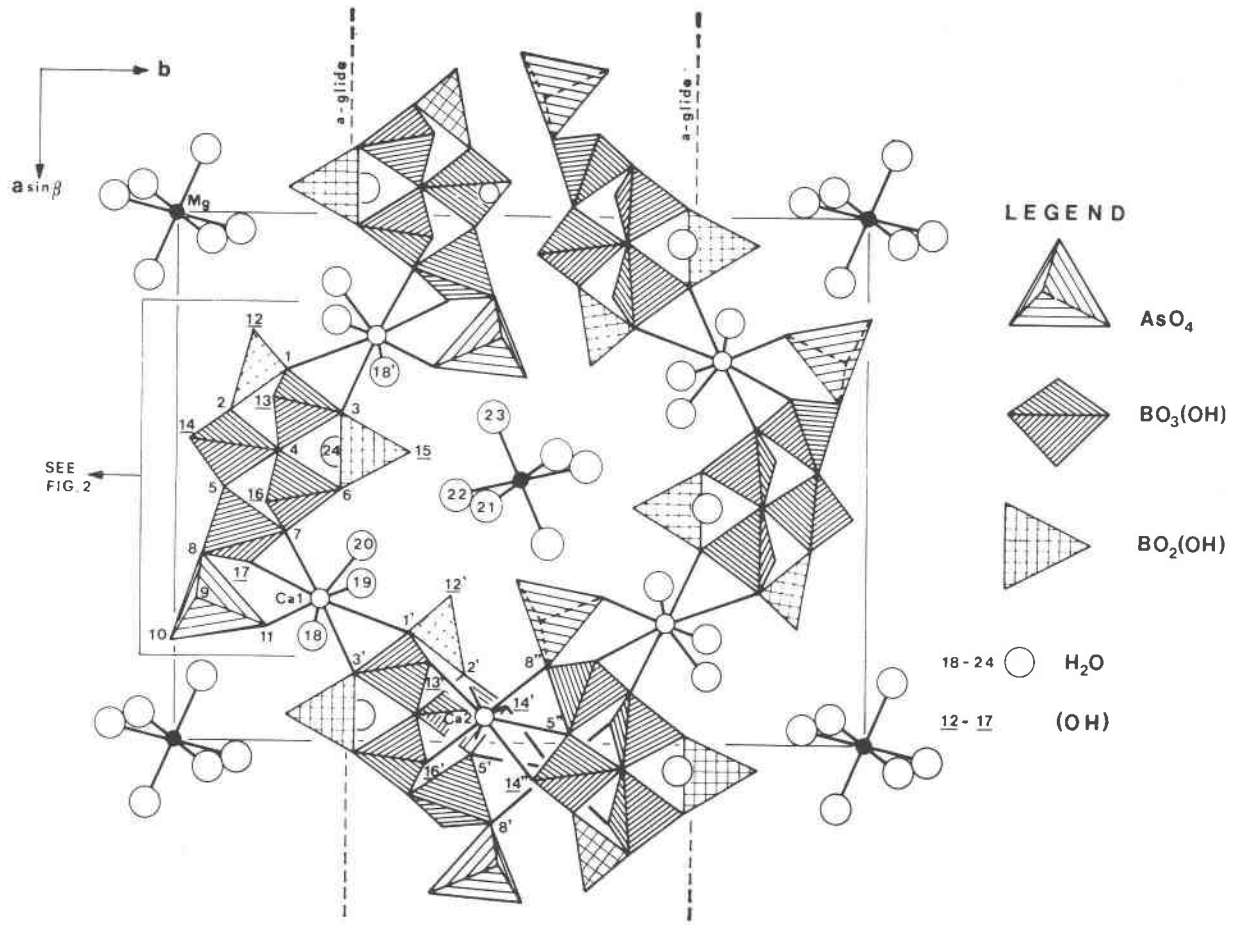

FIG. 1. Projection along [001] of the crystal structure of teruggite. Unconnected bonds are to atoms related by + 1 in z to those shown.

determined from the three-dimensional difference Fourier synthesis on the basis of chemical considerations and taking into account the O–O distances. The hydrogen atoms were included in the structure factor calculation with isotropic temperature factors fixed at 3.0 Å^2. The reliability index for the observed reflections decreased to a final value $R = 0.030$ 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 positional and thermal parameters with their standard deviations are listed in Table 1. The observed and calculated structure factors are listed in Table 2.[2]

[2] To obtain a copy of Table 2 (26 pages), order NAPS Document 02202 from National Auxiliary Publications Service of the A.S.I.S., c/o Microfiche Publications, 305 East 46th Street, New York, N. Y. 10017; remitting in advance $1.50 for microfiche or $5.00 for photocopies.

Description of the Structure

The main structural features of teruggite are illustrated in Figure 1. The polyanion, $[AsB_6O_{11}(OH)_6]^{5-}$, consists of one AsO_4 tetrahedron, four $BO_3(OH)$ tetrahedra, and two $BO_2(OH)$ triangles arranged to form three six-membered B–O rings (Figure 2). Two of them are formed by corner-sharing among two tetrahedra and one triangle; the third one is formed by corner-sharing of three tetrahedra. One oxygen atom, O(4), is common to three tetrahedra and is the central point of the three six-membered boron-oxygen rings. A similar feature occurs in the structures of tunellite (Clark, 1964), macallisterite (Dal Negro, Sabelli and Ungaretti, 1969), and aksaite (Dal Negro, Sabelli and Ungaretti, 1971).

The AsO_4 tetrahedron is linked through the O(8) oxygen atom (Fig. 2) to the ring formed by three B–O tetrahedra. The atoms shared by tetrahedral or triangular cations are not hydroxyl ions.

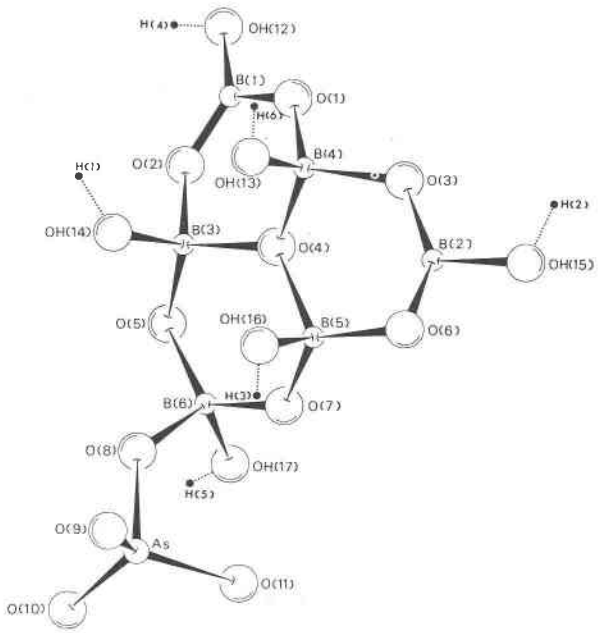

FIG. 2. Projection of the $[AsB_6O_{11}(OH_6]^{5-}$ unit along [001].

The main difference between the B–O polyanion found in teruggite and those found in macallisterite and aksaite is the presence, in the former case, of one ring built up by three tetrahedra instead of two tetrahedra and one triangle.

The angles between the normals to the planes of bridging oxygen atoms are 21°, 24°, and 19° (see Table 3), with a mean value of 21°. This situation is quite similar to that found in aksaite.

Hydroxyl ions show the greatest deviations from the planes of the rings, O(14), O(16), and O(13) on one side and O(12), O(15), and O(18) on the opposite side. In this way there are three hydroxyls above the planes of the rings and three below, the polyanion assuming therefore the well known configuration $[B_6O_7(OH)_6]^{2-}$ found in tunellite, macallisterite, aksaite, and rivadavite (Dal Negro, Sabelli and Ungaretti, 1973).

All interatomic distances and angles with their standard deviations were calculated by using Busing, Martin, and Levy's (1964) program ORFFE. The superscripts in Figures 1, 3, and 4 and in Table 9 refer to the following equivalent positions relative to

TABLE 6. Boron-Boron Distances within the Polyanion
(Standard Deviations in Parentheses)

B(1) - B(3)	2.487(6) Å
B(1) - B(4)	2.482(6)
B(2) - B(4)	2.497(6)
B(2) - B(5)	2.492(6)
B(3) - B(4)	2.591(6)
B(3) - B(5)	2.656(6)
B(3) - B(6)	2.571(6)
B(4) - B(5)	2.630(6)
B(5) - B(6)	2.527(6)
Average	2.548

TABLE 7. Oxygen-Oxygen Distances within the B–O Polyanion
(Standard Deviations in Parentheses)

Triangle around B(1)		Triangle around B(2)	
O(1) - O(2)	2.394(4) Å	O(3) - O(6)	2.378(4) Å
O(1) - O(12)	2.330(4)	O(3) - O(15)	2.372(4)
O(2) - O(12)	2.387(4)	O(6) - O(15)	2.353(4)
Tetrahedron around B(3)		**Tetrahedron around B(4)**	
O(2) - O(4)	2.417(3) Å	O(1) - O(3)	2.334(4) Å
O(2) - O(5)	2.367(3)	O(1) - O(4)	2.422(3)
O(2) - O(14)	2.398(4)	O(1) - O(13)	2.416(4)
O(4) - O(5)	2.428(3)	O(3) - O(4)	2.414(4)
O(4) - O(14)	2.455(4)	O(3) - O(13)	2.433(4)
O(5) - O(14)	2.395(4)	O(4) - O(13)	2.388(4)
Tetrahedron around B(5)		**Tetrahedron around B(6)**	
O(4) - O(6)	2.431(3) Å	O(5) - O(7)	2.445(3) Å
O(4) - O(7)	2.402(3)	O(5) - O(8)	2.364(3)
O(4) - O(16)	2.375(4)	O(5) - O(17)	2.451(4)
O(6) - O(7)	2.359(4)	O(7) - O(8)	2.466(4)
O(6) - O(16)	2.424(4)	O(7) - O(17)	2.294(4)
O(7) - O(16)	2.445(4)	O(8) - O(17)	2.457(4)

TABLE 8. Magnesium-Oxygen and Calcium-Oxygen Distances
(Standard Deviations in Parentheses)

	Mg - O(21)	2.070(3) Å	x2
	Mg - O(22)	2.091(3)	x2
	Mg - O(23)	2.060(3)	x2
	Average	2.074	
Ca(1) - O(1')	2.709(3) Å	Ca(2) - O(2^{VII})	2.404(3) Å
Ca(1) - O(3')	2.453(3)	Ca(2) - O(5^{VII})	2.443(3)
Ca(1) - O(7)	2.421(3)	Ca(2) - O(5'')	2.689(3)
Ca(1) - O(11)	2.401(3)	Ca(2) - O(8'')	2.364(3)
Ca(1) - O(17)	2.437(3)	Ca(2) - O(13')	2.447(3)
Ca(1) - O(18)	2.434(3)	Ca(2) - O(14')	2.447(3)
Ca(1) - O(19)	2.428(4)	Ca(2) - O(14'')	2.434(3)
Ca(1) - O(20)	2.355(3)	Ca(2) - O(16')	2.357(3)
Average	2.455	Average	2.448

the reference atoms at x, y, z:

(′)	$1/2 + x$	$1/2 - y$	z
(″)	$1/2 - x + 1$	$1/2 + y$	$1 - z$
(‴)	x	y	$z - 1$
(iv)	$x - 1/2$	$1/2 - y$	z
(v)	$1 - x$	$-y$	$1 - z$
(vi)	$1/2 - x + 1$	$1/2 + y$	$-z$
(vii)	$1/2 + x$	$1/2 - y$	$1 + z$

B–O distances in teruggite (Table 4), for both triangular and tetrahedral boron coordination, are within the range of the values found in other borates. For the triply linked oxygen atom, O(4), the three tetrahedral B–O distances are 1.523, 1.515, and 1.551 Å (all ± 0.005); the average of 1.529 Å is slightly higher than for tunellite, macallisterite, and aksaite, but this difference can be explained by the fact that O(4) is receiving additional positive charge from a hydrogen atom of the O(24) water molecule [O(24)–O(4) = 2.967 Å].

The O–B–O angles (Table 5) fall within the expected ranges.

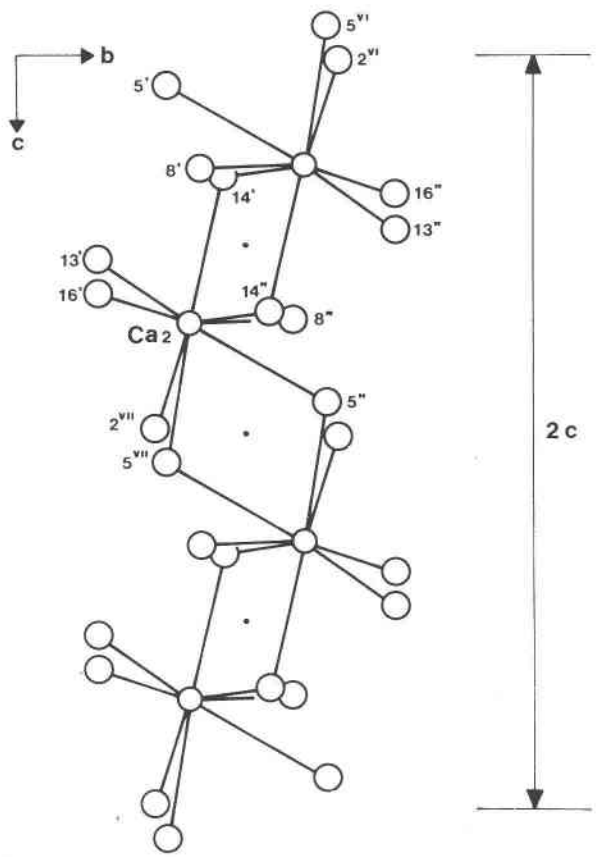

FIG. 3. Schematic view of the Ca(2) polyhedra linked to form an infinite chain along c direction.

TABLE 9. Distances Related to the Hydrogen Bonds

Atoms	O---H	O·····O
	Å	Å
O(14)-------H(1)·····O(9^{V})	0.957	2.734(4)
O(15)-------H(2)·····O(11^{IV})	0.946	2.629(4)
O(16‴)----H(3)·····O(17)	1.045	2.849(4)
O(12′)------H(4)·····O(10^{VI})	0.973	2.635(4)
O(17)-------H(5)·····O(9‴)	0.934	2.807(4)
O(13‴)----H(6)·····O(12)	0.944	3.148(4)
O(18′)------H(7)·····O(24)	1.014	2.770(4)
O(18)-------H(8)·····O(11‴)	1.037	3.005(4)
O(19)-------H(9)·····O(6)	1.008	2.765(4)
O(19)···············O(13′)	-	2.901(4)
O(20)-------H(10)·····O(24)	0.984	2.796(4)
O(20)-------H(11)·····O(12′)	1.034	2.886(4)
O(21^{IV})-----H(12)·····O(10^{V})	0.968	2.736(4)
O(21^{IV})-----H(13)·····O(15^{IV})	0.988	2.982(4)
O(22)-------H(14)·····O(12′)	0.989	2.997(4)
O(22)-------H(15)·····O(15‴)	0.977	2.781(4)
O(23′)------H(16)·····O(10)	1.011	2.771(4)
O(23′)------H(17)·····O(9‴)	0.961	2.739(4)
O(24)-------H(18)·····O(4)	1.011	2.967(4)
O(24)-------H(19)·····O(16‴)	0.975	3.019(4)

The As–O distances in the arsenic-oxygen tetrahedron are given in Table 4; the values of the distances are within the expected ranges, except that bond length As–O(8) is longer than the others. Oxygen atom O(8) is shared by an arsenic atom, a boron atom, and the Ca(2) atom. The Ca–O bond distance (2.364 Å) is rather short and therefore the associated B–O (1.541 Å) and As–O (1.735 Å) distances are considerably larger than usual.

The distances between boron atoms are given in Table 6. The average B–B separation of 2.548 Å is similar to values found in borate structures where one oxygen atom is linked to three boron atoms, as in tunellite and macallisterite; the three largest B–B separations (2.591, 2.656 and 2.630 Å) are around the triply linked oxygen. In addition there are two long B–B distances (2.571 and 2.527 Å) from the boron atom B(6) which is an element of the ring formed by three B–O tetrahedra.

In Table 7 are listed the O–O distances within the B–O polyhedra. All distances fall within the expected ranges. The fairly short O–O distances correspond to edges shared with the Ca–O polyhedra.

Ca–O Coordination

There are two crystallographically non-equivalent Ca^{2+} cations. Both have eight-fold coordination. Ca(1)–O and Ca(2)–O distances (Table 8) range from 2.36 to 2.45 Å, except for one in each polyhedron which has a value around 2.70 Å. The

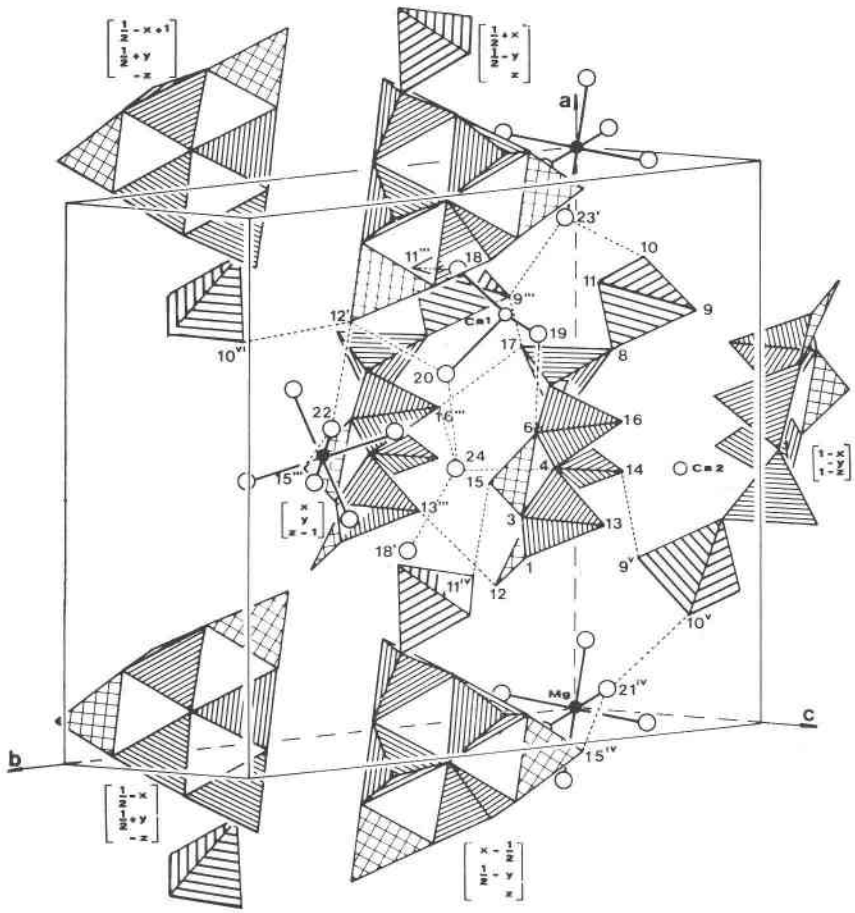

FIG. 4. Clinographic projection of the crystal structure of teruggite showing some $[AsB_6O_{11}(OH)_6]^{5-}$ polyanions, some MgO_6 octahedra, and one Ca(1) surrounded by its water molecules. All the hydrogen bonds are also shown.

TABLE 10. Fractional Coordinates of Hydrogen Atoms

Atom	x/a	y/b	z/c
H(1)	0.377	0.004	0.295
H(2)	0.394	0.364	0.463
H(3)	0.589	0.141	-0.237
H(4)	0.225	0.075	-0.245
H(5)	0.680	0.084	-0.070
H(6)	0.295	0.134	-0.415
H(7)	0.359	0.276	-0.098
H(8)	0.790	0.158	-0.197
H(9)	0.636	0.266	0.497
H(10)	0.567	0.270	-0.070
H(11)	0.656	0.318	-0.080
H(12)	0.092	0.034	0.415
H(13)	0.015	0.080	0.357
H(14)	0.593	0.403	-0.148
H(15)	0.502	0.386	-0.275
H(16)	0.854	0.027	0.170
H(17)	0.835	0.026	-0.090
H(18)	0.453	0.210	0.040
H(19)	0.481	0.204	-0.193

average value is 2.455 Å in the Ca(1) polyhedron and 2.448 Å in the Ca(2) polyhedron.

Ca(1) is coordinated by four oxygen atoms, three water molecules, and one hydroxyl ion. It links two polyanions that are equivalent through a glide plane (see Figure 1), but is otherwise isolated in the structure.

Ca(2) is coordinated by four oxygen atoms and four hydroxyl ions. It links two centrosymmetrically related polyanions, sharing three oxygen atoms with each of them, and it is bonded through two oxygen atoms to a third polyanion in the adjacent cell along *c*. Thus it builds up a three-dimensional network in the structure. In addition, two centrosymmetrically related Ca(2) polyhedra share two edges, O(14′)–O(14″) and O(5″)–O(5^{vii}) to create an infinite chain along the *c* axis as shown in Figure 3. In this way all polyanions are linked together through the Ca polyhedra.

Mg–O Coordination

Six water molecules are coordinated to magnesium in the form of a regular octahedron. It is linked to the polyanions only by hydrogen bonds (see Figure 4). The six water molecules link ten polyanions through their hydrogen atoms. The Mg–O distances are given in Table 8.

Hydrogen Bonds

Nineteen hydrogen atoms in the structure were located using a three-dimensional difference Fourier synthesis and chemical considerations. The twentieth, associated with the O(19) water molecule, did not appear on the difference Fourier synthesis. Its presence was inferred from the value of the O(19)–O(13′) distance of 2.901 Å.

There is one hydrogen bond between the polyanions as shown by the dashed line joining corners O(15) and O(11^{iv}), in Figure 4. In addition to the linkages formed through the Ca(2) polyhedra that share two oxygen atoms, each polyanion has three hydrogen bonds with the adjacent polyanions along the *c* axis; these are between O(13‴)–O(12), O(16‴)–O(17), and O(17)–O(9‴).

The hydrogen bonds associated with the oxygen atoms of the Mg–octahedron (see Figure 4) correspond to the dashed lines linking: O(22)–O(15‴), O(22)–O(12′), O(23′)–O(10), O(23′)–O(9‴), O(21^{iv})–O(10^{v}), and O(21^{iv})–O(15^{iv}). The Mg–octahedron is thus linked to four polyanions in the two adjacent cells along the *c* axis, in addition to the six surrounding polyanions shown in Figure 1.

The three water molecules—O(18), O(19), O(20)—of the polyhedron around Ca(1) participate (1) in two hydrogen bonds, O(20)–O(12′) and O(19)–O(6), to link two glide-plane equivalent polyanions and (2) in another hydrogen bond, O(18)–O(11‴), to link a *c*-translated polyanion. Two of these water molecules, O(20) and O(18′), acting as donors, form hydrogen bonds with the water molecule O(24), which in turn acts as a donor in the hydrogen bonding with O(4) and O(16‴).

TABLE 11. Charge Balance

	B(1)*	B(2)*	B(3)**	B(4)**	B(5)**	B(6)**	As^{5+}	$1/2Mg^{2+}$	$Ca(1)^{2+}$	$Ca(2)^{2+}$	H bond	H^{+}	Σ
O(1)	1.01	—	—	0.78	—	—	—	—	0.15	—	—	—	1.94
O(2)	0.98	—	0.76	—	—	—	—	—	—	0.27	—	—	2.01
O(3)	—	0.99	—	0.75	—	—	—	—	0.25	—	—	—	1.99
O(4)	—	—	0.66	0.67	0.61	—	—	—	—	—	0.10	—	2.04
O(5)	—	—	0.82	—	—	0.76	—	—	—	0.25+0.16	—	—	1.99
O(6)	—	1.05	—	—	0.75	—	—	—	—	—	0.20	—	2.00
O(7)	—	—	—	—	0.88	0.80	—	—	0.26	—	—	—	1.94
O(8)	—	—	—	—	—	0.63	1.15	—	—	0.28	—	—	2.06
O(9)	—	—	—	—	—	—	1.31	—	—	—	0.69	—	2.00
O(10)	—	—	—	—	—	—	1.27	—	—	—	0.65	—	1.92
O(11)	—	—	—	—	—	—	1.26	—	0.27	—	0.43	—	1.96
(OH)													
O(12)	1.01	—	—	—	—	—	—	—	—	—	1.01	—	2.02
O(13)	—	—	—	0.80	—	—	—	—	—	0.25	0.92	—	1.97
O(14)	—	—	0.76	—	—	—	—	—	—	0.25+0.25	0.77	—	2.03
O(15)	—	0.96	—	—	—	—	—	—	—	—	1.06	—	2.02
O(16)	—	—	—	—	0.75	—	—	—	—	0.29	0.98	—	2.02
O(17)	—	—	—	—	—	0.81	—	—	0.26	—	0.97	—	2.04
H_2O													
O(18)	—	—	—	—	—	—	—	—	0.26	—	1.68	—	1.94
O(19)	—	—	—	—	—	—	—	—	0.26	—	0.80	1.00	2.06
O(20)	—	—	—	—	—	—	—	—	0.29	—	1.67	—	1.96
O(21)	—	—	—	—	—	—	—	0.33	—	—	1.65	—	1.98
O(22)	—	—	—	—	—	—	—	0.32	—	—	1.70	—	2.02
O(23)	—	—	—	—	—	—	—	0.34	—	—	1.62	—	1.96
O(24)	—	—	—	—	—	—	—	—	—	—	2.10	—	2.10
Σ	3.00	3.00	3.00	3.00	2.99	3.00	4.99	0.99	2.00	2.00	19.00	1.00	47.97

*Triangular B
**Tetrahedral B

Therefore the O(24) water molecule does not participate in any coordination around the cations. The same feature has been already observed in other hydrated borates, such as macallisterite and rivadavite.

The presence of a water molecule linked only through hydrogen bonds explains the doubts of Aristarain and Hurlbut (1968) about whether to assign 18 or 20 water molecules to the chemical formula of teruggite, because the O(24) water molecule can be easily removed from the structure by a small increase in temperature. In fact, the behavior of this water molecule linked to the rest of the structure only through hydrogen bonds does not differ from that of the adsorbed water. Several DTA and DTG curves (rate of temperature increase varying from 0.3 to 10°C min^{-1}) revealed a continuous weight loss in the range 40–125°C (40°C was the temperature of incipient weight loss). A new determination of the density was performed in order to verify the structural results; by using heavy liquids a specific gravity of 2.20 (±0.03) has been obtained which is in good agreement with the value of 2.192 g/cm^3 calculated for the formula 4 [$CaO \cdot MgO \cdot 6B_2O_3 \cdot As_2O_5 \cdot 20H_2O$].

In Table 9 are listed all the distances related to the hydrogen bonds, and in Table 10 are listed the fractional coordinates of hydrogen atoms.

Charge Balance Considerations

On the basis of the suggestions given by Donnay and Allmann (1970), a curve for bond-lengths *vs* bond-strengths was computed for the cations B, As, Mg, Ca. For the hydrogen-oxygen bonds the correlations given by Zachariasen (1963b) were used. As shown in Table 11, the range in valence units for the oxygen atoms is 1.92 to 2.10, and the summation of 47.97 for anions and cations is within the validity conditions (±0.1) generally accepted.

In compiling the table, one proton of the O(19) water molecule was considered not to be participating in hydrogen bond formation, and for this reason a value of 1.0 was assigned to the O(19)–H bond.

Temperature Factors

As Table 12 reveals, the atoms in the teruggite structure do not have large thermal anisotropies. The largest thermal motion is exhibited by the water molecules and, among the hydroxyls, by O(12) and O(15), which are not linked to the calcium

TABLE 12. Analysis of the Anisotropic Thermal Parameters[1]

Atom	r.m.s.	U_ia	U_ib	U_ic	Atom	r.m.s.	U_ia	U_ib	U_ic	Atom	r.m.s.	U_ia	U_ib	U_ic
Mg	0.105(4)	109	139	124	O(3)	0.085(8)	85	16	74	O(14)	0.099(7)	165	75	87
	0.151(4)	69	62	144		0.111(6)	173	87	84		0.104(6)	75	19	78
	0.159(3)	144	54	91		0.173(5)	95	83	171		0.130(6)	80	80	166
As	0.091(1)	101	98	165	O(4)	0.084(6)	84	22	111	O(15)	0.082(8)	59	34	75
	0.105(1)	99	11	96		0.088(7)	149	96	119		0.126(6)	148	63	73
	0.122(1)	156	96	67		0.125(6)	120	78	33		0.204(5)	102	77	162
Ca(1)	0.095(2)	85	121	148	O(5)	0.086(7)	144	63	111	O(16)	0.103(6)	129	53	60
	0.121(2)	127	49	116		0.100(6)	55	60	131		0.119(6)	83	45	134
	0.140(2)	142	117	66		0.137(5)	75	48	45		0.162(5)	130	119	125
Ca(2)	0.100(2)	84	86	173	O(6)	0.093(7)	143	124	80	O(17)	0.108(6)	169	100	90
	0.104(3)	159	109	96		0.099(6)	120	36	72		0.121(6)	100	16	102
	0.109(2)	110	23	79		0.148(5)	99	76	162		0.134(6)	78	100	164
B(1)	0.102(10)	84	52	131	O(7)	0.093(7)	136	133	87	O(18)	0.150(6)	115	37	65
	0.111(10)	138	99	130		0.106(6)	127	51	118		0.164(6)	137	92	132
	0.133(9)	65	149	105		0.145(5)	100	61	30		0.277(5)	116	136	57
B(2)	0.093(11)	96	7	93	O(8)	0.073(8)	143	86	126	O(19)	0.126(7)	142	119	69
	0.123(9)	157	97	111		0.115(6)	92	10	80		0.170(6)	126	59	128
	0.142(9)	110	97	22		0.163(5)	116	99	28		0.286(5)	89	39	50
B(3)	0.084(13)	100	17	104	O(9)	0.113(7)	74	15	85	O(20)	0.139(6)	52	43	71
	0.106(10)	94	105	164		0.128(5)	91	84	174		0.163(6)	127	46	113
	0.120(9)	159	108	81		0.155(5)	173	84	87		0.316(5)	66	99	154
B(4)	0.082(12)	151	88	118	O(10)	0.106(7)	153	75	111	O(21)	0.129(6)	144	87	54
	0.100(11)	62	70	145		0.149(5)	64	66	144		0.161(6)	117	56	133
	0.115(9)	73	159	103		0.169(5)	78	33	59		0.254(5)	102	145	121
B(5)	0.023(47)	135	133	97	O(11)	0.093(7)	122	42	113	O(22)	0.151(6)	98	34	122
	0.112(8)	134	45	84		0.129(6)	147	118	76		0.177(6)	137	117	119
	0.126(9)	82	74	162		0.203(5)	85	70	20		0.270(5)	128	78	41
B(6)	0.079(12)	142	80	125	O(12)	0.095(7)	138	119	116	O(23)	0.124(6)	149	60	85
	0.098(10)	83	10	82		0.121(6)	100	37	125		0.156(6)	95	89	174
	0.140(9)	117	94	27		0.199(5)	120	64	41		0.207(5)	110	159	88
O(1)	0.091(7)	156	95	112	O(13)	0.102(7)	120	128	126	O(24)	0.146(6)	68	114	146
	0.114(6)	82	32	121		0.121(6)	103	40	127		0.167(5)	95	29	118
	0.168(5)	102	57	35		0.160(5)	25	93	115		0.198(5)	166	101	97
O(2)	0.090(7)	171	85	97										
	0.103(6)	81	57	145										
	0.125(5)	81	35	55										

[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.

atoms. As expected, among the oxygen atoms, the smallest thermal amplitude is shown by O(4) which is linked to three boron atoms, and among the hydroxyls, by O(14) which is linked to two calcium atoms.

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