

Veatchite: Structural relationships of the three polytypes

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ABSTRACT

Crystal structures of the three polytypes of veatchite, $\text{Sr}_2\text{B}_{11}\text{O}_{16}(\text{OH})_5 \cdot \text{H}_2\text{O}$, are determined by X-ray, single-crystal studies. The polytypes are: veatchite-1A, triclinic space group $P\bar{1}$, with $a = 6.6378(6)$, $b = 6.7387(6)$, $c = 20.982(2)$ Å, $\alpha = 87.860(1)$, $\beta = 82.696(12)$, $\gamma = 60.476(1)^\circ$, $V = 809.7(2)$ Å³; veatchite-1M, monoclinic space group $P2_1$, with $a = 6.7127(4)$, $b = 20.704(1)$, $c = 6.6272(4)$ Å, $\beta = 119.209(1)^\circ$, $V = 805.4(2)$ Å³; and veatchite-2M, monoclinic space group Cc with $a = 6.6070(3)$, $b = 11.7125(5)$, $c = 20.6848(9)$ Å, $\beta = 91.998(1)^\circ$, $V = 1599.7(2)$ Å³. The crystal structures have two layer types with similar fundamental building blocks: **A** layer FBB = $3\Delta 2\square : \langle \Delta 2\square \rangle - \langle 2\Delta\square \rangle$ and **B** layer FBB = $3\Delta 2\square, 1\Delta : \langle \Delta 2\square \rangle - \langle 2\Delta\square \rangle, \Delta$ (Grice et al. 1999). Unique in this FBB is the lone polyhedron with triangular coordination, which consists of a neutrally charged $[\text{B}(\text{OH})_3]$ group. Layering has a directional component and depending on layer sequence the symmetry may be centrosymmetric or non-centrosymmetric. Related layered borate structures, biringuccite, nasinite, gowerite, and volkovskite, are compared. Observations indicate that veatchite-1A is the low-temperature and low-pressure polytype, veatchite-1M the high-temperature polytype, and veatchite-2M the moderate temperature and higher pressure polytype.

Keywords: Veatchite, crystal structures, polytype, borate, fundamental building block

INTRODUCTION

Veatchite was first described by Switzer (1938) from a locality at Lang, Los Angeles County, California. These evaporate borate deposits are formed in association with volcanic activity. The crystal structure of this polytype, now called veatchite-2M, was first determined by Clark and Christ (1971). The second polytype, *p*-veatchite and now called veatchite-1M, was found in the Königshall-Hindenburg potash-salt mine, near Reyershausen, Göttingen, Lower Saxony, Germany, as described by Braitsch (1959). The structure was first solved by Gandymov et al. (1968) using material that was most likely from a Russian deposit. The structure was refined, and H positions determined, by Rastsvetaeva et al. (1993) using a crystal from the Nepskii, East Siberia, deposit in a potash-marine evaporite. The most recent polytype described occurs in the Emet deposit, Kütahya, Turkey. This deposit formed as a playa lake associated with volcanic activity. Kumbasar (1979) named this “modification” veatchite-A. He was unable to determine the crystal structure, and it remained unsolved until this study. The proper polytype name is veatchite-1A. The three polytypes have very similar X-ray powder diffraction patterns that do not satisfactorily differentiate them. Having solved the fundamental, triclinic structure of veatchite-1A now enables us to compare the structural relationships and properly designate the three polytypic names.

MATERIAL STUDIED

Type material was obtained from the Smithsonian Institution for all three polytypes. The authors used the type material for

both *p*-veatchite and veatchite-A, but the crystal for the veatchite (NMNH 105697) from California was too large and in the interest of preserving this crystal the authors selected substitute material from the Penobsquis deposit at Sussex, New Brunswick (Grice et al. 2005). Sample numbers, localities, and crystal sizes are given in Table 1. No further chemical analyses could be performed on the type material, and the structure refinement

TABLE 1. Veatchite data collection and structure refinement information

Polytype name	veatchite-1A	veatchite-1M	veatchite-2M
Original name	veatchite-A	<i>p</i> -veatchite	veatchite
Specimen number	NMNH 145911	NMNH 113264	RG701/1
Locality	Emet, Turkey	Reyershausen, Germany	Sussex, NB
Crystal size (μm)	150 × 100 × 25	400 × 400 × 170	250 × 160 × 120
Space group	$P\bar{1}$ (no. 2)	$P2_1$ (no. 4)	Cc (no. 9)
<i>a</i> (Å)	6.6378(6)	6.7127(4)	6.6070(3)
<i>b</i> (Å)	6.7387(6)	20.704(1)	11.7125(5)
<i>c</i> (Å)	20.982(2)	6.6276(4)	20.6848(9)
α (°)	87.860(1)	90	90
β (°)	82.696(1)	119.209(1)	91.998(1)
γ (°)	60.476(1)	90	90
<i>V</i> (Å ³)	809.7(2)	805.4(2)	1599.7(2)
<i>Z</i>	2	2	4
Measured reflections	9356	9451	9398
Unique reflections	4796	4726	4458
Observed reflections [$>4\sigma(F)$]	4679	4600	4107
<i>R</i> _{int} (%)	0.039	0.014	0.036
Goodness of fit on <i>F</i> ²	0.91	1.02	0.987
<i>R</i> index for all data	0.034	0.024	0.035
<i>R</i> index	0.034	0.025	0.031
<i>wR</i> ² (%) for all data	0.093	0.060	0.072
<i>D</i> _{calc} (ideal cell contents)	2.68	2.69	2.71
Ideal cell contents: (Sr,Ca) ₂ B ₁₁ O ₁₆ (OH) ₅ ·H ₂ O	$\mu = 6.7 \text{ mm}^{-1}$		

Note: $w = 1/[\sigma^2 F^2 + (0.05 \times F^2)^2]$.

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supported the nearly end-member formula determined in the original description. Similarly for veatchite-2M, the Sr:Ca ratio refined in the structure analysis agreed well with the chemical analysis in Grice et al. (2005).

X-RAY DIFFRACTION STUDIES

For the two monoclinic polytypes, veatchite-1M and veatchite-2M, data collection, structure solution and refinement was quite routine. Intensity data were collected on a fully automated Siemens P4 four-circle diffractometer equipped with an APEX 4K CCD detector and operated at 50 kV, 40 mA, with graphite-monochromated MoK α radiation. A full sphere of intensity data was collected up to $2\theta = 60^\circ$ using 5 and 15 s frames (1M and 2M polytypes, respectively) at frame widths of 0.2° . It is of note that the polytype veatchite-1A is much more difficult to work with and hence the long-term delay in a structure solution. The crystal problems include small size, ubiquitous twinning, and sub-parallel growth on platy crystal faces. The crystallography given in Kumbasar (1979) is correct, including the observation of the twin law. In the present study, we have adopted a reduced primitive cell instead of the non-conventional $A\bar{1}$ space group of Kumbasar (1979). The transformation matrix from the original A cell to the conventional P cell is: $001/0^{1/2}/\bar{1}00$, which gives $a = 6.630$, $b = 6.733$, $c = 20.80$ Å, $\alpha = 87.90$, $\beta = 89.10$, and $\gamma = 60.50^\circ$. To overcome the problems indicated above a very small crystal (Table 1) was mounted on a Bruker D8 three-circle diffractometer equipped with a rotating anode generator, multi-layer optics and an APEX-II CCD detector. This setup yields a very intense X-ray beam.

Information relevant to the data collection and structure determination is given in Table 1. The three-dimensional data were corrected for Lorentz, polarization, and background effects, and multiple-measured reflections were averaged using the Bruker program SAINT. An empirical absorption-correction was applied (SADABS, Sheldrick 1998). All calculations were done with the Siemens SHELXTL 5.1 system of programs (Sheldrick 1997), with scattering factors of neutral atoms taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). The twinned crystal, veatchite-1A, required the newer programs of Sheldrick (2008a, 2008b), CELL_NOW and TWINABS, as the twin law, twofold rotation about $[1\bar{2}0]$, is not a merohedral twin thus requiring individual data sets for each domain. Of the three domains in the sample one minor component is removed as its relationship to the other two is non-crystallographic. The twin related domains are partitioned into the proportion 0.88:0.12, refined value is 0.1166(4). All three structures have been checked for higher symmetry by MYSSM (LePage 1987) and determined to be correct.

In all three structures, anisotropic displacement parameters were refined for all atomic sites except those of H atoms. The H-atom sites were found using difference Fourier maps and the H-atom positions were allowed to refine without any constraints.

The final positional and isotropic displacement parameters of atoms are given in Table 2. Site occupancies were refined for each of the two Sr sites in all three structures. Only for the veatchite-2M polytypes was the refinement significant. In the Sr2 site, there were almost equal proportions of Sr and Ca, i.e., nearly a new mineral species. Veatchite-2M from the type

locality, Sterling mine, California, has very little Ca. Selected bond-lengths and angles are given in Table 3. Tables listing the observed and calculated structure-factors and the anisotropic displacement parameters (CIF) are available on deposit.¹

DESCRIPTION OF THE STRUCTURES

In the structural hierarchy of borate structures Grice et al. (1999) classify veatchite as a sheet structure with the fundamental building block: $FBB = 3\Delta 2\Box, 1\Delta < \Delta 2\Box > < 2\Delta\Box >, \Delta$. This notation indicates two-connected three-member borate rings, one ring consisting of one triangular and two tetrahedral borate polyhedra, the other ring consisting of two triangular and one tetrahedral borate polyhedra with a separate, isolated triangular borate polyhedra. Two other borate minerals have this identical structural FBB, gowerite and volkovskite, but the layer morphol-

¹Deposit item AM-12-015, CIFs. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 2a. Atomic coordinates and isotropic displacement parameters for veatchite-1A

Atom	x	y	z	U_{eq}
Sr1	0.31005(3)	0.34956(3)	0.05959(1)	0.01024(4)
Sr2	0.34464(3)	0.84380(3)	0.44782(1)	0.00982(4)
B1	0.2661(3)	1.3453(3)	0.4268(1)	0.0091(4)
B2	0.6548(4)	0.4989(4)	0.1908(1)	0.0140(5)
B3	-0.1229(4)	0.9461(4)	0.3066(1)	0.0157(5)
B4	0.2076(3)	0.9394(3)	0.0662(1)	0.0090(4)
B5	-0.1370(3)	1.4311(3)	0.4312(1)	0.0096(4)
B6	0.2322(4)	0.3299(4)	0.2135(1)	0.0166(5)
B7	-0.1080(3)	0.8550(3)	0.0714(1)	0.0103(4)
B8	0.0425(3)	1.2606(3)	0.5915(1)	0.0084(4)
B9	0.8023(3)	0.2545(3)	0.0910(1)	0.0090(4)
B10	0.2856(3)	0.8396(3)	0.5912(1)	0.0078(4)
B11	0.6242(3)	0.6757(3)	0.0868(1)	0.0083(3)
O1	0.4851(2)	1.1727(2)	0.43212(7)	0.0109(3)
O2	0.0996(2)	1.2730(2)	0.42602(7)	0.0107(3)
O3	0.1963(2)	0.5713(2)	0.42408(7)	0.0120(3)
O4	0.7694(2)	0.2861(2)	0.16202(7)	0.0139(3)
O5	0.5750(2)	0.6933(2)	0.15660(7)	0.0146(3)
OH6	0.6143(4)	0.5253(3)	0.25625(8)	0.0297(5)
O7	0.2443(2)	0.8454(2)	0.66116(7)	0.0128(3)
O8	-0.0350(2)	0.7461(2)	0.33865(7)	0.0143(3)
OH9	-0.0855(4)	0.9280(3)	0.24113(8)	0.0314(6)
O10	0.0515(2)	1.1665(2)	0.06762(7)	0.0120(3)
O11	0.4396(2)	0.8727(2)	0.05696(7)	0.0105(3)
O12	0.1290(2)	0.7837(2)	0.07103(7)	0.0126(3)
O13	0.3028(2)	0.6311(2)	0.56376(7)	0.0107(3)
O14	0.7927(2)	0.6582(2)	0.43436(7)	0.0114(3)
OH15	0.3392(3)	1.1444(3)	0.17376(8)	0.0230(4)
OH16	0.2062(4)	0.3221(3)	0.27882(9)	0.0355(6)
OH17	0.1559(4)	0.5254(3)	0.17982(8)	0.0295(5)
O18	0.8451(2)	0.6819(2)	0.06545(7)	0.0126(3)
O19	0.7353(2)	0.0824(2)	0.07612(7)	0.0124(3)
O20	0.1069(2)	1.0415(2)	0.56264(7)	0.0089(3)
O21	0.6523(2)	0.4646(2)	0.06122(7)	0.0101(3)
OW22	0.3696(4)	0.8974(3)	0.33220(9)	0.0347(6)
H6	0.656(4)	0.437(4)	0.274(1)	0.010(6)
H9	-0.154(6)	1.053(6)	0.224(2)	0.051(11)
H15	0.414(5)	1.016(5)	0.185(2)	0.021(7)
H16	0.150(6)	0.438(6)	0.289(2)	0.039(10)
H17	0.068(9)	0.688(9)	0.212(3)	0.099(20)
H22a	0.418(7)	0.814(7)	0.307(2)	0.060(13)
H22b	0.320(6)	1.011(6)	0.314(2)	0.038(10)

Note: Site occupancy factors: Sr1 0.985(1); Sr2 0.975(1).

TABLE 2b. Atomic coordinates and isotropic displacement parameters for veatchite-1M

Atom	x	y	z	U_{eq}
Sr1	0.37767(3)	0.73570(1)	0.18596(4)	0.01213(7)
Sr2	0.92811(4)	0.34853(1)	0.48201(4)	0.01199(7)
B1	0.3912(4)	0.8850(2)	0.1924(4)	0.0104(5)
B2	0.3402(4)	0.3632(1)	0.3808(4)	0.0120(4)
B3	0.1906(5)	0.9875(1)	0.1080(6)	0.0182(5)
B4	0.9707(4)	0.8862(1)	0.0120(4)	0.0109(4)
B5	0.4264(4)	0.3688(1)	0.0670(4)	0.0120(4)
B6	0.5242(4)	0.2040(1)	0.3087(4)	0.0118(4)
B7	0.7875(4)	0.7291(1)	0.0843(4)	0.0116(4)
B8	0.1268(4)	0.2236(1)	0.2291(4)	0.0127(4)
B9	0.0537(4)	0.7070(2)	0.5105(4)	0.0110(5)
B10	0.4123(6)	0.5816(2)	0.1770(5)	0.0204(6)
B11	0.7550(5)	0.1036(1)	0.4056(5)	0.0158(5)
O1	0.0458(3)	0.6374(1)	0.4946(3)	0.0158(4)
O2	0.7372(2)	0.2338(1)	0.4728(3)	0.0122(3)
O3	0.8540(3)	0.7372(1)	0.3124(3)	0.0126(3)
O4	0.5960(3)	0.8574(1)	0.3919(3)	0.0134(3)
O5	0.4980(3)	0.3689(1)	0.3043(3)	0.0141(3)
O6	0.9541(3)	0.2293(1)	0.2784(3)	0.0137(3)
O7	0.4402(3)	0.2289(1)	0.0715(3)	0.0147(3)
O8	0.3938(3)	0.9558(1)	0.2068(3)	0.0166(4)
O9	0.5997(3)	0.3635(1)	0.0180(3)	0.0144(3)
O10	0.3528(3)	0.2193(1)	0.3832(3)	0.0134(3)
O11	0.7996(3)	0.8711(1)	0.0881(3)	0.0142(3)
O12	0.9444(3)	0.7241(1)	0.0081(3)	0.0149(4)
O13	0.1139(3)	0.3606(1)	0.2256(3)	0.0139(3)
OH14	0.5950(4)	0.6212(1)	0.2592(4)	0.0249(4)
O15	0.1849(3)	0.8571(1)	0.1781(3)	0.0114(3)
OH16	0.1795(4)	0.0538(1)	0.1027(5)	0.0353(6)
O17	0.9858(3)	0.9563(1)	0.0020(3)	0.0169(4)
OH18	0.2154(4)	0.6155(1)	0.0865(5)	0.0320(5)
OH19	0.7708(4)	0.0380(1)	0.4098(4)	0.0318(5)
OW20	0.8608(4)	0.4639(1)	0.4488(5)	0.0380(6)
O21	0.5472(3)	0.1334(1)	0.3049(3)	0.0168(4)
OH22	0.4278(4)	0.5164(1)	0.1884(5)	0.0362(6)
H14	0.738(9)	0.607(3)	0.334(9)	0.06(2)
H16	0.288(8)	0.070(2)	0.150(7)	0.03(1)
H18	0.089(7)	0.594(2)	0.019(7)	0.027(9)
H19	0.656(7)	0.015(2)	0.355(7)	0.026(9)
H20a	0.76(1)	0.476(3)	0.35(1)	0.08(2)
H20b	0.965(9)	0.495(2)	0.496(8)	0.03(1)
H22	0.31(1)	0.500(3)	0.147(9)	0.06(2)

Note: Site occupancy factors: Sr1 0.967(1); Sr2 0.891(2).

TABLE 2c. Atomic coordinates and isotropic displacement parameters for veatchite-2M

Atom	x	y	z	U_{eq}
Sr1	0.93247(1)	0.31029(1)	0.71241(1)	0.01153(3)
Sr2	0.90052(3)	-0.03726(2)	0.59968(1)	0.01339(6)
B1	0.6300(3)	0.1049(2)	0.7182(1)	0.0122(4)
B2	0.9203(4)	0.2922(2)	0.8666(1)	0.0181(5)
B3	1.2056(3)	0.1695(2)	0.5853(1)	0.0126(4)
B4	0.7731(3)	0.5618(2)	0.7241(1)	0.0130(4)
B5	0.5624(3)	0.2132(2)	0.5803(1)	0.0127(4)
B6	0.9169(4)	0.4062(2)	0.4601(1)	0.0177(5)
B7	1.4132(3)	0.3764(2)	0.8444(1)	0.0166(5)
B8	0.9241(3)	-0.0289(2)	0.7400(1)	0.0117(4)
B9	0.9101(3)	0.3046(2)	0.5633(1)	0.0113(4)
B10	1.3916(3)	0.2605(2)	0.7432(1)	0.0111(4)
B11	0.9421(3)	0.4861(2)	1.0624(1)	0.0114(4)
O1	0.5875(2)	0.2185(1)	0.71915(7)	0.0141(3)
O2	0.9762(2)	0.5266(1)	0.72357(6)	0.0144(3)
O3	0.8239(2)	0.0721(1)	0.70927(6)	0.0122(3)
OH4	0.9166(3)	0.2002(1)	0.82654(7)	0.0268(4)
OH5	0.9258(3)	0.3907(1)	0.83315(7)	0.0333(5)
OH6	0.9193(3)	0.2842(1)	0.93220(8)	0.0357(5)
O7	0.8596(2)	-0.2513(1)	0.57955(7)	0.0135(3)
O8	1.2473(2)	0.0561(1)	0.58786(7)	0.0145(3)
O9	1.0081(2)	0.2020(1)	0.59055(6)	0.0134(3)
O10	1.2314(2)	0.1750(1)	0.72730(7)	0.0137(3)
O11	0.6370(2)	0.4750(1)	0.71913(6)	0.0141(3)
O12	0.6060(2)	0.0998(1)	0.57788(6)	0.0135(3)
O13	0.6956(2)	0.3007(1)	0.58476(7)	0.0144(3)
O14	0.9147(2)	0.3044(1)	0.49215(6)	0.0167(3)
OH15	0.4135(3)	0.0874(1)	0.89403(8)	0.0342(5)
O16	0.9181(2)	0.4915(1)	0.99185(6)	0.0165(3)
O17	1.4115(2)	0.2727(1)	0.81442(6)	0.0159(3)
O18	0.9142(2)	-0.0234(1)	0.81022(6)	0.0154(3)
OH19	0.9189(3)	0.1150(1)	0.41022(7)	0.0306(4)
O20	1.0042(2)	0.4068(1)	0.59166(6)	0.0117(3)
O21	1.3326(2)	0.3675(1)	0.71301(6)	0.0120(3)
OW22	0.8907(3)	-0.0669(2)	0.48719(8)	0.0348(5)
H4	0.911(4)	0.129(2)	0.834(1)	0.025(7)
H5	0.925(4)	0.471(2)	0.860(1)	0.085(8)
H6	0.883(4)	0.352(2)	0.948(2)	0.062(8)
H15	0.391(4)	0.134(2)	0.877(1)	0.032(7)
H19	0.884(7)	0.166(4)	0.433(2)	0.12(2)
H22a	0.895(6)	-0.016(3)	0.459(2)	0.07(1)
H22b	0.883(4)	-0.133(2)	0.480(1)	0.024(7)

Notes: Site occupancy factors: Sr1 0.9376(5); Sr2 0.6935(6). Coupled site occupancy refinement: Sr1 0.9032(6), Ca2 0.0968; Sr2 0.4870(6), Ca2 0.5130.

ogy differs. This layer type is labeled layer **B** in Figure 1. There is another very closely related FBB, $FBB = 3\Delta 2\Box : <\Delta 2\Box> : <2\Delta\Box>$. This FBB is typified in biringuccite and nasinite but as will be described later this layer type is also an essential component of the veatchite structure. This layer is labeled **A** in Figure 1.

To better compare the three veatchite polytypes the authors have reoriented two of the unit cells to correspond to standard crystallographic space groups; veatchite-1A (formerly veatchite-A) and veatchite-2M (formerly veatchite) (Table 1). In all three structures the layering is perpendicular to the long axis of 20 Å and in each there are two, non-equivalent Sr sites. The Sr1 site has 11-fold coordination with O atoms and a grand average (all three structures) Sr1-O bond length of 2.735 Å. The Sr2 site has 10-fold coordination with O atoms and a grand average (all three structures) Sr2-O bond length of 2.676 Å. The Sr2 site has a propensity toward Ca substitution. This is particularly evident in veatchite-2M where the Ca content is higher than the other two polytypes. In fact this particular sample would qualify as a new mineral species as the Sr2 site is dominated, slightly, by Ca.

Veatchite-1A

Veatchite-1A is the only veatchite polytype that is centrosymmetric. Layering is perpendicular to [001] (Fig. 1a) with **A** and **B** layers alternating along [001] in antipodal pairs: i.e., **A+A-B+B-A+A-B+B-A+A-B+B-**. The antipodal arrangement of layers-in-kind yields a centrosymmetric structure. The two Sr atom sites are between **A+A-** or **B+B-** pairs of layers. Veatchite-1A is invariably twinned on a fine scale. Kumbasar (1979) observed twin lamellae perpendicular to the long axis. This is not a twin plane but a composition plane with the twin law a rotation of 180° about the $[1\bar{2}0]$ axis in the present cell orientation.

Veatchite-1M

Veatchite-1M has non-centrosymmetric space group $P2_1$. Differing from veatchite-1A the layering is perpendicular to [010] (Fig. 1b) with **A** and **B** layers alternating along [010]: i.e., **...A+B-A+B-A+B...**. The consistent directional orientation of each layer-type yields a polar structure. The two Sr atom sites are between **A+B-** pairs of layers.

TABLE 3a. Selected bond lengths (Å) for veatchite-1A

Sr1-O10	2.548(2)	Sr2-OW22	2.436(2)		
Sr1-O19	2.554(1)	Sr2-O3	2.562(2)		
Sr1-O12	2.564(1)	Sr2-O14	2.576(1)		
Sr1-OH17	2.681(2)	Sr2-O2	2.584(1)		
Sr1-OH15	2.701(2)	Sr2-O20	2.696(1)		
Sr1-O21	2.742(2)	Sr2-O20	2.739(1)		
Sr1-O18	2.769(1)	Sr2-O1	2.792(2)		
Sr1-O11	2.788(1)	Sr2-O13	2.830(2)		
Sr1-O21	2.823(2)	Sr2-O1	2.866(2)		
Sr1-O11	2.889(1)	Sr2-O13	2.882(1)		
Sr1-O18	2.989(2)				
<Sr1-O>	<2.7316>	<Sr2-O>	<2.6963>		
B1-O3	1.358(2)	B7-O18	1.361(3)		
B1-O1	1.358(2)	B7-O19	1.361(2)		
B1-O2	1.412(3)	B7-O12	1.400(2)		
B2-O5	1.362(3)	B8-O20	1.452(2)		
B2-OH6	1.366(3)	B8-O8	1.460(3)		
B2-O4	1.368(3)	B8-O14	1.486(3)		
		B8-O3	1.496(2)		
B3-OH9	1.364(3)				
B3-O8	1.366(3)	B9-O21	1.447(2)		
B3-O7	1.377(2)	B9-O10	1.472(2)		
		B9-O4	1.485(3)		
B4-O10	1.360(2)	B9-O19	1.491(3)		
B4-O11	1.363(2)				
B4-O12	1.379(3)	B10-O7	1.457(2)		
		B10-O20	1.466(2)		
B5-O13	1.348(3)	B10-O13	1.486(2)		
B5-O14	1.364(2)	B10-O1	1.498(2)		
B5-O2	1.389(2)				
		B11-O5	1.455(2)		
B6-OH15	1.347(3)	B11-O21	1.455(3)		
B6-OH16	1.361(3)	B11-O11	1.479(2)		
B6-OH17	1.363(3)	B11-O18	1.498(2)		
D-H	d(D-H)	d(H--A)	<DHA	d(D--A)	A
OH6-H6	0.645	2.170	173.25	2.811	O7
OH9-H9	0.826	1.914	160.49	2.706	O4
OH15-H15	0.803	1.968	143.85	2.659	O5
OH16-H16	0.709	2.054	166.16	2.748	O8
OH17-H17	1.151	1.521	165.93	2.652	OH9
OH17-H17	1.151	2.653	130.98	3.516	O8
OW22-H22a	0.702	1.982	163.63	2.663	OH6
OW22-H22b	0.782	1.990	169.94	2.763	OH16

TABLE 3b. Selected bond lengths for veatchite-1M

Sr1-O7	2.542(2)	Sr2-OW20	2.425(2)		
Sr1-O10	2.550(2)	Sr2-O13	2.564(2)		
Sr1-O12	2.561(2)	Sr2-O5	2.566(2)		
Sr1-OH18	2.671(2)	Sr2-O11	2.568(2)		
Sr1-OH14	2.703(2)	Sr2-O2	2.689(2)		
Sr1-O2	2.723(2)	Sr2-O15	2.711(2)		
Sr1-O6	2.786(2)	Sr2-O3	2.716(2)		
Sr1-O15	2.820(2)	Sr2-O9	2.792(2)		
Sr1-O3	2.883(2)	Sr2-O6	2.862(2)		
Sr1-O4	2.904(2)	Sr2-O4	2.886(2)		
Sr1-O9	3.013(2)				
<Sr1-O>	<2.7415>	<Sr2-O>	<2.6779>		
B1-O15	1.461(3)	B6-O2	1.446(3)		
B1-O8	1.470(4)	B6-O21	1.475(3)		
B1-O4	1.480(3)	B6-O7	1.480(3)		
B1-O9	1.493(3)	B6-O10	1.491(3)		
B2-O4	1.355(3)	B7-O3	1.362(3)		
B2-O13	1.358(3)	B7-O7	1.364(3)		
B2-O5	1.385(3)	B7-O12	1.376(3)		
B3-O8	1.360(3)	B8-O6	1.354(3)		
B3-O17	1.364(3)	B8-O10	1.356(3)		
B3-OH16	1.376(3)	B8-O12	1.402(3)		
B4-O15	1.448(3)	B9-O1	1.446(4)		
B4-O17	1.461(3)	B9-O2	1.463(3)		
B4-O13	1.487(3)	B9-O3	1.482(3)		
B4-O11	1.496(3)	B9-O6	1.499(3)		
B5-O11	1.355(3)	B10-OH14	1.351(4)		
B5-O9	1.357(3)	B10-OH18	1.352(4)		
B5-O5	1.402(3)	B10-OH22	1.355(4)		
		B11-O1	1.361(3)		
		B11-OH19	1.363(3)		
		B11-O21	1.365(3)		
D-H	d(D-H)	d(H--A)	<DHA	d(D--A)	A
OH14-H14	0.887	1.914	141.09	2.664	O1
OH16-H16	0.721	2.013	165.2	2.717	O21
OH18-H18	0.866	1.781	174.16	2.644	OH16
OH19-H19	0.825	1.971	174.44	2.793	O8
OW20-H20a	0.739	2.104	151.93	2.778	OH22
OW20-H20b	0.884	1.806	163.14	2.664	OH19
OH22-H22	0.757	1.975	172.65	2.727	O17

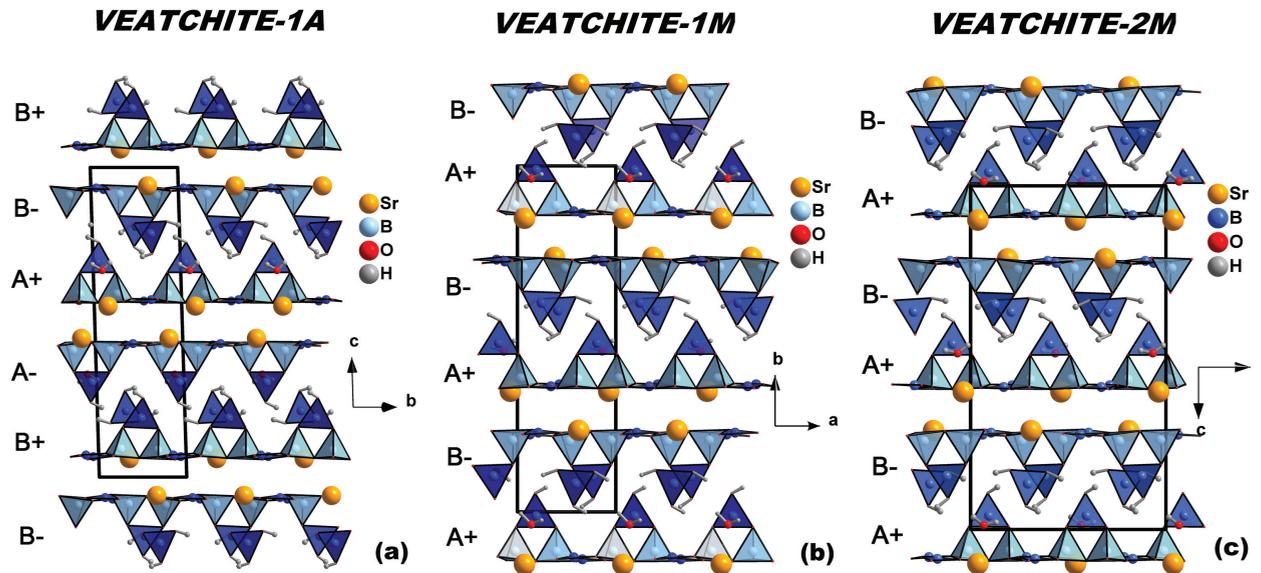


FIGURE 1. Veatchite polytypes showing the layered aspect perpendicular to the long axis. Boron in triangular coordination with oxygen is a darker shade than that of boron in tetrahedral coordination. The layer type, A or B, is indicated as is the directional aspect, + for up and – for down. Polytypes are (a) veatchite-1A, (b) veatchite-1M, and (c) veatchite-2M.

TABLE 3c. Selected bond lengths for veatchite-2M

Sr1-O1	2.528(1)	Sr2-OW22	2.351(2)		
Sr1-O10	2.542(1)	Sr2-O12	2.551(1)		
Sr1-O2	2.560(1)	Sr2-O7	2.554(1)		
Sr1-OH5	2.671(2)	Sr2-O8	2.558(1)		
Sr1-OH4	2.695(2)	Sr2-O21	2.649(1)		
Sr1-O21	2.727(1)	Sr2-O3	2.668(1)		
Sr1-O11	2.752(1)	Sr2-O20	2.698(1)		
Sr1-O20	2.797(1)	Sr2-O13	2.746(1)		
Sr1-O3	2.880(1)	Sr2-O11	2.880(1)		
Sr1-O9	2.881(1)	Sr2-O9	2.898(1)		
Sr1-O13	3.024(2)				
<Sr1-O>	<2.7328>	<Sr2-O>	<2.6552>		
B1-O3	1.357(2)	B7-OH19	1.363(3)		
B1-O1	1.360(2)	B7-O17	1.365(3)		
B1-O2	1.378(2)	B7-O18	1.370(3)		
B2-OH5	1.347(3)	B8-O21	1.458(2)		
B2-OH6	1.360(3)	B8-O18	1.457(2)		
B2-OH4	1.359(3)	B8-O11	1.487(2)		
		B8-O3	1.488(2)		
B3-O8	1.358(2)				
B3-O9	1.367(2)	B9-O20	1.462(3)		
B3-O7	1.385(2)	B9-O9	1.469(3)		
		B9-O14	1.473(3)		
B4-O10	1.357(2)	B9-O13	1.500(2)		
B4-O11	1.358(2)				
B4-O2	1.402(2)	B10-O21	1.447(2)		
		B10-O17	1.482(2)		
B5-O13	1.351(2)	B10-O1	1.486(2)		
B5-O12	1.361(2)	B10-O10	1.486(2)		
B5-O7	1.403(2)				
		B11-O20	1.446(2)		
B6-O14	1.364(3)	B11-O16	1.465(2)		
B6-O16	1.366(2)	B11-O8	1.491(2)		
B6-OH15	1.369(3)	B11-O12	1.504(2)		
D-H	d(D-H)	d(H--A)	<DHA	d(D--A)	A
OH4-H4	0.851	1.850	153.7	2.640	O18
OH5-H5	1.093	1.538	175.1	2.628	OH15
OH6-H6	0.898	1.875	156.9	2.724	O16
OH15-H15	0.663	2.084	162.5	2.724	O17
OH19-H19	0.798	2.039	157.3	2.792	O14
OW22-H22a	0.843	1.840	168.6	2.671	OH19
OW22-H22b	0.793	2.044	158.5	2.796	OH6

Veatchite-2M

Veatchite-2M is non-centrosymmetric. Similar to veatchite-1A, the layering is perpendicular to [001] (Fig. 1c), but the A and B layers alternating along [001]: i.e., ... A+B- A+B- A+B- ... are like those of veatchite-1M. The consistent directional orientation of each layer-type yields a polar structure. As in veatchite-1M, the two Sr atom sites are between A+B- pairs of layers. The relationship between the unit cells of the monoclinic polytypes veatchite-2M and veatchite-1M is: $a_{2M} = c_{1M}$; $b_{2M} = 2[a_{1M} \times \cos(\gamma - 90^\circ)]$; and $c_{2M} = b_{1M}$. The transformation $2M \rightarrow 1M$ is: $100/00\bar{1}/\sqrt{2}/2_0$.

DISCUSSION

Polytypic relationships in veatchite and a comparison with other layered borate structures

The polytypes of veatchite each have two types of layer. Layer A with FBB = $3\Delta 2\Box : <\Delta 2\Box > - <2\Delta\Box >$ and layer B with FBB = $3\Delta 2\Box, 1\Delta : <\Delta 2\Box > - <2\Delta\Box >, \Delta$. To compare the topologies of the veatchite polytypes and related to similar borate structures, a diagram is constructed ignoring oxygen atoms and using just the large, low-valence cations and the boron atoms. In this simplified topology diagram, the nodes represent boron in tetrahedral or triangular coordination with oxygen. These representations are

clearer, thus leading to a cleaner determination of the net topology.

Veatchite-1A polytype is quite distinct from either veatchite-1M or veatchite-2M polytypes in having double A and double B layers alternating vs. single A and B layers alternating. The differences between polytypes-1M and -2M are much more subtle. Although both monoclinic polytypes are non-centrosymmetric they belong to different crystal classes; veatchite-1M is in the sphenoidal class, 2, and veatchite-2M is in the domatic class, *m*. It is of note that the unique axis, **b**, changes in the two structures. One might expect that these major changes in crystallography would in fact bring about major changes in the crystal structure, but the difference between polytypes 1M and 2M is due to a slight shift between layers.

In layered borate structures, there are two species with only A-type layers, biringuccite and nasinite (Fig. 2). In biringuccite, the layers have a polar component and they alter in stacking (Fig. 2a), ...A+A- A+A- A+A-..., while in nasinite there is no polar

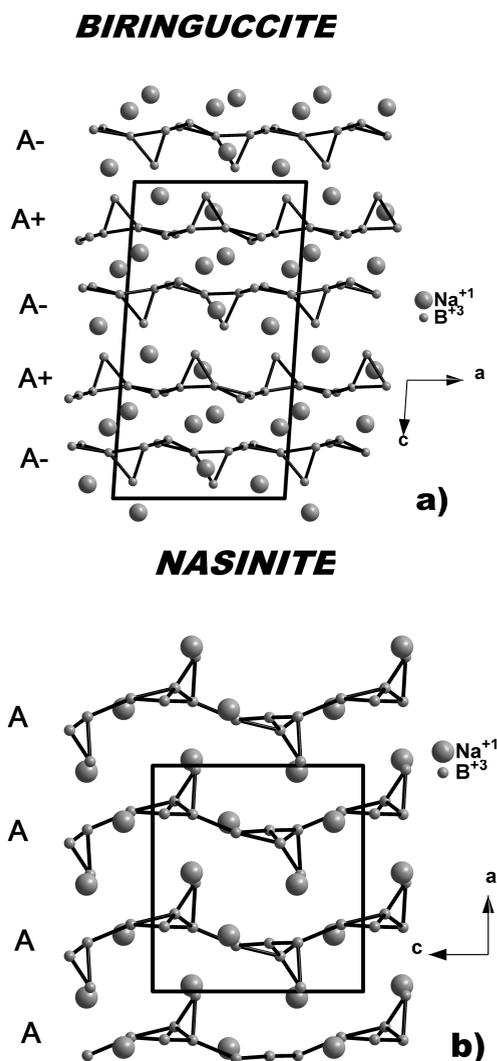


FIGURE 2. Net topology diagram for (a) biringuccite and (b) nasinite. The layer type, A, is indicated as is the directional aspect if there is one, + for up and - for down.

component to the layers as the layer is twisted (Fig. 2b). Gowerite is the only borate species that is entirely built with **B**-type layers (Fig. 3). Like nasinite, there is no polar component to the layer as it is twisted giving equal numbers of triangular coordination up and down. The borate layer arrangement in volkovskite (Fig. 4a) is isostructural with that observed in veatchite-1A (Fig. 4b) (Grice et al. 1999) but, unlike veatchite-1A, volkovskite is non-centrosymmetric due to the asymmetric arrangement of Ca atoms.

Occurrences of veatchite polytypes and their origin

Polytypes of veatchite do not coexist at a single deposit and are therefore expected to be unique to a particular environment.

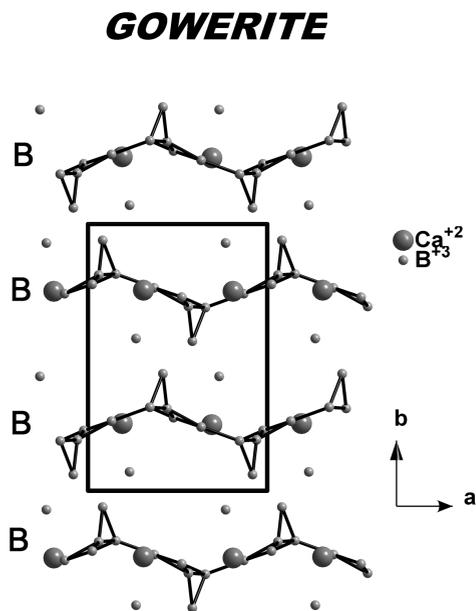


FIGURE 3. Net topology diagram for gowerite. The layer type, **B**, is indicated but there is no directional aspect.

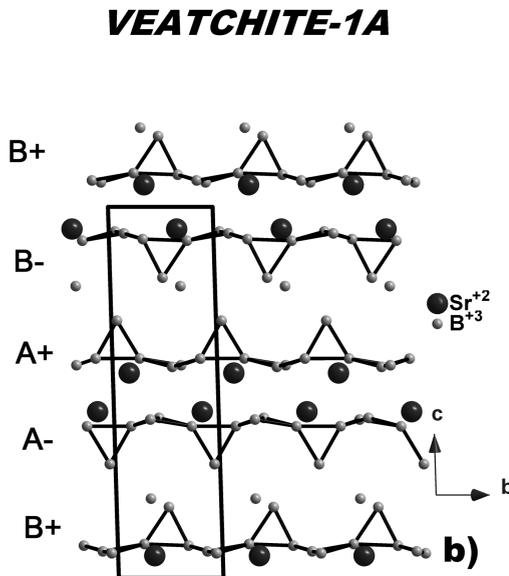
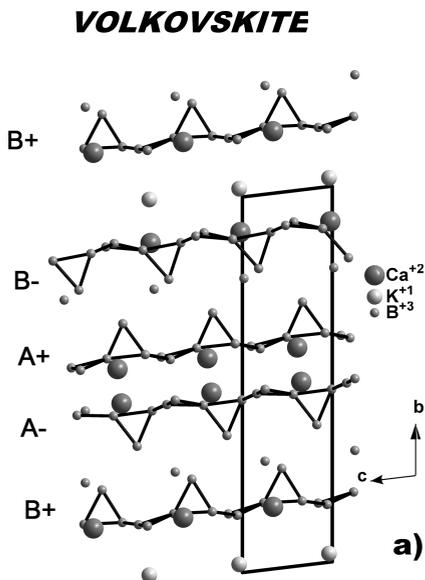


FIGURE 4. Net topology diagram for (a) volkovskite and (b) veatchite-1A. The layer type, **A** or **B**, is indicated as is the directional aspect, + for up and - for down.

To date there is only one occurrence of veatchite-1A: Emet, Turkey. Here the borate minerals are intercalated with lacustrine playa lake sediments (Helvacı and Alfonso 2000). Veatchite-1A partially replaced colemanite by low-temperature, diagenetic alteration. Veatchite-1M occurs at Reyershausen, Germany, and Yorkshire, England (Garrett 1998). Both of these are marine potash deposits and they have undergone high-temperature metamorphism. Veatchite-2M occurs in sediment buried playa lakes at Lang, Four Corners, and Billie, California. It also occurs in the marine evaporates of Inder, Kazakhstan, Russia, and Sussex, New Brunswick, Canada. All five of these deposits have been subjected to moderate temperatures and folded under pressure (Garrett 1998). From these observations, it appears temperature and pressure control the occurrence of each polytype, but precise parameters are not known.

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