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VOLKOVSKITE, A COMPLEX BORATE MINERAL: REFINED CRYSTALLOGRAPHIC DATA AND OPTICS

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ABSTRACT

Volkovskite [$KCa_4B_{22}O_{32}(OH)_{10}Cl{\cdot}4H_2O$] has been identified among numerous borate minerals obtained from potash deposits in New Brunswick. The crystals are vitreous, translucent, and colorless, varying from pale to deep orange.

The crystals possess perfect {010} and {100} cleavages occurring as thinly layered pseudohexagonal/triangular, elongated platy masses. Volkovskite is biaxial positive, with indices of refraction α 1.539(2), β 1.540(2), and γ 1.605(2); $2V_{Meas.} = 14.6°(7.2°)$, $2V_{Calc.} = 14.4°$. There is no dispersion and no pleochroism. Volkovskite is triclinic, space group *P*1 with cell parameters refined from the X-ray powder-diffraction pattern: *a* 6.539(3), *b* 24.194(5), *c* 6.576(3) Å, α 92.2(4.4), β 119.1(1.3), γ 97.4(5.4)°, *V* 894.7(6) Å^3. The six strongest lines of the X-ray powder diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 11.937(28.8)(020), 7.938(100)(030), 5.951(31.4)(040), 3.400(73.6)(070), 2.644(74.3)(090), and 1.983(13.0)(0120).

A crystal structure refinement confirms the basic model of Rastsvetaeva *et al.* (1992). The crystal structure determination refined to $R = 2.1\%$ for 5266 unique reflections. The layered borate structure consists of a double layer of borate sheets parallel to (010). Between the double layers there are two types of cross linkage: Ca polyhedra bond two double layer slabs and K polyhedra bond the double slabs. Many borate minerals found in potash deposits form layered structures, such as biringuccite, nasinite, gowerite, veatchite polytypes, and volkovskite. The volkovskite structure obtained in this study is compared to related layered borates.

Keywords: volkovskite, borate, crystal structure, related structures, H-bonding

INTRODUCTION

The crystal structure of volkovskite was determined by Rastsvetaeva *et al.* (1992) from a crystal found at the Nepskii deposit, eastern Siberia. With an *R* index of 0.065 the H positions would be very questionable. They are reported, but some are incorrect and all are with significant positional errors. The structure was refined by Le Page & Lee (1985), but was only ever published as a conference abstract (see Mandarino *et al.* 1990). With the availability of good material from the Sussex area evaporites it was opportune to refine the structure, define the H-bonding, and compare the structure to related layered borates.

GEOLOGICAL SETTING AND OCCURRENCE

The Carboniferous (~300 m.y.) sedimentary rocks of eastern Canada extend from southern New Brunswick to the western margin of Newfoundland (Fig. 1). Two major evaporite units are hosted in the Moncton subbasin. The first evaporite unit was deposited regionally and hosted in a carbonate/sulfate sequence, while the second unit is comprised of argillaceous halite and sylvite (Fig. 2). In Figure 2, and in what follows, the term, "sylvinite" refers to an evaporite rock rich in sylvite and halite. The evaporite deposits of the Windsor Group in the Sussex area are stratigraphically related (Fig. 2).

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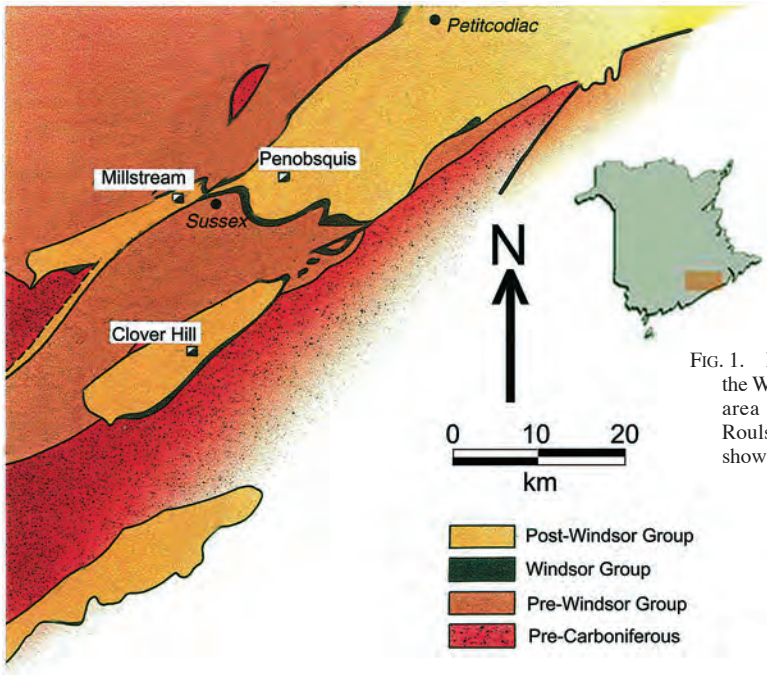

FIG. 1. Location of the potash deposits within the Windsor Group evaporites in the Sussex area of New Brunswick (after Webb & Roulston 1994). The insert map in green shows the province of New Brunswick.

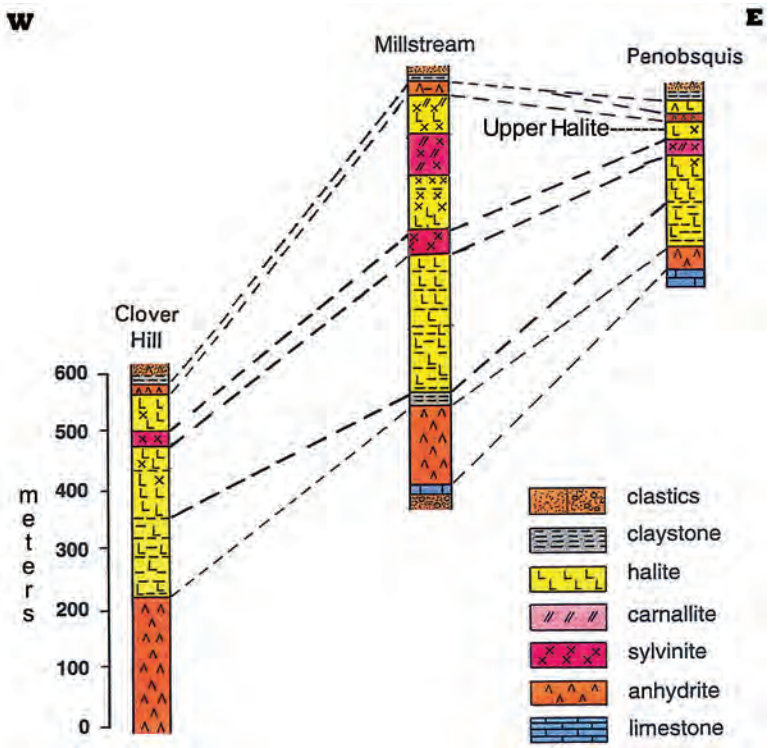

FIG. 2. Stratigraphic correlation of the three potash deposits in the Sussex area of New Brunswick (after Webb & Roulston 1994).

The major borate mineralization can be isolated to the uppermost portion of the Cassidy Lake Formation. This upper unit hosts a relatively thick unit of "sylvinite" (~100 m), where borate mineralization is concentrated. The source of the boron has been determined to be marine and not volcanic (Grice *et al*. 2005). Volkovskite is intimately associated with halite, sylvite, hilgardite, boracite, and anhydrite.

Deep depressions with marine brines characterize the deposit, which allowed progressive concentration in a series of fore-basins and proximal hydrothermal fluid flow. The depositional events of the Moncton subbasin were brought to a halt with a major influx of the Windsor Sea into the basin.

Mineral Description

General appearance and physical properties

Volkovskite occurs as granular masses composed of thinly layered, pseudohexagonal/triangular, elongated platy crystals. Most crystals occur as masses of interlayered and overlapping platelets up to 5 mm. Crystal faces display a certain amount of iridescence, varying from yellow to light orange. Crystals are vitreous, translucent, and color varies from colorless to shades of pale to deep orange. The crystals have perfect {010} and {100} cleavages.

Optical Properties

An optical study, using the spindle stage and extinction curves described by Bloss (1981), gave the following results: biaxial positive, α 1.539(2), β 1.540(2), and γ 1.605(2); $2V_{meas.}$ = 14.6° (7.2°), $2V_{calc.}$ = 14.41°. Measurements were made using a filter that transmits light with a wavelength of 590 nm.

Chemical composition

The chemical analyses were performed with a JEOL 8230 electron microprobe in wavelength-dispersion (WD) mode using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine (Pouchou & Pichoir 1984) in XMAQNT (C. Davidson, CSIRO, pers. commun.). The operating voltage was 20 kV, and the beam current was 20 nA. The beam diameter varied from 20 to 40 μm. The following standards were used: albite (Na$K\alpha$), sanidine (K$K\alpha$), celestine (Sr$L\alpha$), diopside (Ca$K\alpha$), and tugtupite (Cl$K\alpha$). Several 100s energy-dispersion (ED) scans were made, and indicated no elements with Z > 8 other than those reported here. Data for all elements in the samples were collected for 20 to 25 s or 0.50% precision, whichever was attained first. Five electron-microprobe analyses were performed on one crystal from the crystal-structure analysis sample, which was used to establish the amount of H and B (Hawthorne & Grice 1990). The chemical composition is: Na_2O 0.01 (0.01–0.02), K_2O 3.75 (3.69–3.82), CaO 17.76 (17.62–17.95), SrO 0.00 (0.00–0.02), Cl 2.81 (2.78–2.85), (B_2O_3) 60.70, and (H_2O) 12.85, for a total of 97.25 wt.%. The empirical formula based on 47 anions is: $K_{1.00}Ca_{4.00}B_{22.00}O_{32}(OH)_{10}Cl_{1.00}\bullet 4H_2O$.

Crystallography

X-ray powder diffraction

X-ray diffraction data for volkovskite were collected using a Siemens D5000 powder diffractometer using Cu radiation (λ = 1.54184 Å) with a scintillation detector, graphite monochromator, and operating at 40 kV and 40 mA. Data were collected from 3–70° 2θ using a step-width of 0.02° 2θ and a dwell time of 2s/step. Divergence and anti-scatter slits were both set to 1 mm. The X-ray diffraction data are available in Table 1. The unit cell parameters obtained by refining the X-ray powder diffraction data are compared in Table 2 with those derived from the crystal structure determination and the data given by Rastsvetaeva *et al*. (1992) and by Le Page & Lee (1985).

Crystal-structure determination

A single crystal of volkovskite used for the collection of X-ray intensity data measured 300 × 200 × 30 μm. Intensity data were collected using a fully automated Bruker D8 three circle diffractometer equipped with a rotating anode generator operating at 50 kV, 40 mA, with graphite-monochromated Mo$K\alpha$ radiation, multi-layer optics, and an APEX-II CCD detector. This setup yields a very intense X-ray beam. A full sphere of intensity data was collected up to 2θ = 60° using 1 s frames at frame widths of 0.2°. With these operating conditions, no deterioration in the degree of crystallinity was evident in the final analysis of the reflections used as intensity standards. Information relevant to the data collection and structure determination is given in Table 3. The three-dimensional data were corrected for Lorentz, polarization, and background effects, and a multiple-measured reflection was averaged using the Bruker program SAINT. An empirical absorption-correction was applied (SADABS, Sheldrick 1998), which reduced the internal residual for merging data from 11.2% before the absorption correction to 3.7% after the absorption correction. All calculations were done with the Siemens SHELXTL 5.1 system of programs (Sheldrick 1997), with scattering factors for neutral atoms taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.777, which suggests the non-centrosymmetric space-group *P*1. The phase normalized structure factors were used to construct an *E*-map on which were located positions for 4 calcium atoms, 1 potassium atom, and 29

TABLE 1. VOLKOVSKITE: X-RAY POWDER DIFFRACTION DATA (D5000-PXRD)

Tolerance of 0.03 I Obs.	I Calc. *	d Obs.	d Calc. **	h	k	l	Ř	I Obs.	I Calc. *	d Obs.	d Calc. **	h	k	l	Ř
7.4	37.8	23.95	23.79	0	1	0			10.2		2.787	$\bar{2}$	1	2	
28.8	43.0	11.94	11.90	0	2	0		0.7	8.3	2.780	2.780	$\bar{2}$	$\bar{2}$	2	
100	100	7.938	7.931	0	3	0		74.3	52.2	2.644	2.644	0	9	0	
31.4	22.6	5.951	5.948	0	4	0			4.8		2.597	1	5	1	
	11.5		5.444	0	1	1		3.4	2.7	2.379	2.379	0	10	0	
	10.1		5.449	0	$\bar{2}$	1		1.0	0.5	2.162	2.163	0	11	0	
0.3	0.2	4.758	4.759	0	5	0			4.9		2.147	$\bar{3}$	0	1	
3.2	1.9	3.968	3.966	0	6	0			5.0		2.132	1	$\bar{4}$	2	
73.6	41.7	3.400	3.399	0	7	0			5.2		2.125	$\bar{3}$	2	1	
	4.5		3.318	1	0	1			4.1		2.111	$\bar{2}$	$\bar{3}$	3	
1.0	88.0	3.269	3.269	$\bar{2}$	0	1			6.1		2.102	$\bar{3}$	$\bar{2}$	1	
	0.3		3.243	$\bar{2}$	1	1		0.9	2.9	2.110	2.110	0	10	1	
	5.8		3.007	$\bar{1}$	$\bar{4}$	2			9.1		2.016	1	$\bar{6}$	2	
	0.2		2.982	$\bar{1}$	$\bar{7}$	1		13.0	10.8	1.983	1.983	0	12	0	
4.0	2.7	2.974	2.975	0	8	0		0.7	0.6	1.832	1.830	0	13	0	
	5.8		2.934	$\bar{1}$	3	2		1.5	1.3	1.699	1.700	0	14	0	
	10.4		2.899	0	$\bar{1}$	2		0.6	0.4	1.580	1.580	0	$\overline{15}$	1	
	2.3	2.838	2.838	1	7	0		1.2	1.6	1.487	1.487	0	16	0	

Refined cell parameters: *a* 6.539(3), *b* 24.194(5), *c* 6.576(3) Å, α 92.2(4.4), β 119.1(1.3), γ 97.4(5.4) °, *V* 894.7(6) Å^3
* Calculated based on results from crystal-structure determination
** Calculated from XRPD, unit-refinement with Cu*K*α radiation.
Ř R indicates rejected from refinement due to multiple, possible indices

TABLE 2. UNIT-CELL DATA FOR VOLKOVSKITE

Parameters	1	2	3
a	6.50 Å	6.575(2) Å	6.539(3) Å
b	23.96	23.921(8)	24.194(5)
c	6.62	6.522(2)	6.576(3)
α	95.68	90.58(3)°	92.2(4.44)°
β	119.6	119.10(2)	119.1(1.3)
γ	90.59	95.56(3)	97.4(5.4)
V	889.96 Å^3	890.15 Å^3	894.7(6) Å^3
Z	1	1	1

Notes:
1. Cell parameters derived from the crystal structure determination by Rastsvetaeva *et al.* (1992).
2. Cell parameters derived from the crystal structure determination by Le Page & Lee (1985).
3. Cell parameters derived from the X-ray powder diffraction (This study).

oxygen atoms. Additional atom sites from a series of difference-Fourier maps were added in, and subsequent refinements conducted. By paying close attention to coordination complexes, bond lengths, and scattering power during the refinement, the correct atom assignment could be made. The H atoms were refined with an isotropic displacement factor and with constraints on the O–H distance of 0.980(3) Å. The addition of an isotropic extinction correction improved the refinement, attesting to the perfection of the crystal. There was no evidence of twinning. The maximum and minimum electron densities in the final cycle of refinement were +0.51 and –0.38 e$^-$/Å^3. With all atoms located and assigning anisotropic displacement factors to all non-hydrogen atoms, the structure refined to $R = 0.029$.

The final positional and anisotropic displacement parameters for the atoms are given in Table 4 and selected bond-lengths and angles are given in Table 5 and 6. Tables listing the observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, on the MAC website [document Volkovskite CM51_157].

Description of the Structure

The crystal structure of volkovskite is a layered borate (Grice *et al.* 1999). The layering parallels (010) (Fig. 3) and consists of a double layer of borate sheets. Each sheet in the double layer varies only slightly. Between the double layers there are two types of cross linkage: Ca polyhedra bond two double layer slabs and K polyhedra bond the double slabs (Fig. 3). In Figure 3 it is evident that the plane of K polyhedra with the Cl atoms is much more open (weaker bonded) than the Ca polyhedral layers.

Borate polyanions

The borate polyanions consist of two distinct polyhedra, one triangularly coordinated and the other tetrahedrally coordinated. Of the 22 crystallographically distinct B-sites, 13 have triangular coordination, and 9 have tetrahedral coordination. There are three sub-types of triangular coordination, the common $[BO_3]^{-3}$, the rarer $[BO_2(OH)]^{-2}$, and the even rarer $[B(OH)_3]^0$. Each of the three sub-types has a distinct bond topology since H atoms act as net terminations. Thus the $[B(OH)_3]$ polyhedra are isolated from the borate sheets. The $[BO_2(OH)]^{-2}$ polyhedra act as apical polyhedra on pairs of $[BO_4]$ polyhedra and the $[BO_3]$ polyhedra are cross-linkages within the polyhedral sheets. The tetrahedral group is always $[BO_4]$ and it is always linked to another borate group. There are no H_2O groups bonded to B in any borate mineral structure.

In the structural hierarchy of borate structures Grice *et al*. (1999) classify volkovskite as a sheet structure with the fundamental building block: FBB = 3Δ2□,1Δ:<Δ2□>–<2Δ□>,Δ. This notation indicates two-connected three-member borate rings, one ring consisting of one triangular and two tetrahedral borate polyhedra, and a second ring consisting of two triangular and one tetrahedral borate polyhedra with a separate, isolated triangular borate polyhedra.

Ca and K polyhedra

The four Ca-atom sites have nine-fold coordination, a $[Ca\Phi_9]$ polyhedra, with Φ vertices as O atoms, Cl atoms, OH anions or water groups. This polyhedron describes a bifurcated hexagonal dipyramid. The single K atom site has eight-fold coordination with bonds

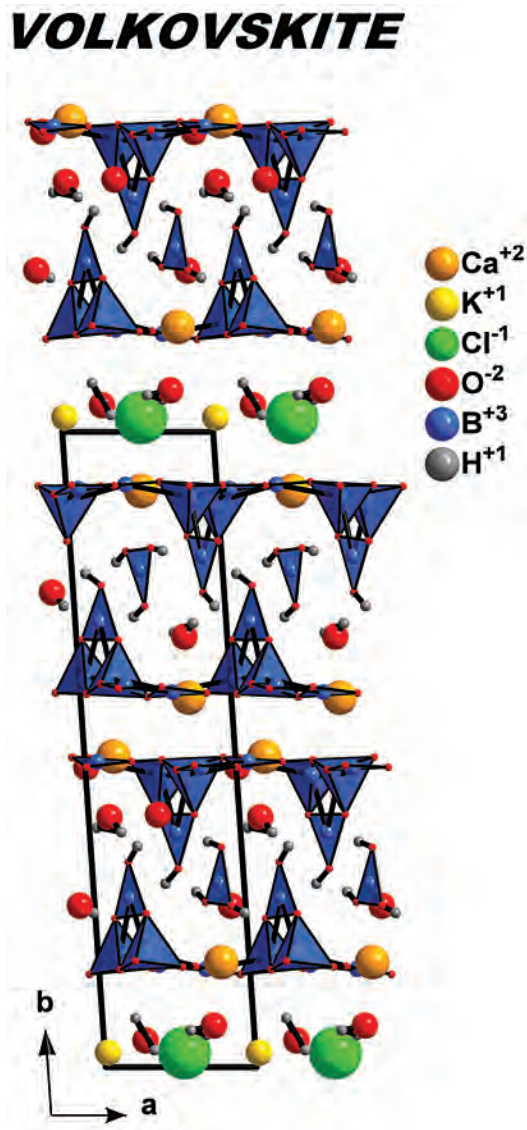

FIG. 3. Volkovskite: a [001] projection showing the borate layering of triangular and tetrahedral polyhedra. Between the borate sheets and Ca atoms is a layer of Cl atoms (large green circles), K atoms (small yellow circles), and H_2O groups (medium sized red circles).

TABLE 3. VOLKOVSKITE: DATA COLLECTION AND STRUCTURE REFINEMENT INFORMATION

Space Group	*P1*	Measured reflections	32201
a (Å)	6.535(3)	Unique reflections	10512
b (Å)	24.185(13)	Observed reflections [> 4σ(*F*)]	10452
c (Å)	6.589(4)	*R*(int) (%)	2.82
α (°)	92.626(14)	Goodness of fit on F^2	1.03
β (°)	119.132(11)	*R* index (%) for all data	2.89
γ (°)	97.298 (9)	wR^2 (%) for all data	7.38
V (Å^3)	895.28(14)	Refinement by full-matrix least squares on F^2	

Ideal unit-cell contents, $KCa_4B_{22}O_{32}(OH)_{10}$ Cl•$4H_2O$, μ = 1.41 mm^{-1}

TABLE 4. VOLKOVSKITE ATOMIC COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å)^3

Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca1	0.8127(1)	0.1649(1)	0.6598(1)	0.0125(3)	0.0153(3)	0.0103(3)	0.0021(2)	0.0059(2)	0.0014(3)	0.0125(2)
Ca2	0.7163(1)	0.5816(1)	0.3900(1)	0.0114(3)	0.0146(3)	0.0106(3)	0.0023(2)	0.0055(2)	0.0006(2)	0.0121(2)
Ca3	0.4952(1)	0.9069(1)	0.0217(1)	0.0120(3)	0.0146(3)	0.0104(3)	0.0012(2)	0.0059(2)	0.0009(2)	0.0122(2)
Ca4	0.1913(1)	0.4891(1)	0.3453(1)	0.0113(3)	0.0145(3)	0.0103(3)	0.0007(2)	0.0053(2)	0.0012(2)	0.0121(2)
K1	0.0213(2)	0.0228(1)	0.0364(2)	0.0257(4)	0.0235(5)	0.0274(4)	0.0053(4)	0.0102(4)	0.0018(4)	0.0266(3)
B1	0.3001(7)	0.5993(2)	0.9027(7)	0.0074(13)	0.0153(17)	0.0065(13)	0.0014(12)	0.0038(11)	0.0008(13)	0.0095(8)
B2	0.3921(7)	0.9167(2)	0.4268(7)	0.0091(13)	0.0124(17)	0.0077(14)	0.0022(12)	0.0038(11)	0.0022(13)	0.0098(8)
B3	0.7658(7)	0.4710(2)	0.8406(7)	0.0084(13)	0.0136(17)	0.0074(13)	0.0016(12)	0.0044(11)	0.0012(13)	0.0096(8)
B4	0.3997(7)	0.1603(2)	0.1575(7)	0.0092(13)	0.0156(18)	0.0079(13)	0.0012(13)	0.0048(11)	0.0005(13)	0.0107(8)
B5	0.2369(8)	0.2648(2)	0.5598(8)	0.0162(16)	0.0174(19)	0.0079(15)	0.0023(14)	0.0040(13)	0.0009(15)	0.0146(9)
B6	0.7085(7)	0.1537(2)	0.0586(7)	0.0096(13)	0.0135(17)	0.0075(13)	0.0017(12)	0.0049(11)	0.0007(13)	0.0098(8)
B7	0.1590(8)	0.7007(2)	0.3302(8)	0.0179(16)	0.0139(18)	0.0090(15)	0.0013(14)	0.0051(13)	0.0004(15)	0.0143(9)
B8	0.5700(8)	0.3693(2)	0.1692(8)	0.0181(16)	0.0142(18)	0.0083(15)	0.0014(14)	0.0048(13)	0.0009(15)	0.0142(9)
B9	0.0792(7)	0.4800(2)	0.7489(7)	0.0078(13)	0.0124(17)	0.0058(13)	0.0020(12)	0.0033(10)	0.0010(13)	0.0086(8)
B10	0.8743(8)	0.8040(2)	0.8213(8)	0.0170(16)	0.0146(18)	0.0098(15)	0.0021(14)	0.0050(13)	0.0017(15)	0.0145(9)
B11	0.6090(7)	0.5900(2)	0.8024(7)	0.0083(13)	0.0125(16)	0.0059(13)	0.0014(12)	0.0040(10)	0.0009(13)	0.0087(8)
B12	0.8347(8)	0.2889(2)	0.7479(8)	0.0181(16)	0.0164(19)	0.0117(16)	0.0030(14)	0.0058(13)	0.0018(15)	0.0159(10)
B13	0.4549(8)	0.7819(2)	0.9840(8)	0.0178(16)	0.0169(19)	0.0113(16)	0.0003(14)	0.0061(13)	0.0009(15)	0.0159(10)
B14	0.0784(7)	0.9106(2)	0.5200(7)	0.0096(14)	0.0155(18)	0.0063(14)	0.0017(13)	0.0035(11)	0.0018(14)	0.0106(8)
B15	0.0375(7)	0.6112(2)	0.0812(7)	0.0082(13)	0.0128(17)	0.0058(13)	0.0011(12)	0.0040(10)	0.0004(12)	0.0087(8)
B16	0.9865(7)	0.8899(2)	0.1057(7)	0.0085(14)	0.0153(18)	0.0053(13)	0.0017(13)	0.0025(11)	0.0011(13)	0.0100(8)
B17	0.2203(7)	0.6126(2)	0.506097)	0.0083(13)	0.0118(16)	0.0064(13)	0.0017(12)	0.0036(11)	0.0009(13)	0.0088(8)
B18	0.495997)	0.4588(2)	0.0067(7)	0.0069(13)	0.0142(17)	0.0058(13)	0.0019(12)	0.0030(11)	0.0014(13)	0.0090(8)
B19	0.1356(7)	0.1714(2)	0.3345(7)	0.0079(13)	0.0156(18)	0.0061(13)	0.0019(12)	0.0035(11)	0.0004(13)	0.0098(8)
B20	0.3168(7)	0.1788(2)	0.7629(7)	0.0083(13)	0.0160(18)	0.0074(14)	0.0034(13)	0.0044(11)	0.0018(13)	0.0102(8)
B21	0.8098(7)	0.8975(2)	0.6853(7)	0.0082(13)	0.0154(18)	0.0047(13)	0.0017(12)	0.0025(11)	0.0008(13)	0.0097(8)
B22	0.6774(7)	0.4576(2)	0.4307(7)	0.0083(13)	0.0115(16)	0.0072(13)	0.0012(12)	0.0032(11)	0.0006(13)	0.0092(8)
O1	0.1362(5)	0.1526(1)	0.5386(5)	0.0099(9)	0.0160(13)	0.0052(9)	0.0021(9)	0.0035(8)	0.0003(9)	0.0104(6)
O2	0.8165(5)	0.9147(1)	0.9059(5)	0.0096(9)	0.0152(12)	0.0048(9)	0.0015(9)	0.0034(8)	0.0026(9)	0.0099(6)
O3	0.0353(5)	0.9162(2)	0.7014(5)	0.0087(9)	0.0245(14)	0.0068(10)	0.0016(10)	0.0046(8)	0.0004(10)	0.0130(6)
O4	0.0383(5)	0.5866(1)	0.2787(5)	0.0081(9)	0.0131(12)	0.0044(9)	0.0011(8)	0.0028(7)	–0.0003(9)	0.0087(6)
O5	0.9155(5)	0.4876(1)	0.5228(5)	0.0071(9)	0.0172(13)	0.0057(9)	0.0024(9)	0.0024(7)	–0.0003(9)	0.0103(6)
O6	0.6037(5)	0.4675(1)	0.6101(5)	0.0081(9)	0.0188(13)	0.0055(9)	0.0012(9)	0.0033(8)	0.0010(9)	0.0109(6)
O7	0.1405(5)	0.6026(1)	0.6757(5)	0.0079(9)	0.0188(13)	0.0057(9)	0.0027(9)	0.0033(8)	0.0014(9)	0.0107(6)
OH8	0.9045(7)	0.2535(2)	0.9137(6)	0.0300(15)	0.0181(14)	0.0101(12)	0.0036(11)	0.0055(11)	0.0012(13)	0.0211(8)
O9	0.8351(5)	0.5888(1)	0.8553(5)	0.0073(9)	0.0182(13)	0.0062(10)	0.0001(9)	0.0028(8)	0.0003(9)	0.0109(6)
O10	0.5405(5)	0.5983(1)	0.9708(5)	0.0076(9)	0.0204(14)	0.0067(10)	0.0008(9)	0.0039(8)	0.0010(9)	0.0115(6)
O11	0.3187(5)	0.9153(1)	0.5913(5)	0.0089(10)	0.0252(15)	0.0074(10)	0.0029(10)	0.0042(8)	0.0014(10)	0.0137(6)
O12	0.2415(5)	0.1666(2)	0.9329(5)	0.0087(9)	0.0251(15)	0.0068(10)	0.0042(10)	0.0049(8)	0.0028(10)	0.0129(6)
O13	0.0340(5)	0.6727(1)	0.1105(5)	0.0188(11)	0.0114(12)	0.0086(10)	0.0020(9)	0.0055(9)	0.0015(10)	0.0134(6)
O14	0.7819(5)	0.8348(1)	0.6378(5)	0.0205(12)	0.0141(13)	0.0072(10)	0.0008(9)	0.0052(9)	0.0015(11)	0.0146(7)
OH15	0.5312(6)	0.8170(2)	0.1835(6)	0.0287(14)	0.0173(14)	0.0102(12)	–0.0002(11)	0.0060(11)	0.0019(12)	0.0204(8)
O16	0.2297(5)	0.9140(1)	0.1939(5)	0.0080(9)	0.0210(14)	0.0061(10)	0.0015(9)	0.0030(8)	–0.0005(10)	0.0119(6)
O17	0.7214(5)	0.4750(1)	0.0203(5)	0.0088(9)	0.0210(14)	0.0072(10)	0.0012(9)	0.0050(8)	–0.0001(10)	0.0119(6)
O18	0.3525(5)	0.1553(2)	0.3333(5)	0.0087(9)	0.0263(15)	0.0075(10)	0.0042(10)	0.0053(8)	0.0030(10)	0.0134(6)
O19	0.2712(5)	0.6721(1)	0.5221(5)	0.0167(11)	0.0113(12)	0.0080(11)	0.0011(9)	0.0032(9)	–0.0013(10)	0.0133(6)
O20	0.4415(5)	0.5823(1)	0.5691(5)	0.0068(9)	0.0170(13)	0.0053(10)	0.0005(9)	0.0020(8)	0.0027(9)	0.0102(6)
O21	0.6202(5)	0.9211(1)	0.4880(5)	0.0071(9)	0.0202(14)	0.0077(10)	0.0041(9)	0.0030(8)	0.0019(10)	0.0117(6)
O22	0.5104(5)	0.4833(1)	0.2283(5)	0.0091(9)	0.0132(12)	0.0048(9)	0.0015(9)	0.0035(8)	0.0027(9)	0.0090(6)
O23	0.0061(5)	0.4718(1)	0.9095(5)	0.0076(9)	0.0191(13)	0.0071(10)	0.0033(9)	0.0037(8)	0.0015(10)	0.0111(6)
O24	0.6387(5)	0.1586(1)	0.2269(5)	0.0081(10)	0.0226(14)	0.0069(10)	0.0020(10)	0.0041(8)	0.0017(10)	0.0123(6)
O25	0.9184(5)	0.9009(1)	0.2890(5)	0.0084(9)	0.0238(14)	0.0058(10)	0.0008(9)	0.0038(8)	–0.0002(10)	0.0126(6)
OH26	0.3691(7)	0.8119(2)	0.7961(6)	0.0400(18)	0.0156(15)	0.0109(12)	0.0009(11)	0.0069(12)	0.0023(14)	0.0246(9)
O27	0.2546(5)	0.5951(1)	0.0794(5)	0.0082(9)	0.0215(14)	0.0072(10)	0.0031(9)	0.0050(8)	0.0021(10)	0.0116(6)
O28	–0.0197(5)	0.8278(1)	0.0486(5)	0.0185(12)	0.0145(13)	0.0078(11)	0.0018(10)	0.0039(9)	0.0017(11)	0.0147(7)
OH29	0.5648(8)	0.3121(2)	0.1580(6)	0.0515(22)	0.0122(14)	0.0098(13)	0.0002(11)	0.0040(14)	0.00002(15)	0.0294(10)
O30	0.5512(5)	0.1576(1)	0.8302(5)	0.0088(5)	0.0213(14)	0.0069(10)	0.0031(8)	0.0040(8)	0.0030(10)	0.0121(6)

O31	0.9345(5)	0.1458(1)	0.1147(5)	0.0072(9)	0.0189(13)	0.0073(10)	0.0005(9)	0.0030(8)	0.0011(10)	0.0115(6)
O32	0.1291(6)	0.2338(1)	0.3465(5)	0.0210(12)	0.0137(13)	0.0075(10)	0.0020(9)	0.0048(9)	0.0010(11)	0.0149(7)
O33	0.3350(5)	0.2411(1)	0.7636(5)	0.0188(12)	0.0139(12)	0.0075(11)	0.0015(9)	0.0034(9)	0.0008(10)	0.0147(7)
O34	0.6954(5)	0.3979(1)	0.3891(5)	0.0168(11)	0.0114(12)	0.0074(11)	0.0012(9)	0.0029(9)	0.0024(10)	0.0131(6)
OH35	0.8578(8)	0.7466(2)	0.7707(6)	0.0529(22)	0.0144(15)	0.0114(13)	0.0015(11)	0.0085(14)	0.0024(15)	0.0293(10)
OH36	0.2440(8)	0.3223(2)	0.5641(6)	0.0486(21)	0.0153(15)	0.0110(13)	0.0013(11)	0.0062(14)	–0.0003(15)	0.0286(10)
O37	0.3054(5)	0.4811(1)	0.8030(5)	0.0072(9)	0.0179(13)	0.0072(10)	0.0034(9)	0.0034(8)	0.0017(9)	0.0107(6)
OH38	0.7356(8)	0.2591(2)	0.5308(6)	0.0425(18)	0.0159(14)	0.0104(13)	0.0028(11)	0.0068(13)	0.0017(14)	0.0255(9)
OW39	0.7159(7)	0.6769(2)	0.3867(6)	0.0382(18)	0.0154(14)	0.0134(14)	0.0005(11)	0.0065(13)	0.0030(13)	0.0250(9)
OH40	0.8613(8)	0.3459(2)	0.7909(7)	0.0524(22)	0.0158(16)	0.0137(14)	0.0006(12)	0.0083(14)	–0.0010(16)	0.0308(11)
OH41	0.1827(8)	0.7579(2)	0.3724(6)	0.0499(21)	0.0127(14)	0.0105(13)	0.0023(11)	0.0058(13)	0.0007(14)	0.0282(10)
O42	0.4596(5)	0.3970(1)	0.9764(5)	0.0178(11)	0.0119(12)	0.0071(10)	0.0008(9)	0.0044(9)	–0.0004(10)	0.0130(6)
OW43	0.7371(7)	0.0651(2)	0.6034(7)	0.0335(16)	0.0195(16)	0.0220(15)	–0.0004(12)	0.0113(13)	–0.0021(14)	0.0262(9)
OW44	0.2711(9)	0.0419(2)	0.5207(8)	0.0567(24)	0.0259(19)	0.0246(17)	0.0032(15)	0.0155(17)	0.0054(19)	0.0376(12)
OH45	0.4643(8)	0.7253(2)	0.9727(7)	0.0512(22)	0.0157(16)	0.0131(14)	0.0008(12)	0.0091(14)	0.0045(16)	0.0296(10)
OW46	0.1379(7)	0.3934(2)	0.2510(6)	0.0393(19)	0.0145(15)	0.0139(13)	0.0024(11)	0.0059(13)	–0.0021(14)	0.0256(9)
Cl1	0.5277(2)	0.0221(1)	0.0626(2)	0.0296(4)	0.0174(4)	0.0217(4)	0.0005(4)	0.0130(4)	0.0003(4)	0.0229(2)
H8	0.9981(144)	0.2606(43)	1.0832(56)	0.05						
H15	0.6179(149)	0.8111(35)	0.3477(60)	0.05						
H26	0.5134(169)	0.3029(46)	0.0566(187)	0.05						
H29	0.3196(146)	0.7916(30)	0.6438(71)	0.05						
H35	0.8925(143)	0.7265(25)	0.9048(77)	0.05						
H36	0.3166(151)	0.3434(28)	0.7210(70)	0.05						
H38	0.6763(151)	0.2742(26)	0.3830(69)	0.05						
H39A	0.7656(152)	0.7070(21)	0.5123(90)	0.05						
H39B	0.6427(153)	0.6932(20)	0.2396(54)	0.05						
H40	0.8202(139)	0.3636(26)	0.6495(72)	0.05						
H41	0.1086(152)	0.7805(21)	0.2439(82)	0.05						
H43A	0.5834(56)	0.0551(39)	0.5840(128)	0.05						
H43B	0.7618(138)	0.1047(14)	0.5966(157)	0.05						
H44A	0.2184(112)	0.0796(16)	0.5229(169)	0.05						
H44B	0.2992(160)	0.0321(45)	0.6516(185)	0.05						
H45	0.3947(152)	0.7033(27)	0.8202(72)	0.05						
H46A	0.0589(155)	0.3763(32)	0.0905(65)	0.05						
H46B	0.1692(156)	0.3650(19)	0.3562(91)	0.05						

TABLE 5. VOLKOVSKITE SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Calcium bonding							
Ca1–OW43	2.395(4)	Ca2–OW39	2.286(4)	Ca3–OH15	2.456(5)	Ca4–OW46	2.294(4)
Ca1–OH8	2.445(7)	Ca2–O7	2.488(4)	Ca3–O25	2.467(4)	Ca4–O6	2.490(4)
Ca1–OH38	2.460(4)	Ca2–O10	2.498(18)	Ca3–OH26	2.487(5)	Ca4–O23	2.502(18)
Ca1–O30	2.473(7)	Ca2–O4	2.548(5)	Ca3–O16	2.492(7)	Ca4–O4	2.545(3)
Ca1–O12	2.483(4)	Ca2–O22	2.561(3)	Ca3–O11	2.519(18)	Ca4–O22	2.552(5)
Ca1–O24	2.492(18)	Ca2–O20	2.584(7)	Ca3–O2	2.571(5)	Ca4–O5	2.585(7)
Ca1–O1	2.601(5)	Ca2–O5	2.621(4)	Ca3–O3	2.733(5)	Ca4–O20	2.605(4)
Ca1–O18	2.705(5)	Ca2–O27	2.745(4)	Ca3–Cl1	2.744(2)	Ca4–O17	2.751(4)
<Ca1–O>	<2.507>	<Ca2–O>	<2.541>	<Ca3–O>	<2.559>	<Ca4–O>	<2.541>
Potassium bonding							
K1–O2	2.759(4)	K1–B16	3.282(5)				
K1–OW44	2.773(20)	K1–Cl1	3.313(2)				
K1–OW43	2.837(15)	K1–B21	3.426(8)				
K1–O16	2.991(4)	K1–Ca3	4.212(2)				
K1–O31	3.050(4)	K1–Ca1	4.248(9)				
K1–Cl1	3.229(2)	K1–B6	3.052(19)				
K1–O3	3.244(10)	<K1–O>	<3.263>				

Triangular boron bonding

B1–O27	1.347(10)	O27–O7	126.61(5)	B2–O21	1.342(5)	O21–O16	118.07(4)
B1–O7	1.355(9)	O27–O10	113.58(4)	B2–O16	1.371(9)	O21–O10	121.92(4)
B1–O10	1.401(5)	O7–O10	119.77(4)	B2–O11	1.386(9)	O16–O21	120.01(5)
<B1–O>	<1.368>	<O–O>	<119.99>	<B2–O>	<1.366>	<O–O>	<120.00>
B3–O17	1.345(10)	O17–O6	126.21(5)	B4–O18	1.351(10)	O18–O12	126.44(5)
B3–O6	1.358(9)	O17–O23	113.88(4)	B4–O12	1.356(9)	O18–O24	113.29(4)
B3–O23	1.405(5)	O6–O23	119.91(4)	B4–O24	1.400(5)	O12–O24	120.27(4)
<B3–O>	<1.369>	<O–O>	<120.00>	<B4–O>	<1.369>	<O–O>	<120.00>
B5–O32	1.359(9)	O32–O33	122.58(5)	B6–O31	1.358(5)	O31–O30	117.75(4)
B5–O33	1.362(9)	O32–OH36	117.26(4)	B6–O30	1.361(9)	O31–O24	121.69(4)
B5–OH36	1.376(6)	O33–OH36	120.16(4)	B6–O24	1.386(9)	O30–O24	120.55(5)
<B5–O>	<1.366>	<O–O>	<120.00>	<B6–O>	<1.368>	<O–O>	<120.00>
B7–OH41	1.364(6)	OH41–O13	122.77(4)	B8–O42	1.363(8)	O42–OH29	123.02(4)
B7–O13	1.366(9)	OH41–O19	116.25(4)	B8–OH29	1.365(6)	O42–O34	121.26(5)
B7–O19	1.371(8)	O13–O19	120.98(5)	B8–O34	1.372(9)	OH29–O34	115.72(4)
<B7–O>	<1.367>	<O–O>	<120.00>	<B8–O>	<1.367>	<O–O>	<120.00>
B9–O37	1.340(5)	O37–O5	117.53(4)	B10–O14	1.356(8)	O14–O28	122.72(5)
B9–O5	1.379(9)	O37–O23	122.82(4)	B10–O28	1.366(10)	O14–OH35	117.20(5)
B9–O23	1.384(9)	O5–O23	119.64(5)	B10–OH35	1.375(6)	O28–OH35	120.08(4)
<B9–O>	<1.368>	<O–O>	<120.00>	<B10–O>	<1.366>	<O–O>	<120.00>
B11–O9	1.344(5)	O9–O20	117.39(4)	B12–OH8	1.351(8)	OH8–OH40	124.94(5)
B11–O20	1.378(9)	O9–O10	122.86(4)	B12–OH40	1.360(6)	OH8–OH38	110.11(6)
B11–O10	1.384(9)	O20–O10	119.74(5)	B12–OH38	1.366(10)	OH40–OH38	124.94(5)
<B11–O>	<1.369>	<O–O>	<120.00>	<B12–O>	<1.359>	<O–O>	<120.00>
B13–OH15	1.351(9)	OH15–OH45	124.84(5)	B14–O3	1.350(10)	O3–O25	127.24(5)
B13–OH45	1.356(6)	OH15–OH26	110.05(6)	B14–O25	1.357(9)	O3–O11	112.87(4)
B13–OH26	1.366(9)	OH45–OH26	125.11(5)	B14–O11	1.402(5)	O25–O11	119.89(4)
<B13–O>	<1.358>	<O–O>	<120.00>	<B14–O>	<1.370>	<O–O>	<120.00>

Tetrahedral boron bonding

B15–O13	1.470(5)	O13–O9	108.91(3)	B16–O2	1.436(7)	O2–O25	106.39(5)
B15–O9	1.473(7)	O13–O4	110.98(4)	B16–O25	1.480(10)	O2–O16	112.47(4)
B15–O4	1.478(10)	O13–O27	110.21(3)	B16–O16	1.488(5)	O2–O28	110.70(4)
B15–O27	1.479(5)	O9–O4	111.84(5)	B16–O28	1.494(6)	O25–O16	109.74(4)
<B15–O>	<1.475>	O9–O27	108.30(4)	<B16–O>	<1.475>	O25–O28	108.81(4)
		O4–O27	106.55(3)			O16–O28	108.66(3)
		<O–O>	<109.47>			<O–O>	<109.46>
B17–O19	1.443(5)	O19–O4	115.60(4)	B18–O37	1.471(7)	O37–O42	108.88(3)
B17–O4	1.455(8)	O19–O7	108.9(4)	B18–O42	1.474(6)	O37–O17	108.44(4)
B17–O7	1.482(9)	O19–O20	109.32(3)	B18–O17	1.478(5)	O37–O22	111.87(5)
B17–O20	1.511(5)	O4–O7	106.46(5)	B18–O22	1.478(11)	O42–O17	109.95(3)
<B17–O>	<1.473>	O4–O20	107.90(3)	<B18–O>	<1.475>	O42–O22	111.10(4)
		O7–O20	108.45(3)			O17–O22	106.54(3)
		<O–O>	<109.44>			<O–O>	<109.46>
B19–O1	1.457(10)	O1–O31	112.01(5)	B20–O1	1.442(8)	O1–O12	105.88(5)
B19–O31	1.470(7)	O1–O18	109.05(3)	B20–O12	1.476(9)	O1–O30	112.76(4)
B19–O18	1.477(5)	O1–O32	109.59(4)	B20–O30	1.484(5)	O1–O33	110.76(4)
B19–O32	1.492(6)	O31–O18	107.95(4)	B20–O32	1.494(6)	O12–O30	110.50(4)
<B19–O>	<1.474>	O31–O32	109.30(3)	<B20–O>	<1.474>	O12–O33	108.68(4)
		O18–O32	108.88(3)			O30–O33	108.19(3)
		<O–O>	<109.46>			<O–O>	<109.46>
B21–O2	1.452(11)	O2–O21	113.01(5)	B22–O34	1.448(5)	O34–O22	115.32(4)
B21–O21	1.460(7)	O2–O3	109.35(3)	B22–O22	1.450(7)	O34–O6	108.87(4)
B21–O3	1.486(6)	O2–O14	109.43(4)	B22–O6	1.472(10)	O34–O5	109.10(3)
B21–O14	1.498(6)	O21–O3	107.91(4)	B22–O5	1.510(5)	O22–O6	106.86(5)
<B21–O>	<1.474>	O21–O14	108.96(3)	<B22–O>	<1.470>	O22–O5	108.00(3)
		O3–O14	108.05(3)			O6–O5	108.49(4)
		<O–O>	<109.45>			<O–O>	<109.44>

TABLE 6. VOLKOVSKITE HYDROGEN INTERATOMIC DISTANCES (Å) AND ANGLES (º)

D–H….A	OH8–H8...O32	OH15–H15...O14	OH29–H29...O33	OH26–H26...OH41
D–H (Å)	0.973	0.973	0.600	0.968
D–A (Å)	2.590	2.606	2.684	2.630
H–A (Å)	1.713	1.706	2.123	1.673
<D–H...A (º)	147.9	152.2	156.6	169.1
D–H….A	OH35–H35...O13	OH36–H36...O42	OH38–H38...OH29	OW39–H39A...OH35
D–H (Å)	0.975	0.982	0.966	0.964
D–A (Å)	2.786	2.803	2.616	2.631
H–A (Å)	1.869	1.841	1.665	1.686
<D–H...A (º)	155.5	165.6	167.8	166.0
D–H….A	OW39–H39B...OH45	OH40–H40...O34	OH41–H41...O28	OW43–H43A...OW44
D–H (Å)	0.973	0.977	0.969	0.973
D–A (Å)	2.787	2.757	2.663	2.858
H–A (Å)	1.823	1.790	1.701	1.890
<D–H...A (º)	170.5	169.6	171.4	173.3
D–H….A	OW43–H43B...O24	OW44–H44A...O1	OW44–H44B...Cl1	OH45–H45...O19
D–H (Å)	0.970	0.971	0.847	0.970
D–A (Å)	3.338	2.815	3.210	2.761
H–A (Å)	2.641	1.845	2.412	1.798
<D–H...A (º)	129.0	176.6	157.1	171.51
D–H….A	OW46–H46A...OH40	OW46–H46B...OH36		
D–H (Å)	0.966	0.970		
D–A (Å)	2.777	2.635		
H–A (Å)	1.821	1.670		
<D–H...A (º)	169.5	172.9		

to four O atoms, two water groups, and two chlorine atoms. This polyhedron is described as a bifurcated tetragonal dipyramid.

H_2O and OH groups and hydrogen bonding

In volkovskite, there are four (H_2O) groups and ten (OH) groups. With the superior data all H positions could be found making it possible to discuss the complex H-bonding. Table 6 gives the appropriate bond lengths for both the H-bond donor and H-bond acceptor. Two of the (H_2O) groups are intra-borate-layer, OW43 and OW44, as part of the K polyhedra, and two are inter-borate-layer, OW39 and OW46. Both of the intralayer water groups are only partially H-bonded. Figure 4 shows that there is an H-bond for one H atom and not for the other. In contrast the inter-layer water groups are more substantially anchored with H-bonds for both H atoms (Fig. 5).

Discussion

In the structural hierarchy of borate crystal structures Grice *et al*. (1999) classify volkovskite as a sheet structure with the fundamental building block: FBB = 3Δ2□,1Δ:<Δ2□>–<2Δ□>,Δ. This layer type is labeled layer **B** in Figure 3 and it is the only layer type present in gowerite (Grice & Pring 2012). There is another very closely related FBB, FBB = 3Δ2□:<Δ2□>–<2Δ□> (labeled **A** in Fig. 3). This FBB is typified in biringuccite and nasinite (Grice & Pring 2012). Both layer **A** and **B** are present in the volkovskite and veatchite structures. To compare these two structure topologies a diagram is constructed ignoring oxygen atoms and using just the large, low-valence, cations and the boron atoms (Fig. 6). As shown in Grice & Pring (2012) only the layer sequence of veatchite-1*A* matches that of volkovskite… **AABBAABB**… . For the other two veatchite polytypes, –1*M* and –2*M*, the layer sequence is different ..**ABABABAB**… . As expected, similarities exist in the formulae of the two

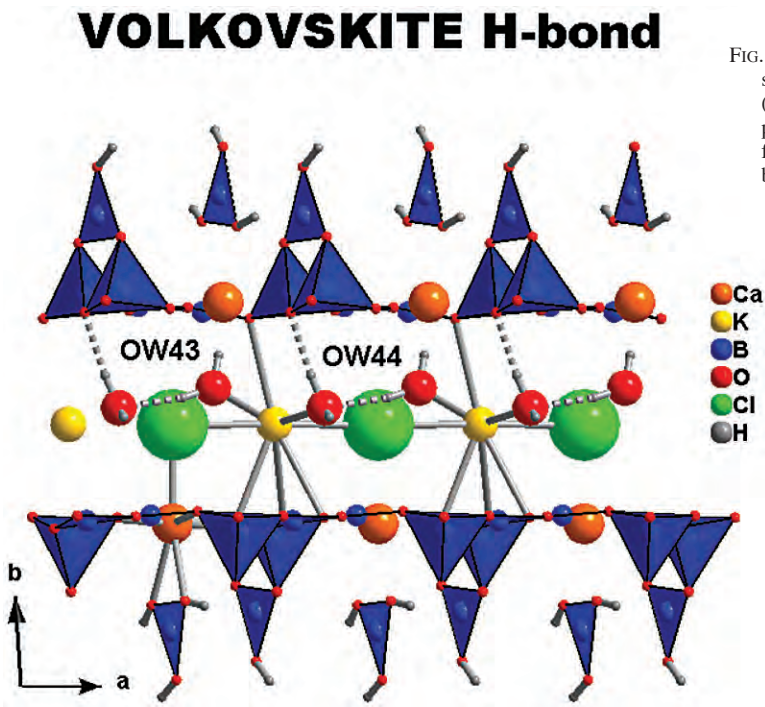

FIG. 4. Volkovskite: a [001] projection showing the intra-layered H_2O groups (OW43 & OW43) part of the K polyhedra. Note that there is an H-bond for one H atom and not for the other for both water groups.

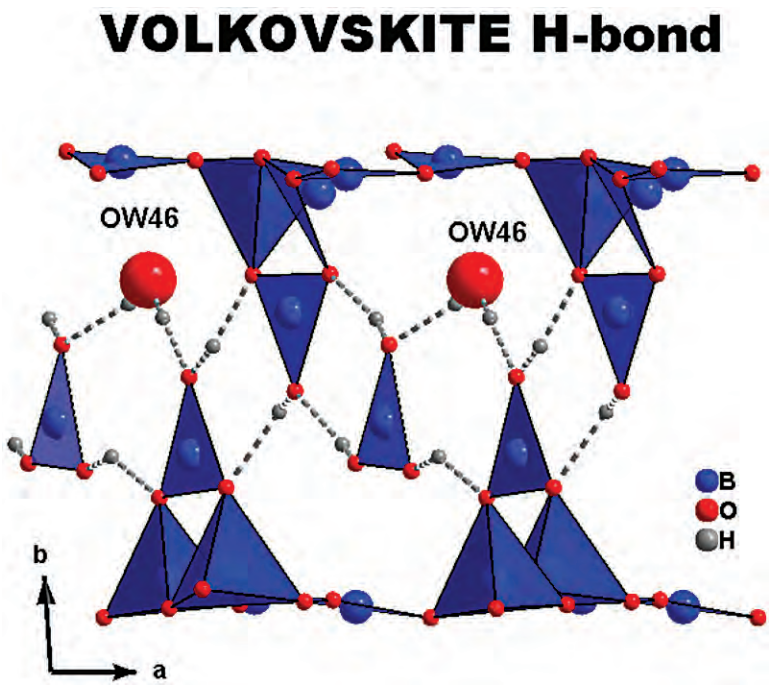

FIG. 5. Volkovskite: a [001] projection showing the inter-layered H_2O group (OW46). This inter-layered H_2O group is firmly anchored with H-bonds for both H atoms in comparison to the intra-layered H_2O groups.

species: volkovskite, $KCa_4B_{22}O_{32}(OH)_{10}Cl{\bullet}4H_2O$, and veatchite, $Sr_4B_{22}O_{32}(OH)_{10}{\bullet}2H_2O$. Volkovskite has an additional large cation, K, and additional large anion, Cl, and two more water groups. The interlayer cell parameters of the two species are similar as this is controlled by the borate layer, volkovskite 6.53 × 6.59 Å and veatchite 6.64 × 6.74 Å, but the cell parameter perpendicular to the layering is necessarily expanded in volkovskite to accommodate the extra ions and water groups, 23.96 *versus* 20.98 Å. Although volkovskite and veatchite-1*A* are both triclinic, volkovskite is non-centrosymmetric and veatchite-1*A* is centrosymmetric. This shift of symmetry is not due to the borate layers, but to the intra-layer constituents. This is readily seen in Figure 6; for veatchite-1*A* the Sr atoms are related by a center of symmetry, while in volkovskite there is no such symmetry relationship for the Ca atoms.

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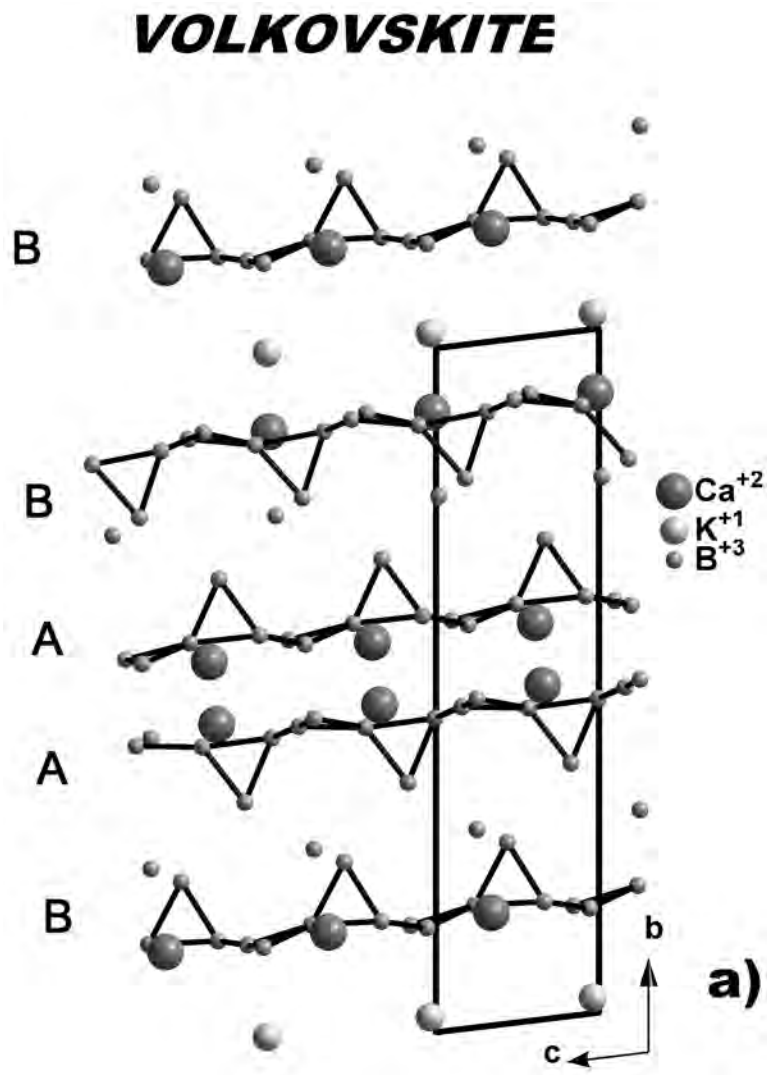
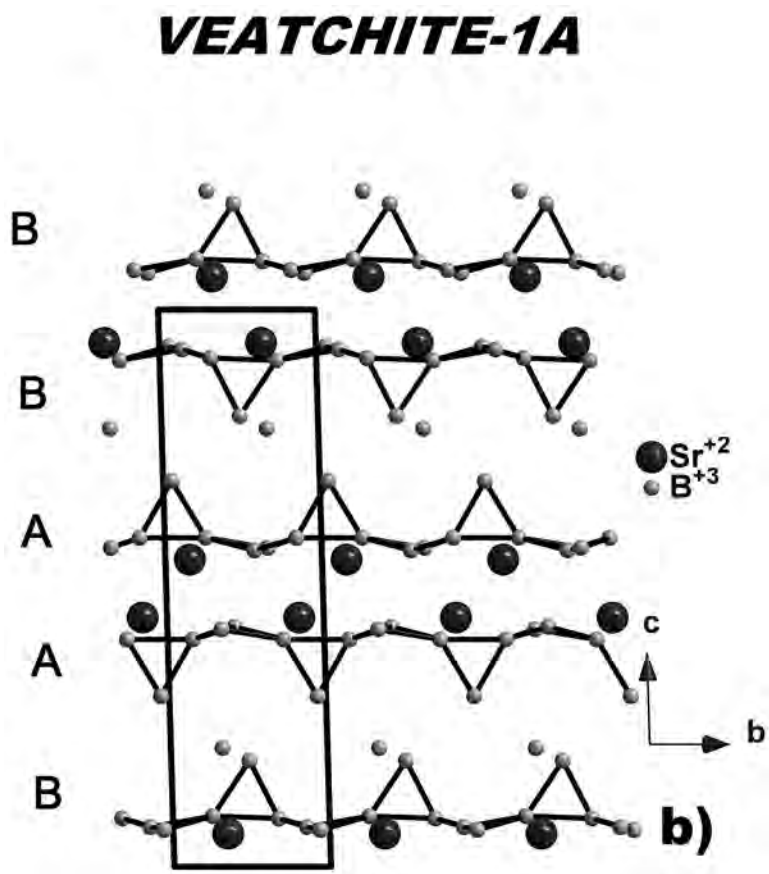


FIG. 6. Structure topologies of volkovskite (a) and veatchite-1*A* (b). The topologies only show large, low-valence cations and boron atoms.



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