# From structure topology to chemical composition. VI. Titanium silicates: the crystal structure and crystal chemistry of bornemanite, a group III Ti-disilicate mineral

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# ABSTRACT

The crystal structure of bornemanite, ideally Na<sub>6</sub> BaTi<sub>2</sub>Nb(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(PO<sub>4</sub>)O<sub>2</sub>(OH)F, a = 5.4587(3), b = 7.1421(5), c = 24.528(2) Å,  $\alpha = 96.790(1)$ ,  $\beta = 96.927(1)$ ,  $\gamma = 90.326(1)^{\circ}$ , V = 942.4(2) Å<sup>3</sup>, space group  $P\bar{1}$ , Z = 2,  $D_{calc.} = 3.342$  g cm<sup>-3</sup>, from the Lovozero alkaline massif, Kola Peninsula, Russia, has been solved and refined to  $R_1 = 6.36\%$  on the basis of 4414 unique reflections ( $F_o > 4\sigma F$ ). Electron microprobe analysis yielded the empirical formula (Na<sub>6.07</sub>Mn<sup>0,+2</sup><sub>0.23</sub>Ca<sub>0.06</sub> $\square_{0.64}$ )<sub> $\Sigma$ 7.00</sub> (Ba<sub>0.73</sub>K<sub>0.13</sub>Sr<sub>0.06</sub> $\square_{0.08}$ )<sub> $\Sigma$ 1.00</sub>(Ti<sub>2.05</sub>Nb<sub>0.80</sub>Zr<sub>0.02</sub>Ta<sup>5,+</sup><sub>0.05</sub>Fa<sup>3,+</sup><sub>0.03</sub>Al<sub>0.02</sub>Mn<sup>0,06</sup>Mg<sub>0.01</sub>)<sub> $\Sigma$ 3.00</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>0.97</sub>O<sub>4</sub>)O<sub>2</sub> [F<sub>1.27</sub>(OH)<sub>0.74</sub>]<sub> $\Sigma$ 2.01</sub>. The crystal structure of bornemanite is a combination of a TS (titanium silicate) block and an I (intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The TS block exhibits linkage and stereochemistry typical for Group III (Ti = 3 a.p.f.u.) of Ti-disilicate minerals: two H sheets connect to the O sheet such that two (Si<sub>2</sub>O<sub>7</sub>) groups link to the *trans* edges of a Ti octahedron of the O sheet. The O sheet cations give Na<sub>3</sub>Ti (4 a.p.f.u.). The TS block has two different H sheets, H<sub>1</sub> and H<sub>2</sub>, where (Si<sub>2</sub>O<sub>7</sub>) groups link to <sup>[5]</sup>Ti and <sup>[6]</sup>Nb polyhedra, and there are two peripheral sites which are occupied by Ba and Na, respectively. There are two I blocks: the I<sub>1</sub> block is a layer of Ba atoms; the I<sub>2</sub> block consists of Na polyhedra and (PO<sub>4</sub>) tetrahedra.

**Keywords:** bornemanite, Ti-disilicate minerals, crystal structure, EMP analysis, chemical formula, TS block, Group III.

#### Introduction

BORNEMANITE was described as a new mineral by Men'shikov *et al.* (1975). It was found in a natrolite zone of the Yubileinaya pegmatite, Mt. Karnasurt, Lovosero alkaline massif, Kola peninsula, Russia as yellow 10 mm  $\times$  8 mm  $\times$  0.2 mm plates associated with lomonosovite and natrolite, and containing microscopic inclusions of aegirine and lomonosovite. Based on precession photographs, the authors reported orthorhombic symmetry, a = 5.48(5), b = 7.10(5), c =

\* E-mail: camara@crystal.unipv.it DOI: 10.1180/minmag.2007.071.6.593 48.2(1) Å, V = 1875.4 Å<sup>3</sup>, and possible space groups *Imma* and *Ima2*. Men'shikov *et al.* (1975) stated that elongation and flattening of bornemanite crystals are parallel to [100] and perpendicular to [001], respectively. They gave a chemical analysis of bornemanite (quoted in Table 1) and the ideal formula Na<sub>7</sub>BaTi<sub>2</sub>NbPSi<sub>4</sub>O<sub>21</sub>F, Z = 4,  $D_{calc} =$ 3.49 g cm<sup>-3</sup>,  $D_{meas.} = 3.47-3.50$  g cm<sup>-3</sup>. Men'shikov *et al.* (1975) emphasized the chemical and structural similarity of bornemanite with the seidozerite and lomonosovite groups of minerals, especially with lomonosovite, Na<sub>10</sub>Ti<sub>4</sub>(Si<sub>2</sub>O<sub>7)2</sub> (PO<sub>4</sub>)<sub>2</sub>O<sub>4</sub> (Belov *et al.*, 1977), murmanite, Na<sub>4</sub>Ti<sub>4</sub>(Si<sub>2</sub>O<sub>7)2</sub>O<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub> (Khalilov, 1989), epistolite, Na<sub>4</sub>TiNb<sub>2</sub>(Si<sub>2</sub>O<sub>7)2</sub>O<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> (Sokolova

|                                | Men'shikov e | t al. (1975)* | Ferraris et al. |        | — This work** -       |      |
|--------------------------------|--------------|---------------|-----------------|--------|-----------------------|------|
|                                | (1)          | (2)           | (2001)**        |        |                       |      |
| $P_2O_5$                       | 6.57         | 6.80          | 6.44            | 7.22   | Si                    | 4.07 |
| $Nb_2O_5$                      | 9.22         | 8.86          | 10.13           | 11.18  | Р                     | 0.97 |
| Ta <sub>2</sub> O <sub>5</sub> | n.d.         | 0.66          | n.a.            | 0.14   |                       |      |
| TiO <sub>2</sub>               | 18.72        | 18.00         | 19.94           | 17.29  | Na                    | 6.07 |
| ZrO <sub>2</sub>               | 0.20         | 0.25          | 0.06            | 0.20   | $Mn^{2+}$             | 0.23 |
| SiO <sub>2</sub>               | 23.96        | 25.00         | 26.42           | 25.76  | Ca                    | 0.06 |
| $Al_2O_3$                      | 0.55         | 0.00          | 0.15            | 0.12   | ∑~Na                  | 6.36 |
| Fe <sub>2</sub> O <sub>3</sub> | n.d.         | 0.30          | n.a.            | 0.24   |                       |      |
| FeO                            | 0.17         | n.d.          | 0.22            | n.a.   | Ba                    | 0.73 |
| MnO                            | 2.97         | 2.48          | 2.37            | 2.17   | K                     | 0.13 |
| MgO                            | 0.04         | 0.06          | 0.02            | 0.03   | Sr                    | 0.06 |
| BaO                            | 12.05        | 13.00         | 12.02           | 11.76  | $\Sigma A^{P}(1)$     | 0.92 |
| SrO                            | 0.70         | 0.68          | 0.72            | 0.63   |                       |      |
| CaO                            | 0.33         | 0.77          | 0.26            | 0.33   | Ti                    | 2.05 |
| Na <sub>2</sub> O              | 19.62        | 20.00         | 18.64           | 19.84  | Nb                    | 0.80 |
| K <sub>2</sub> O               | 0.65         | 0.67          | 0.61            | 0.62   | Zr                    | 0.02 |
| Li <sub>2</sub> O              | 0.10         | n.d.          | n.a.            | n.d.   | Та                    | 0.01 |
| Rb <sub>2</sub> O              | 0.0025       | n.d.          | n.a.            | n.d.   | Fe <sup>3+</sup>      | 0.03 |
| Cs <sub>2</sub> O              | 0.002        | n.d.          | n.a.            | n.d.   | Al                    | 0.02 |
| $H_2O^+$                       | 2.44         | n.a.          | n.a.            | n.a.   | Mn <sup>2+</sup>      | 0.06 |
| $H_2O^-$                       | 0.30         | 0.70          | 0.7***          | 0.7*** | Mg                    | 0.01 |
| F                              | 1.52         | 1.64          | 1.29            | 2.54   | $\Sigma \sim (Ti+Nb)$ | 3.00 |
| Cl                             | n.a.         | n.a.          | 0.03            | n.a.   |                       |      |
| $-O=F_2$                       | 0.64         | 0.69          | 0.54            | 1.07   | F                     | 1.27 |
| $-O=Cl_2$                      |              |               | 0.01            |        | OH                    | 0.74 |
| Total                          | 99.47        | 99.18         | 99.47           | 99.70  | $\Sigma X_A^O$        | 2.01 |

TABLE 1. Chemical composition (wt.%) and unit formula (a.p.f.u.) for bornemanite.

\* Wet chemistry + flame photometry for alkaline and alkali-earth elements,  $D_{\text{meas}} = 3.47$  (sample 1) and 3.50 g cm<sup>-3</sup> (sample 2).

\*\* Electron microprobe analyses.

\*\*\* Taken from analysis (sample 2) of Men'shikov et al. (1975).

n.d.: not detected

n.a.: not analysed

and Hawthorne, 2004), vuonnemite, Na<sub>11</sub>Nb<sub>2</sub>Ti(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>3</sub>F (Ercit *et al.*, 1998), and seidozerite, Na<sub>4</sub>MnZr<sub>2</sub>Ti(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>F<sub>2</sub> (Christiansen et al., 2003). In this study, we quote the latest structure work. However, Men'shikov et al. (1975) noted that the final formula of bornemanite could be written only after structure investigation. Pekov (2000) reported bornemanite from two other localities in the Lovozero massif, specifically the Shkatulka and Sirenevaya veins. It was difficult to find crystals of bornemanite suitable for crystal-structure work and Ferraris et al. (2001) proposed a model for the crystal structure of bornemanite using selected-area electron diffraction (SAED), powder X-ray diffraction (XRD) data and a polysomatic model-building approach. They examined a bornemanite sample (NH-10) from the type locality described by Men'shikov et al. (1975) from the collection of the Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM, Moscow, Russia). They reported the symmetry of bornemanite as monoclinic, space group I11b, a = 5.498(4), b = 7.120(6), c = 47.95(4) Å,  $\gamma = 88.1(1)^{\circ}, V =$ 1876  $Å^3$ , and gave the crystal-chemical formula,  $(Na_{2,83}Ba_{0,71}K_{0,12}Sr_{0,06}Ca_{0,04}Mg_{0,01})_{\Sigma_{3,77}}$  $\{(Na_{2.64}Ti_{1.00}Mn_{0.30}Fe_{0.03}Al_{0.03})_{\Sigma 4.00}[(Ti_{1.27})_{\Sigma 4.00}]$  $Nb_{0.69}Zr_{0.01})_{\Sigma1.97}O_{2}Si_{4}O_{14}](O_{0.38}(OH)_{0.71}F_{0.62}$  $Cl_{0.01}$ )<sub> $\Sigma 1.72$ </sub>}(PO<sub>4</sub>)<sub>0.82</sub>, Z = 4, D<sub>calc</sub> = 3.203 g cm<sup>-3</sup>. Note that the calculated density is significantly smaller than that of Men'shikov et al. (1975). Ferraris et al. (2001) approximated the chemical

composition of bornemanite as  $BaNa_{2.5}Mn_{0.5}$  {Na\_3Ti[TiNbO\_2Si\_4O\_{14}](O\_{0.5}OH\_{0.75}F\_{0.75})}PO\_4 and proposed a structure model of bornemanite based on seidozerite and lomonosovite modules.

Sokolova (2006) questioned the validity of this model of the bornemanite structure. She considered the structural hierarchy and stereochemistry of 24 titanium disilicate minerals containing the TS (titanium-silicate) block, built up by a trioctahedral central (O) sheet and two adjacent heteropolyhedral (H) sheets containing different polyhedra including (Si<sub>2</sub>O<sub>7</sub>) groups. She established the relation between structure topology and chemical composition for those minerals and divided them into four groups, characterized by different topology and stereochemistry of the TS block. Each group of structures has a different linkage of H and O sheets in the TS block and a different arrangement of Ti (= Ti + Nb) polyhedra. In a structure, the TS block can alternate with another block, an intermediate (I) block, so called as it is intercalated between two TS blocks. In Groups I, II, III and IV, Ti equals 1, 2, 3 and 4 a.p.f.u. (atoms per formula unit), respectively. Sokolova (2006) pointed out that in bornemanite, Ti equals 3 a.p.f.u. (see ideal formula of bornemanite above, where Ti + Nb equals 3 a.p.f.u.). Hence, bornemanite belongs to Group III and the TS block has to exhibit linkage 1 and the stereochemistry of Group III: Ti occurs in both the H and O sheets, and two  $(Si_2O_7)$ groups link to trans edges of a Ti octahedron in the O sheet. In the bornemanite model of Ferraris et al. (2001), the TS block has linkage 3, as in Group IV where Ti equals 4 a.p.f.u. Sokolova (2006) considered the proposed model of the crystal structure of bornemanite extremely unlikely, and suggested that this issue should be reexamined.

This work is a continuation of our interest in Ti disilicates in which we have recently revised the crystal structure and crystal chemistry of delindeite (Sokolova and Cámara, 2007), barytolamprophyllite (Sokolova and Cámara, 2008), nacareniobsite-(Ce) (Sokolova and Hawthorne, 2008*a*) and nabalamprophyllite (Sokolova and Hawthorne, 2008*b*). Here, we present results of a direct determination of the crystal structure of bornemanite on holotype sample #75318 (from the Yubileinaya vein, Karnasurt Mt., Lovosero alkaline massif, Kola Peninsula, Russia), obtained from the Fersman Mineralogical Museum, Moscow, Russia and discuss its crystal chemistry and relation to the other TS-block minerals.

### **Experimental details**

### Sample description

The single crystal of bornemanite used in this work is a transparent yellow plate with dimensions 0.165 mm  $\times$  0.065 mm  $\times$  0.010 mm. The crystal is of good quality and shows no evidence of elongated lamellae as described by Men'shikov *et al.* (1975) and Ferraris *et al.* (2001). However, some other crystals did show the presence of several darker coloured lamellae  $\sim$ 5 µm wide.

### Electron microprobe (EMP) analysis

A fragment of the bornemanite crystal previously used for the structure determination was analysed with a Cameca SX-100 EMP operating in wavelength-dispersive spectroscopy (WDS) mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 µm and count times on peak and background of 20 and 30 s for major and minor elements (<1 wt. %), respectively. The following standards and crystals were used for K or L X-ray lines: F: topaz; Na: jadeite; Nb, Ba: Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub>; Si, Ca: diopside; Fe: fayalite; Mn: spessartine; K: orthoclase; Ti: titanite; Zn: zircon; Mg: forsterite; Sr: SrTiO<sub>3</sub>; Al: andalusite; P: apatite; Zr: ZrO2; Ta: MnTa2O6. Data were reduced using the PAP procedure of Pouchou and Pichoir (1985). The chemical composition of bornemanite is given in Table 1 and is the mean of seven determinations. The empirical formula is  $(Na_{6.07}Mn_{0.23}^{2+}Ca_{0.06}\Box_{0.64})_{\Sigma7.00}(Ba_{0.73}K_{0.13})$  $Sr_{0.06} \square_{0.08})_{\Sigma 1.00} (Ti_{2.05}Nb_{0.80}Zr_{0.02}Ta_{0.01}^{5+}Fe_{0.03}^{3+}$  $Al_{0.02}Mn_{0.06}^{2+}Mg_{0.01})_{\Sigma 3.00}(Si_2O_7)_2(P_{0.97}O_4)O_2$  $[F_{1,27}(OH)_{0,74}]_{\Sigma 2.01}$ , Z = 2, calculated on the basis of 22 (O + F) a.p.f.u., and the ideal formula is Na<sub>6</sub> BaTi<sub>2</sub>Nb(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(PO<sub>4</sub>)O<sub>2</sub>(OH)F, which is in good agreement with the structure data.

### Data collection and crystal structure refinement

A single crystal of bornemanite was mounted on a Bruker AXS SMART APEX diffractometer with a CCD detector and Mo- $K\alpha$  radiation. The reflection intensities were collected to 55.99°2 $\theta$  using 30 s per 0.2° frame, and an empirical absorption correction (SADABS; Sheldrick, 1998) was applied. The refined unit-cell parameters for the triclinic cell (Table 2) were obtained from 8055 reflections with  $I > 10\sigma$ . The crystal structure of bornemanite was solved by direct methods with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick, 1997) and refined in space group  $P\overline{1}$  to

| 5.4587(3)                                      |
|--|
| 7.1421(5)                                      |
| 24,528(2)                                      |
| 96.790(1)                                      |
| 96.927(1)                                      |
| 90.326(1)                                      |
| 942.4(2)                                       |
| PĪ   |
| 2  |
| 3.92   |
| 902  |
| 3.342  |
| $0.165 \times 0.065 \times 0.010$              |
| Mo-Ka/graphite                                 |
| 56.00*(55.99)                                  |
| 2.82   |
| 14405  |
| 5457   |
| 4540   |
| 4414   |
| Full-matrix least squares on $F^2$ ,           |
| fixed weights proportional to $1/\sigma F_o^2$ |
| 1.323  |
| D (2)  |
| $R_1 = 6.36$                                   |
| $R_1 = 6.53$                                   |
| $wR^2 = 13.10$                                 |
| GoF = 1.323                                    |
|  |

TABLE 2. Miscellaneous refinement data for bornemanite.

\* Used for the structure refinement

 $R_1 = 6.36\%$  and a GooF of 1.32. As there were hardly any observed reflections at large  $2\theta$  values, the structure refinement was based on 4414 intensities of unique observed reflections ( $F_{0}$  $>4\sigma F$ ) with  $-7 \leq h \leq 7, -9 \leq k \leq 9, -32$  $\leq l \leq 32, 2\theta \leq 56^{\circ}$ . Scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography (1992). The R indices are given in Table 2, and expressed as percentages. Site occupancies for the  $M^{\rm H}(1,2)$  and  $M^{\rm O}(1)$  sites were refined with the scattering curves of Ti, Nb;  $M^{O}(2-3)$  and  $A^{P}(2)$  sites with the scattering curve of Na;  $M^{O}(4)$  site with the scattering curve of Ca; and  $A^{P}(1)$  site with the scattering curves of Ba. In the final stages of the refinement, four peaks with magnitudes from 3 to 2  $e^{-}$ Å<sup>-3</sup> were found in the difference-Fourier map and they were labelled  $A^{P}(1A)$ ,  $M^{H}(2A)$ ,  $M^{H}(2B)$  and  $M^{H}(2C)$  sites. Refined occupancies of these subsidiary sites are 1% for the  $A^{P}(1A)$  site and 1.2–2% for the  $M^{\rm H}(2A), M^{\rm H}(2B)$  and  $M^{\rm H}(2C)$  sites.

Details of the data collection and structure refinement are given in Table 2, final atom and subsidiary-atom parameters are given in Table 3, selected interatomic distances and angles in Table 4, refined site-scattering values and assigned populations for selected sites in Table 5, and bond-valence values in Table 6. A list of observed and calculated structure factors has been deposited with the Principal Editor of the *Mineralogical Magazine* and is available from w w . minersoc.org/pages/e\_journals/ dep\_mat.html.

#### Structure description

#### Cation sites

#### Site nomenclature

The crystal structure of bornemanite can be described as a combination of a TS block and an (intermediate) I block. The TS (titanium silicate) block consists of HOH sheets (H-heteropolyhedral,

| $U_{\rm eq}$ | $\begin{array}{c} 0.0193(4) \\ 0.0186(7) \\ 0.0188(8) \end{array}$      | 0.0090(8)          | 0.0064(5)                                | 0.0068(4)  | 0.0081(4)  | 0.0060(4)  | 0.0082(4)  | 0.0074(2)           | 0.0214(8)<br>0.0738(8)      | 0.0262(9)   | 0.0180(7)   | 0.0124(4)  | 0.0137(12) | 0.0178(3)  | 0.0106(11) | 0.0100(11) | 0.0105010                | 0.0090(10)  | 0.0160(12) | 0.0095(10) | 0.0105(11) | 0.0198(13) | 0.0092(10)  | 0.0159(12) | 0.0106(11) | 0.0161(12) | 0.0136(11) | 0.0181(13) | 0.0220(14) | 0.0223(14) | 0.0151(12) | 0.0144(12)          | 0.0080(10)          |                 |                  |                   |
|--------------|---|--------------------|--|------------|------------|------------|------------|---------------------|-----------------------------|-------------|-------------|------------|------------|------------|------------|------------|--------------------------|-------------|------------|------------|------------|------------|-------------|------------|------------|------------|------------|------------|------------|------------|------------|---------------------|---------------------|-----------------|------------------|-------------------|
| $U_{12}$     | $\begin{array}{c} 0.0016(6) \\ -0.0034(13) \\ -0.0044(13) \end{array}$  | -0.0008(8)         | -0.0001(4)<br>-0.0003(3)                 | 0.0004(7)  | 0.0001(7)  | -0.0005(7) | -0.0001(7) | -0.00002(17)        | -0.0036(15)<br>0 0009(15)   | -0.0031(16) | -0.0002(14) | 0.0001(8)  | -0.000(2)  | 0.007(2)   | 0.001(2)   | -0.002(2)  | -0.002(2)                | -0.0019(19) | -0.006(2)  | 0.0008(19) | -0.002(2)  | -0.007(2)  | -0.0006(19) | 0.005(2)   | 0.003(2)   | 0.001(2)   | 0.000(2)   | -0.003(2)  | 0.001(3)   | 0.003(3)   | 0.003(2)   | -0.001(2)           | -0.004(2)           |                 |                  |                   |
| $U_{13}$     | $\begin{array}{c} 0.0228(7) \\ -0.0029(14) \\ -0.0032(14) \end{array}$  | -0.0013(9)         | 0.0013(3)                                | 0.0027(7)  | 0.0024(8)  | 0.0010(7)  | 0.0019(8)  | 0.00148(18)         | 0.0033(14)<br>0.0037(15)    | 0.0025(17)  | 0.0088(14)  | 0.0026(8)  | 0.003(2)   | 0.010(2)   | 0.001(2)   | -0.001(2)  | (0.001(2))               | 0.003(2)    | 0.004(2)   | 0.002(2)   | 0.000(2)   | 0.006(2)   | 0.004(2)    | 0.003(2)   | 0.002(2)   | 0.002(2)   | 0.003(2)   | 0.002(3)   | 0.002(3)   | 0.009(3)   | 0.001(2)   | -0.002(2)           | 0.0010(19)          |                 |                  |                   |
| $U_{23}$     | $\begin{array}{c} 0.0006(6) \\ 0.0040(14) \\ 0.0090(14) \end{array}$    | 0.0003(9)          | -0.0004(3)                               | 0.0000(7)  | 0.0012(7)  | -0.0002(7) | -0.0007(7) | 0.00023(18)         | 0.0019(15)                  | -0.0023(15) | 0.0053(13)  | 0.0019(8)  | 0.002(2)   | 0.003(2)   | -0.002(2)  | 0.003(2)   | -0.001(2)                | 0.001(2)    | 0.003(2)   | 0.001(2)   | 0.000(2)   | -0.003(3)  | -0.000(2)   | 0.003(2)   | 0.003(2)   | 0.002(2)   | 0.000(2)   | -0.002(2)  | 0.005(3)   | 0.001(2)   | 0.001(2)   | 0.001(2)            | -0.0002(19)         |                 |                  |                   |
| $U_{33}$     | $\begin{array}{c} 0.0220(8)\\ 0.0242(19)\\ 0.028(2)\end{array}$         | 0.0143(14)         | 0.0071(13)                               | 0.0125(10) | 0.0122(10) | 0.0095(10) | 0.0111(10) | 0.0121(4)           | 0.0191(18)<br>0.025(2)      | 0.025(2)    | 0.0150(17)  | 0.0148(10) | 0.016(3)   | 0.026(3)   | 0.013(3)   | 0.014(3)   | 0.010(0)                 | 0.016(3)    | 0.020(3)   | 0.014(3)   | 0.012(3)   | 0.021(3)   | 0.016(3)    | 0.020(3)   | 0.015(3)   | 0.012(3)   | 0.018(3)   | 0.020(3)   | 0.031(4)   | 0.020(3)   | 0.019(3)   | 0.016(3)            | 0.004(2)            |                 |                  |                   |
| $U_{22}$     | 0.0028(6)<br>0.0175(17)<br>0.0157(17)                                   | 0.0056(12)         | 0.0052(4)                                | 0.0025(9)  | 0.0044(9)  | 0.0026(9)  | 0.0046(9)  | 0.0039(3)           | 0.0233(19)<br>0.0234(19)    | 0.0153(18)  | 0.0178(17)  | 0.0093(9)  | 0.005(2)   | 0.015(3)   | 0.004(2)   | 0.009(2)   | (7)00000                 | 0.006(2)    | 0.015(3)   | 0.009(2)   | 0.007(2)   | 0.020(3)   | 0.006(2)    | 0.015(3)   | 0.003(2)   | 0.023(3)   | 0.013(3)   | 0.007(3)   | 0.020(3)   | 0.014(3)   | 0.012(3)   | 0.012(3)            | 0.009(2)            |                 |                  |                   |
| $U_{11}$     | $\begin{array}{c} 0.0377(10)\\ 0.0131(16)\\ 0.0125(16)\end{array}$      | 0.0062(12)         | 0.0066(4)                                | 0.0056(9)  | 0.0081(9)  | 0.0057(9)  | 0.0087(9)  | 0.0060(3)           | 0.0218(18)                  | 0.037(2)    | 0.0235(18)  | 0.0135(10) | 0.021(3)   | 0.015(3)   | 0.014(3)   | 0.007(2)   | (5)600.0                 | 0.006(2)    | 0.013(3)   | 0.006(2)   | 0.012(3)   | 0.018(3)   | 0.007(2)    | 0.013(3)   | 0.014(3)   | 0.013(3)   | 0.010(3)   | 0.026(3)   | 0.015(3)   | 0.034(4)   | 0.014(3)   | 0.014(3)            | 0.010(3)            | 0.02000         | 0.02000          | 0.02000           |
| ы            | $\begin{array}{c} 0.29972(7) \\ 0.29512(15) \\ 0.29439(16) \end{array}$ | 0.29477(10)        | (c)ccc110<br>(0.16855(6)                 | 0.41039(9) | 0.18026(9) | 0.41040(8) | 0.18720(9) | 0.47216(2)          | 0.15697(15)                 | 0.04799(17) | 0.08004(14) | 0.03953(9) | 0.1575(2)  | 0.1673(3)  | 0.3439(2)  | 0.4365(2)  | (2)074700(2)             | 0.4371(2)   | 0.1526(3)  | 0.4354(2)  | 0.2467(2)  | 0.1625(3)  | 0.4356(2)   | 0.1515(3)  | 0.2529(2)  | 0.2405(2)  | 0.3462(3)  | 0.0644(3)  | 0.0335(3)  | 0.9822(3)  | 0.0768(3)  | 0.3444(3)           | 0.2518(2)           | 0.438(2)        | 0.1687(16)       | 0.138(5)          |
| у            | 0.1691(2)<br>0.6635(5)<br>0.9191(5)                                     | 0.4008(3)          | 0./14/9(17)<br>0.60220(11)               | 0.4298(3)  | 0.3213(3)  | 0.9976(3)  | 0.8990(3)  | 0.23880(7)          | 0.0813(5)<br>0.0166(6)      | 0.2903(5)   | 0.5540(5)   | 0.7653(3)  | 0.0932(8)  | 0.8040(9)  | 0.3927(7)  | 0.5371(8)  | 0.9109(6)                | 0.2247(7)   | 0.4093(9)  | 0.5354(8)  | 0.3467(8)  | 0.7733(9)  | 0.9119(7)   | 0.3893(9)  | 0.9448(7)  | 0.6128(9)  | 0.6827(8)  | 0.9636(8)  | 0.7607(9)  | 0.7161(9)  | 0.6111(8)  | 0.1965(8)           | 0.1477(7)           | 0.241(6)        | 0.441(5)         | 0.600(10)         |
| x            | 0.2987(3)<br>0.2825(6)<br>0.7924(6)                                     | 0.7843(4)          | 0.7044(2)<br>0.86010(15)                 | 0.2020(4)  | 0.3572(4)  | 0.2032(4)  | 0.3764(4)  | 0.73357(10)         | 0.8553(7)<br>0.2401(7)      | 0.7923(8)   | 0.2694(7)   | 0.7230(4)  | 0.3549(11) | 0.6205(11) | 0.1636(10) | 0.4609(10) | 0.4611(10)<br>0.1668(10) | 0.2.155(10) | 0.5816(11) | 0.9679(10) | 0.3984(10) | 0.1367(12) | 0.9692(10)  | 0.0950(11) | 0.4020(10) | 0.9066(11) | 0.6677(10) | 0.8229(12) | 0.4413(12) | 0.8101(13) | 0.8175(11) | 0.5966(11)          | 0.9671(10)          | 0.725(7)        | 0.870(7)         | 0.835(14)         |
| Atom         | M <sup>0</sup> (1)<br>M <sup>0</sup> (2)<br>M <sup>0</sup> (3)          | M <sup>O</sup> (4) | M <sup>H</sup> (1)<br>M <sup>H</sup> (2) | Si(1)      | Si(2)      | Si(3)      | Si(4)      | $\mathbf{A}^{L}(1)$ | A <sup>2</sup> (2)<br>Na(1) | Na(2)       | Na(3)       | Р          | 0(1)       | 0(2)       | 0(3)       | 0(4)       | (c)0                     |             | 0(8)       | 0(6)       | O(10)      | 0(11)      | O(12)       | O(13)      | O(14)      | 0(15)      | 0(16)      | 0(17)      | O(18)      | 0(19)      | O(20)      | $X^{O}_{\Delta}(1)$ | $X^{O}_{\Delta}(2)$ | $A_{n}^{P}(1A)$ | $M_{ii}^{H}(2A)$ | $M_{II}^{II}(2B)$ |

 $T^{ABLE}$  3. Atom coordinates and displacement parameters  $({\rm \AA}^2)$  for bornemanite.

 $X^O_A(1)$  +  $X^O_A(2)$  equals 1.27  $\rm F$  + 0.73 OH (a.p.f.u.)

CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY OF BORNEMANITE

| TABLE 4. Selecte | 1 interatomic | distances ( | (A) and | l angles | (°) for | bornemanite. |
|------------------|---------------|-------------|---------|----------|---------|--------------|
|                  |               |             |         | <u> </u> | · · ·   |              |

| $\begin{array}{l} M^{O}(1){-}X^{O}_{A}(1) \\ M^{O}(1){-}O(14)a \\ M^{O}(1){-}O(6)a \\ M^{O}(1){-}O(3) \\ M^{O}(1){-}X^{O}_{A}(2)b \\ M^{O}(1){-}O(10) \\ {<}M^{O}(1){-}\phi{>} \end{array}$ | $\begin{array}{c} 1.843(6) \\ 1.983(6) \\ 2.003(6) \\ 2.016(6) \\ 2.031(6) \\ \underline{2.038(6)} \\ 1.986 \end{array}$  | $\begin{array}{l} M^{O}(2) {-} O(16) \\ M^{O}(2) {-} O(15) b \\ M^{O}(2) {-} O(14) \\ M^{O}(2) {-} O(3) \\ M^{O}(2) {-} O(10) \\ M^{O}(2) {-} O(6) \\ {<} M^{O}(2) {-} O{>} \end{array}$   | 2.308(7)<br>2.313(7)<br>2.484(6)<br>2.513(7)<br>2.548(7)<br><u>2.577(7)</u><br>2.457   | $\begin{array}{l} M^{O}(3){-}O(14) \\ M^{O}(3){-}O(6)c \\ M^{O}(3){-}X^{O}_{A}(2)d \\ M^{O}(3){-}O(16) \\ M^{O}(3){-}X^{O}_{A}(1)d \\ M^{O}(3){-}O(15) \\ {<}M^{O}(3){-}\phi{>} \end{array}$   | $\begin{array}{c} 2.266(7)\\ 2.270(7)\\ 2.301(6)\\ 2.372(7)\\ 2.517(7)\\ \underline{2.540(7)}\\ 2.378\end{array}$                         |
|---|---|--|--|--|---|
| $\begin{array}{l} M^{O}(4) - O(3)c \\ M^{O}(4) - O(15) \\ M^{O}(4) - X^{O}_{A}(2) \\ M^{O}(4) - O(10) \\ M^{O}(4) - X^{O}_{A}(1) \\ M^{O}(4) - O(16) \\ < M^{O}(4) - \phi > \end{array}$    | $\begin{array}{c} 2.271(6) \\ 2.278(7) \\ 2.280(6) \\ 2.294(6) \\ 2.315(6) \\ \underline{2.379(6)} \\ \underline{2.303} \end{array}$  | $\begin{array}{l} M^{H}(1){-}O(16) \\ M^{H}(1){-}O(4) \\ M^{H}(1){-}O(9) \\ M^{H}(1){-}O(12) \\ M^{H}(1){-}O(5) \\ {<}M^{H}(1){-}O{>} \end{array}$   | 1.678(6)<br>1.985(6)<br>1.987(6)<br>1.989(6)<br><u>1.996(6)</u><br>1.927   | $\begin{array}{l} M^{\rm H}(2){-}O(15) \\ M^{\rm H}(2){-}O(2) \\ M^{\rm H}(2){-}O(11)c \\ M^{\rm H}(2){-}O(8) \\ M^{\rm H}(2){-}O(13)c \\ M^{\rm H}(2){-}O(22) \\ {<}M^{\rm H}(2){-}O{>} \end{array}$  | $\begin{array}{c} 1.746(6)\\ 1.953(6)\\ 1.968(6)\\ 2.017(6)\\ 2.033(6)\\ \underline{2.243(6)}\\ 1.993\end{array}$                         |
| $\begin{array}{l} Si(1) - O(3) \\ Si(1) - O(4) \\ Si(1) - O(9)b \\ Si(1) - O(7) \\ < Si(1) - O> \end{array}$  | 1.609(6)<br>1.627(6)<br>1.633(6)<br><u>1.672(6)</u><br>1.635  | $\begin{array}{l} Si(2) - O(10) \\ Si(2) - O(13) \\ Si(2) - O(8) \\ Si(2) - O(1) \\ < Si(2) - O> \end{array}$  | $ \begin{array}{r} 1.606(6) \\ 1.622(6) \\ 1.628(6) \\ \underline{1.658(6)} \\ 1.629 \end{array} $                                   | $\begin{array}{l} Si(3) - O(6)\\ Si(3) - O(5)\\ Si(3) - O(12)b\\ Si(3) - O(7)d\\ <\!Si(3) - O\!> \end{array}$  | 1.593(6)<br>1.624(6)<br>1.630(6)<br><u>1.674(6)</u><br>1.630  |
| $\begin{array}{l} Si(4) - O(14) \\ Si(4) - O(11) \\ Si(4) - O(2) \\ Si(4) - O(1)d \\ < Si(4) - O> \\ P - O(18) \\ P - O(19)e \\ P - O(17) \\ P - O(20) \\ < P - O> \\ \end{array}$          | $\begin{array}{c} 1.596(6) \\ 1.598(6) \\ 1.601(6) \\ 1.640(6) \\ \hline 1.609 \\ \end{array}$ $\begin{array}{c} 1.527(7) \\ 1.540(7) \\ 1.544(6) \\ \hline 1.564(6) \\ \hline 1.544 \end{array}$ | $\begin{array}{l} {\rm Si}(1){\rm -O}(7){\rm -Si}(3){\rm a} \\ {\rm Si}(2){\rm -O}(1){\rm -Si}(4){\rm a} \\ \\ {\rm A}^{P}(2){\rm -O}(17){\rm a} \\ {\rm A}^{P}(2){\rm -X}^{O}_{{\rm A}}(1) \\ {\rm A}^{P}(2){\rm -O}(2){\rm a} \\ {\rm A}^{P}(2){\rm -O}(13){\rm c} \\ {\rm A}^{P}(2){\rm -O}(11){\rm f} \\ {\rm A}^{P}(2){\rm -O}(1){\rm c} \\ {\rm A}^{P}(2){\rm -O}(1) \\ {\rm A}^{P}(2){\rm -O}(1) \\ {\rm A}^{P}(2){\rm -O}(8){\rm g} \\ {\rm } \end{array}$ | $134.6(4) \\134.6(4) \\2.311(7) \\2.324(6) \\2.407(7) \\2.579(7) \\2.697(8) \\2.727(7) \\2.735(7) \\\underline{2.792(7)} \\2.572 \\$ | $\begin{array}{l} A^{P}(1) - O(9) \\ A^{P}(1) - O(5)a \\ A^{P}(1) - O(4) \\ A^{P}(1) - O(12)a \\ A^{P}(1) - O(7) \\ A^{P}(1) - O(7)c \\ A^{P}(1) - O(7)c \\ A^{P}(1) - O(4)g \\ A^{P}(1) - O(5)g \\ A^{P}(1) - O(9)h \\ A^{P}(1) - O(12)h \\ < A^{P}(1) - O \end{array}$ | 2.763(6)<br>2.765(6)<br>2.772(5)<br>2.780(5)<br>2.853(5)<br>2.863(5)<br>2.908(6)<br>2.921(6)<br>2.935(6)<br>2.935(6)<br>2.936(6)<br>2.850 |
|   | 2.209(8)<br>2.278(8)<br>2.325(8)<br>2.398(7)<br>2.303   |  | 2.227(8)<br>2.315(7)<br>2.375(8)<br><u>2.418(7)</u><br>2.333   | Na(3)-O(18)<br>Na(3)-O(19)g<br>Na(3)-O(20)b<br>Na(3)-O(13)a<br>Na(3)-O(11)<br>Na(3)-O(8)<br><na(3)-o></na(3)-o>  | 2.237(7)<br>2.319(7)<br>2.496(7)<br>2.497(7)<br>2.585(7)<br><u>2.619(7)</u><br>2.459  |

φ: O, OH, F

a: x, y-1, z; b: x-1, y, z; c: x+1, y, z; d: x, y+1, z; e: x, y, z-1; f: x+1, y-1, z; g: -x+1, -y+1, -z+1; h: -x+2, -y+1, -z+1; i: x-1, y-1, z; j: -x+1, -y+1, -z.

O-octahedral). Here we use the (HOH) notation of Ferraris *et al.* (1996). We divide the cation sites (Table 3) into 4 groups:  $M^{O}$  sites of the O sheet,  $M^{H}$  and Si sites of the H sheet, peripheral  $A^{P}$  sites, and sites of the I block; site labelling is in accord with Sokolova (2006). Also in accord with

Sokolova (2006), we label anions  $X^O$ ,  $X^H$  and  $X^P$  (anions of O and H sheets and peripheral anions);  $X^O_M$  = common vertices of  $M^O$  and  $M^H$  polyhedra;  $X^O_A$  = common vertices of  $M^O$  and  $A^P$  polyhedra;  $X^P_M$  and  $X^P_A$  = apical anions of  $M^H$  and  $A^P$ polyhedra at the periphery of the TS block.

| Site                        | Refined site-scattering | Site population   | Calculated site-scattering | < <i>X</i> -φ≥ <sub>calc.</sub> *<br>(Å) | < <i>X</i> -φ≥ <sub>obs.</sub><br>(Å) |
|-----------------------------|-------------------------|---|----------------------------|--|---------------------------------------|
| <i>M</i> <sup>O</sup> (1)** | 22.0(4)                 | $\begin{array}{c} 0.85 \text{ Ti} + 0.06 \text{ Mn}^{2+} + \\ 0.05 \text{ Nb}^{5+} + 0.02 \text{ Zr} + \\ 0.01 \text{ Ta}^{5+} + 0.01 \text{ Mg} \end{array}$ | 23.3                       | 1.987                                    | 1.986                                 |
| $M^{O}(2)$                  | 11.0(4)                 | $0.95 \text{ Na} + 0.05 \square$  | 10.5                       | 2.400                                    | 2.457                                 |
| $M^{O}(3)$                  | 11.0(4)                 | $0.90 \text{ Na} + 0.10 \square$  | 9.9                        | 2.400                                    | 2.378                                 |
| $M^{O}(4)$                  | 13.9(2)                 | 0.65 Na + 0.23 $Mn^{2+}$ + 0.12 $\Box$  | 12.9                       | 2.343                                    | 2.303                                 |
| ${}^{[5]}M^{\rm H}(1)$      | 22.0(4)                 | $0.90 \text{ Ti} + 0.05 \text{ Nb}^{5+} + 0.03 \text{ Fe}^{3+} + 0.02 \text{ Al}^{3+}$  | 22.9                       | 1.894                                    | 1.927                                 |
| $M^{\rm H}(2)$              | 35.3(4)                 | $0.70 \text{ Nb}^{5+} + 0.30 \text{ Ti}$  | 35.3                       | 2.009                                    | 1.993                                 |
| ${}^{[10]}\dot{A}^{P}(1)$   | 46.8(2)                 | 0.73 Ba + 0.13 K + 0.06 Sr + 0.08 $\square$   | 45.6                       | 2.899                                    | 2.850                                 |
| ${}^{[8]}A^P(2)^{***}$      | 11.0(5)                 | $0.62 \text{ Na} + 0.06 \text{ Ca} + 0.32 \square$  | 8.0                        | 2.548                                    | 2.572                                 |
| [4]Na(1)                    | 11.0(4)                 | 1.00 Na   | 11.0                       | 2.370                                    | 2.303                                 |
| [4]Na(2)                    | 11.0(4)                 | 1.00 Na   | 11.0                       | 2.370                                    | 2.333                                 |
| Na(3)                       | 11.0(4)                 | 0.95 Na + 0.05 □  | 10.5                       | 2.400                                    | 2.459                                 |
| <sup>[4]</sup> P            | 15.0(2)                 | 1.00 P  | 15.0                       | 1.550                                    | 1.544                                 |

TABLE 5. Refined site-scattering (e.p.f.u.) and assigned site-populations (a.p.f.u.) for bornemanite.

\* Calculated by summing constituent ionic radii; values from Shannon (1976),  $\phi = O$ , (OH), F.

\*\* Coordination number is given only for non-[6]-coordinated sites.

\*\*\* See discussion in the text.

The ideal formula of bornemanite, Na6 BaTi2  $Nb(Si_2O_7)_2(PO_4)O_2(OH)F$ , Z = 2, will be discussed below. We consider it here to explain the rational of the cation site assignment. The anion part of the formula,  $(Si_2O_7)_2(PO_4)$  $O_2(OH)F$ , has an aggregate charge of -21, and the electroneutrality of the formula requires a charge of +21 at 11 cation sites,  $M^{O}(1-4)$ ,  $M^{\rm H}(1,2), A^{\rm P}(1,2), Na(1-3)$  (Table 3). However, the ideal formula lists 10 cations per formula unit, Na<sub>6</sub>BaTi<sub>2</sub>Nb and a vacancy. Three sites, Ti<sub>2</sub>Nb, represent Ti + Nb = 3 a.p.f.u.; one site,  $A^{P}(1)$ , equals ~1 Ba a.p.f.u. We know that Ti(Nb) sites are always fully occupied in Ti-disilicate minerals and we have to assign all Ti, Nb and other minor elements to these three sites. The structure refinement gives seven Na-dominant sites (Tables 3, 4, 5). The chemical analysis gives 6.07 Na + 0.23 Mn<sup>2+</sup> + 0.06 Ca + 0.64  $\Box$  = 6.36 a.p.f.u., i.e. <6.5 a.p.f.u. (Table 1). Therefore we write the total content of seven Na-dominant sites as Na6 in the ideal formula and distribute  $0.64 \square$  (vacancies) over these seven sites in accord with interatomic distances (Table 4) and bond-valence sums on anions and cations.

#### O sheet

In the crystal structure of bornemanite, the  $M^{O}(1)$  site is primarily occupied by Ti, with minor Nb, Mn<sup>2+</sup>, Zr, Ta and Mg, and is coordinated by four O atoms and two monovalent X<sup>O</sup><sub>A</sub> anions (see section on anion sites below) with a  $\langle M^{O}(1) - \phi \rangle$ distance of 1.986 Å ( $\phi$  = unspecified anion) (Tables 3, 4, 5). The occurrence of both Ti and  $Mn^{2+}$  at a single site in the O sheet has been observed previously in another Ti disilicate mineral, sobolevite, Na<sub>12</sub>Ca(Na,Ca,Mn)  $Ti_2(Ti,Mn)(Si_2O_7)_2(PO_4)_4O_3F_3$  (Sokolova et al., 2005). There are three [6]-coordinated sites primarily occupied by Na. The  $M^{O}(2)$  and  $M^{O}(3)$ sites are 90 and 95% occupied by Na, respectively (Table 5). The  $M^{O}(2)$  site is coordinated by six O atoms and the  $M^{O}(3)$  site is coordinated by four O atoms and two  $X_A^O$  anions, with  $\langle M^O(2) - O \rangle$  and <M<sup>O</sup>(3) $-\phi$ > distances of 2.457 and 2.378 Å, respectively. The  $M^{O}(4)$  site, Na<sub>0.65</sub>Mn<sub>0.23</sub><sup>2+</sup> $\square_{0.12}$ a.p.f.u. (Table 5), is coordinated by four O atoms and two  $X_A^O$  anions, with a  $< M^O(4) - \phi >$  distance of 2.303 Å. The occurrence of both Na and  $Mn^{2+}$  at one site is fairly common in Ti-disilicate minerals; it has been described previously in vuonnemite,

|     | Si(1)        | Si(2)        | Si(3)        | Si(4)            | Р            | M <sup>0</sup> (1) | $M^{O}(2)$     | $M^{O}(3)$     | $M^{O}(4)$   | $M^{H}(1)$   | M <sup>H</sup> (2) | $\mathbf{A}^{P}(1)$ | $\mathbf{A}^{P}(2)$ | Na(1)          | Na(2)          | Na(3)          | ω                    |
|-----|--------------|--------------|--------------|------------------|--------------|--------------------|----------------|----------------|--------------|--------------|--------------------|---------------------|---------------------|----------------|----------------|----------------|----------------------|
|     |              | 0.93         |              | 0.97             |              |                    |                |                |              |              |                    |                     | 0.08                | 0.21           |                |                | 2.27                 |
|     | 1.06         |              |              | 1.08             |              | 0.58               | 0.16           |                | 0.24         |              | 0.82               |                     | 0.14                |                |                |                | 2.04<br>2.04         |
|     | 1.01         |              |              |                  |              |                    |                |                |              | 0.62         |                    | $0.23 \\ 0.16$      |                     |                |                |                | 2.02                 |
|     |              |              | 1.02         |                  |              |                    |                |                |              | 09.0         |                    | 0.23                |                     |                |                |                | 2.01                 |
|     |              |              | 1.10         |                  |              | 0.60               | 0.14           | 0.23           |              |              |                    |                     |                     |                |                |                | 2.07                 |
|     | 0.90         |              | 0.89         |                  |              |                    |                |                |              |              |                    | 0.19                |                     |                |                |                | 2.16                 |
|     |              | 1.01         |              |                  |              |                    |                |                |              |              | 0.70               |                     | 0.08                |                |                | 0.13           | 1.92                 |
|     | 0.99         |              |              |                  |              |                    |                |                |              | 0.61         |                    | $0.23 \\ 0.15$      |                     |                |                |                | 1.98                 |
|     |              | 1.07         |              | 1.09             |              | 0.55               | 0.15           |                | 0.22         |              | 0.79               |                     | 0.09                |                |                | 0.14           | 1.99<br>2.11         |
|     |              |              | 1.00         |                  |              |                    |                |                |              | 0.61         |                    | 0.22                |                     |                |                |                | 1.98                 |
|     |              | 1.02         |              | 1 00             |              |                    |                |                |              |              | 0.67               |                     | 0.11                |                |                | 0.16           | 1.96                 |
|     |              |              |              | 1.U <del>9</del> |              | 0.03               | 0.21           | 0.14           | 0.23         |              | 1.40               |                     |                     |                |                |                | 1.98                 |
|     |              |              |              |                  | 1.23<br>1.29 |                    | C7.0           | 0.2.0          | 0.10         | 1.4/         |                    |                     | 0.17                | $0.24 \\ 0.29$ | $0.20 \\ 0.28$ | 0.27           | 2.00<br>1.84<br>2.13 |
|     |              |              |              |                  | 1.24<br>1.16 |                    |                |                |              |              | 0.41               |                     |                     | 0.26           | 0.22           | 0.23           | 1.95                 |
|     |              |              |              |                  |              | $0.86 \\ 0.49$     |                | 0.14<br>0.19   | 0.19<br>0.20 |              |                    |                     | 0.15                |                |                |                | 1.19                 |
| ite | 3.96<br>4.00 | 4.03<br>4.00 | 4.01<br>4.00 | 4.23<br>4.00     | 4.92<br>5.00 | 3.71<br>3.92       | $1.06 \\ 0.95$ | $1.13 \\ 0.90$ | 1.26<br>1.11 | 3.91<br>4.00 | 4.79<br>4.70       | $1.90 \\ 1.71$      | 0.90<br>0.76        | $1.00 \\ 1.00$ | 0.94<br>1.00   | $1.09 \\ 0.95$ |                      |

TABLE 6. Bond-valence\* (v.u.) table for bornemanite.

\* Bond-valence parameters are from Brown (1981).

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 $\begin{array}{l} Na_7(Na,Mn^{2+})_4 Ti^{4+}(Nb,Ti^{4+})_2(Si_2O_7)_2(PO_4)_2 \\ O_3(F,OH) \ (Ercit \ et \ al., \ 1998), \ quadruphite, \\ Na_{14}Ca_2 Ti_4(Si_2O_7)_2(PO_4)_4O_4F_2 \ (Sokolova \ and \\ Hawthorne, \ 2001) \ and \ polyphite, \ Na_5(Na_4Ca_2) \\ Ti_2(Si_2O_7)(PO_4)_3O_2F_2 \ (Sokolova \ et \ al., \ 2005). \end{array}$ 

# H sheet

There are four tetrahedrally coordinated sites occupied by Si with a <Si-O> distance of 1.631 Å (Table 4) and two  $M^{\rm H}$  sites. The [5]-coordinated  $M^{\rm H}(1)$  site is occupied mainly by Ti (Table 5). The  $M^{\rm H}(1)$  site is coordinated by five O atoms, with a  $\langle M^{H}(1) - O \rangle$  distance of 1.927 Å; the very short  $M^{H}(1) - O(16)$  distance of 1.678 Å (Table 4) is in accord with the structure topology of Group III minerals (see figure 32 in Sokolova, 2006). O(16) is the  $X_M^O$  anion in the terminology of Sokolova (2006). The [6]-coordinated Nb-dominant  $M^{\rm H}(2)$  site is coordinated by six O atoms, with a <M<sup>H</sup>(2)-O> distance of 1.993 Å (Table 4); this site is occupied mainly by Nb (see Table 5). The shortest  $M^{H}(2)-O(15)$ distance of 1.746 Å is from the  $M^{\rm H}(2)$  site to another  $X_M^O$  anion. The two  $M^H$  sites occur in different H sheets of one TS block.

# Peripheral A<sup>P</sup> sites

In bornemanite, there are two chemically distinct peripheral sites,  $A^{P}(1)$  and  $A^{P}(2)$ . The [10]-coordinated  $A^{P}(1)$  site is occupied mainly by Ba, Ba<sub>0.73</sub>K<sub>0.13</sub>Sr<sub>0.06</sub> \_\_\_\_0.08</sub> a.p.f.u. There are ten  $A^{P}(1)$ -O distances <3 Å (Table 4), and one longer distance,  $A^{P}(1)-X^{O}_{A}(1) = 3.118$  Å. We consider the  $A^{P}(1)$  site as [10]-coordinated, with a  $\langle A^{P}(1) - O \rangle$  distance of 2.792 Å. At the  $A^{P}(1)$ site,  $Ba^{2+} > Sr^{2+} + Ca^{2+}$  and we write the ideal composition of this site as Ba. The  $A^{P}(2)$  site is coordinated by seven O atoms and the monovalent  $X_A^O(2)$  anion, and it is occupied by  $Na_{0.62}Ca_{0.06} \square_{0.32}$  a.p.f.u., with  $\langle A^{P}(2) - \phi \rangle =$ 2.572 Å. Partial occupancy of the  $A^{P}(2)$  site was also observed in the crystal structure of epistolite (Sokolova and Hawthorne, 2004).

## I block

There are two types of **I** block in the structure of bornemanite,  $\mathbf{I}_1$  and  $\mathbf{I}_2$ . The  $\mathbf{I}_1$  block comprises  $A^P(1)$  sites which are shifted from the H sheet into the intermediate space between two TS blocks (note the long distance from the  $A^P(1)$  site to the  $X_A^O(1)$  anion in the O sheet,  $A^P(1)-X_A^O(1) =$ 3.118 Å. The  $\mathbf{I}_2$  block contains the Na and P sites. There are two Na sites, Na(1) and Na(2), and these are tetrahedrally coordinated by O atoms with a range of <Na-O> distances from 2.209 to 2.418 Å. There is one *Na*(3) site, coordinated by six O-atoms with a <Na(3)-O> distance of 2.459 Å. Coordination numbers of the Na atoms are in reasonable accord with the bond-valence requirements of the O atoms (Table 6). There is one tetrahedrally coordinated *P* site, solely occupied by P, with a <P-O> distance of 1.544 Å, close to the grand <P-O> distance in minerals of 1.537 Å given by Huminicki and Hawthorne (2002).

# Anion sites

There are 18 anion sites, O(1)-O(14) and O(17)-O(20), occupied by O atoms which form the tetrahedral coordination of the Si and P atoms, respectively (Tables 4, 5, 6). There are two O sites, O(15) and O(16), which are common anions for the M<sup>H</sup> polyhedra and three octahedra of the O sheet,  $M^O(2-4)$  (Table 6). There are two  $X_A^O$  sites which receive bond valences of 1.19 and 1.03 v.u., respectively (Table 6), and hence are monovalent anions. The chemical analysis gives F = 1.27 and OH = 0.74 a.p.f.u. (Table 1), and we assign  $F_{1.27}OH_{0.73}$  to these two sites. Ideally, the two  $X_A^O$  sites give F(OH) a.p.f.u.

# Structure topology

## The TS block

In the Ti disilicate minerals (Sokolova, 2006), the TS block consists of HOH sheets where H is a heteropolyhedral sheet including (Si<sub>2</sub>O<sub>7</sub>) groups, and O is a trioctahedral close-packed sheet. In the crystal structure of bornemanite, the O sheet is of the form  $M^{O}X_{2}^{O}$ , where  $M^{O}$  are cations and  $X^{O}$  are anions. Structures with the TS block have a characteristic two-dimensional minimal cell in the plane of the O sheet, with  $t_1 \approx 5.5$  and  $t_2 \approx$ 7.1 Å,  $t_1 \wedge t_2 \approx 90^{\circ}$ , and this minimal cell contains 4 [M<sup>O</sup>X<sub>2</sub><sup>O</sup>]. In bornemanite, the O sheet comprises  $M^{O}(1-4)$  octahedra (Fig. 1*a*) and its cation content is Na<sub>3</sub>Ti (4 a.p.f.u.). In the H sheets,  $(SiO_4)$  tetrahedra link together to form (Si<sub>2</sub>O<sub>7</sub>) groups. There are two distinct H sheets in bornemanite. In the  $H_1$  sheet,  $(Si_2O_7)$  groups and [5]-coordinated Ti-dominant M<sup>H</sup>(1) polyhedra share common vertices to form the sheet as in other Ti disilicate minerals (Fig. 1b). In the H<sub>2</sub> sheet, (Si<sub>2</sub>O<sub>7</sub>) groups share common vertices with Nb-dominant  $M^{H}(2)$  octahedra (Fig. 1c). The topology of both H sheets is identical except for the coordination of the  $M^{\rm H}$  sites. In the H<sub>1</sub> and H<sub>2</sub> sheets, the peripheral  $A^P$  sites are occupied by Ba



FIG. 1. Details of the crystal structure of bornemanite. (*a*) The close-packed octahedral (O) sheet; (*b*) the heteropolyhedral (H) sheets H<sub>1</sub>; and (*c*) H<sub>2</sub>. (*d*) shows the TS block viewed down [100]; (*e*) the intermediate (I) blocks I<sub>1</sub>; and (*f*) I<sub>2</sub>. The (SiO<sub>4</sub>) tetrahedra are orange, Ti<sup>4+</sup>- and Nb<sup>5+</sup>-dominant polyhedra are yellow, Na-dominant octahedra are navy blue, Na tetrahedra are turquoise, atoms at the  $A^P(1)$  and  $A^P(2)$  sites are shown as maroon and navy blue circles, respectively, monovalent  $X^O_A$  anions are shown as small red spheres. In (*a*), labels 1, 2, 3, 4 correspond to  $M^O(1)$ ,  $M^O(2)$ ,  $M^O(3)$  and  $M^O(4)$  octahedra, respectively; in (*b*) and (*c*), labels 1, 2, 3, 4 correspond to Si(1), Si(2), Si(3) and Si(4) tetrahedra, respectively; in (*e*) and (*f*), *m* = number of cation layers in the I block.

and Na, respectively (see discussion of the (I) block below). The [10]-coordinated  $A^P(1)$  cations are shifted from the plane of the H<sub>1</sub> sheet to just above the centres of the large voids in the H<sub>1</sub> sheet. The [8]-coordinated  $A^P(2)$  cations are located in the plane of the H<sub>2</sub> sheet. The H and O sheets link via common vertices of M<sup>H</sup>, Si and M<sup>O</sup> polyhedra to form the TS block parallel to

(001) (Fig. 1*d*). In bornemanite, the TS block exhibits linkage 1 and stereochemistry typical of Group III (Sokolova, 2006): two H sheets connect to the O sheet such that two (Si<sub>2</sub>O<sub>7</sub>) groups link to the *trans* edges of the Ti octahedron of the O sheet. In this case, the H<sub>1</sub> and H<sub>2</sub> sheets are related by a pseudo-mirror plane (*m*) coinciding with the plane of the O sheet.

#### The I blocks

In bornemanite, the TS blocks do not link directly through the apical vertices of the  $M^{H}(2)$  octahedra, they alternate with I blocks,  $I_1$  and  $I_2$ .

A layer of  $A^{P}(1)$  atoms (hereafter called an **I** layer) forms the **I**<sub>1</sub> block (Fig. 1*e*). In the **I**<sub>1</sub> block, which is a layer of  $A^{P}(1)$  atoms (m = 1, where *m* is the number of **I** layers; Sokolova, 2006). The atoms are arranged in a close-packed fashion where each is surrounded by six others at approximately equal distances of 5 Å. There are four  $A^{P}(1)$  cations in the minimal cell. The composition of the **I**<sub>1</sub> block is  $A^{P}(1)_{2}$  or ideally Ba<sub>2</sub>.

The **I**<sub>2</sub> block has two **I** layers (m = 2) between adjacent TS blocks (Fig. 1f). Each I layer consists of [4]- and [6]-coordinated Na(1-3) polyhedra and  $(PO_4)$  tetrahedra. In the I layer, Na polyhedra share vertices, edges and faces, whereas (PO<sub>4</sub>) tetrahedra share common vertices with Na polyhedra and  $M^{H}(2)$  and  $A^{P}(2)$  polyhedra. The two I layers are parallel to (001) and are related by an inversion centre. Therefore the topology and chemical composition of these two I layers of polyhedra are identical. All cations in this I layer are close-packed, and there are four cations, 3 Na<sup>+</sup>  $+ P^{5+}$ , in the minimal cell. Two I-layers link together through common vertices of Na and P polyhedra. The composition of the  $I_2$  block is  $2[Na_3(PO_4)].$ 

#### The general structure

The crystal structure of bornemanite (Fig. 2*a*) consists of TS and I blocks alternating along the *c* axis. There are two TS blocks and two I blocks,  $I_1$  and  $I_2$ , per *c* cell-parameter. Bornemanite is the only Ti disilicate mineral currently known with two different types of I block. Note that the two TS blocks are related by an inversion centre (and hence are identical). The TS block exhibits the stereochemistry of Group III where Ti equals 3 a.p.f.u. (Sokolova, 2006) and this is the key to understanding the relation of bornemanite to other Ti disilicate minerals.

#### The chemical formula of bornemanite

We write the chemical formula of bornemanite as the sum of the TS and I blocks. In accord with Sokolova (2006), the formula for the TS block of Group III minerals is  $A_2^P B_2^P M_2^H M_4^O (Si_2 O_7)_2 X_4^O$  $X_{M2}^P X_{A2}^P$ , where  $A^P$  and  $B^P$  are cations at the peripheral (P) sites;  $M^{H}$  and  $M^{O}$  are cations of the H and O sheets;  $X^{O}$  are anions of the O sheet;  $X^{P}_{M}$ and  $X^{P}_{A}$  are apical anions of the M<sup>H</sup> and A<sup>P</sup> cations at the periphery of the TS block. In bornemanite,  $\begin{array}{l} A_2^P = A^P(1) + A^P(2) = Ba + (Na_{0.62}Ca_{0.06} \square_{0.32}); \\ B_2^P = 0; \ M_2^H = M^H(1) + M^H(2) = Ti, Nb; \ M_4^O = \end{array}$  $(Na_{2.50}Mn_{0.23}\square_{0.27})$  Ti;  $X_4^O = O_2$  (OH)F;  $X_{M2}^P$  and  $X_{A2}^P = O_2$  as only polyhedra of one H sheet, H<sub>2</sub>, have two anions at the periphery of the TS block, they are O(15) and O(16). Hence, we write the ideal composition of the TS block as  $(Na_{0.5} \square_{0.5})$ BaTiNb(Na<sub>2.5</sub> $\square_{0.5}$ )Ti(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)F, Z = 2. There are two I blocks in bornemanite: the  $I_1$ block comprises the  $A^{P}(1)$  sites, which have already been counted in the formula of the TS block; the  $I_2$  block includes Na(1-3) sites and (PO<sub>4</sub>) tetrahedra, hence we write its composition as  $Na_3(PO_4)$  per formula unit. The TS and  $I_2$  blocks are totalled to write the ideal structural and mineral formula for bornemanite: Na<sub>3.5</sub> <sub>0.5</sub> BaTiNbNa<sub>2.5</sub> □0.5Ti(Si2O7)2 (PO4)O2(OH)F and Na6□BaTi2Nb  $(Si_2O_7)_2(PO_4) O_2(OH)F$ , respectively, with Z = 2. These can be compared with the empirical formula from the EMP analysis:  $(Na_{6.07}Mn_{0.23}^{2+}Ca_{0.06})$  $\Box_{0.64})_{\Sigma7.00}(Ba_{0.73}K_{0.13}Sr_{0.06}\Box_{0.08})_{\Sigma1.00}(Ti_{2.05}$  $Nb_{0.80}Zr_{0.02}Ta_{0.01}^{5+}Fe_{0.03}^{3+}Al_{0.02}Mn_{0.06}^{2+}Mg_{0.01})_{\Sigma 3.00}$  $(Si_2O_7)_2(P_{0.97}O_4)O_2 [F_{1.27}(OH)_{0.74}]_{\Sigma 2.01}$ 

#### **Related minerals**

There are six other minerals in Group III: lamprophyllite, nabalamprophyllite, barytolamprophyllite, innelite, epistolite and vuonnemite (listed in Table 7). Apart from innelite, these minerals contain an invariant core of the TS block,  $M_2^H M_4^O(Si_2O_7)_2 X_4^O$ ,  $M_2^H = Ti$ , Nb;  $M_4^O =$ Na<sub>3</sub>Ti (for innelite,  $M_4^O = Na_2CaTi$ , however we believe the crystal structure of innelite requires re-examination). In these minerals, the TS blocks do not link directly. The TS blocks alternate with I blocks as in bornemanite, apart from in the epistolite structure.

There are two types of I block in bornemanite. The I<sub>1</sub> block is of composition  $A^P(1)_2 = Ba_{1.46}K_{0.26}Sr_{0.12}\square_{0.16}$  and is topologically identical and chemically similar to the I block (BaK) in barytolamprophyllite (Fig. 2b). It is interesting that the aggregate charge of the I<sub>1</sub> block is +3.42, i.e. <+4.00 for the ideal composition Ba<sub>2</sub>. Hence the ideal integer charge of the I<sub>1</sub> block can be written as +3.00 rather than +4.00. This is in accord with Sokolova (2006) who wrote the general formula for lamprophyllite, barytolamprophyllite and nabalamprophyllite as



FIG. 2. The crystal structures of: (*a*) bornemanite projected onto (100); and related minerals (*b*) barytolamprophyllite projected onto (001); and (*c*) vuonnemite projected onto (100). Legend as in Fig. 1.

 $(A^{2+}A^+)M_2^HM_4^O(Si_2O_7)_2X_4^O$  where  $A^{2+}$  and  $A^+$  cations constitute the **I** block, and have a total charge of +3. Although in bornemanite the ratio  $A^{2+}:A \neq 1:1$ , the presence of vacancies makes the ideal aggregate charge +3.

The  $I_2$  block is of composition 2[Na<sub>3</sub>(PO<sub>4</sub>)] and is topologically similar to the I block in vuonnemite (Fig. 2*b*) (except for the coordination numbers of the Na atoms). In the  $I_2$  block in bornemanite, two Na atoms, Na(1) and Na(2), are [4]-coordinated and one atom, Na(3), is [6]-coordinated. In vuonnemite, the three Na atoms are [4]-, [5]- and [6]-coordinated (Fig. 2*c*).

In both vuonnemite and barytolamprophyllite, the origin of the unit cell and the corresponding inversion centre occur within the O sheet of the

| Mineral  | Formula   | <i>a</i> (Å)                          | b (Å)                         | c (Å)                            | Sp. gr.                                 | Ζ                                       | α(°)                      | β(°)                   | γ(°)                    | Ref.                           |
|--|---|---------------------------------------|-------------------------------|----------------------------------|---|---|---------------------------|------------------------|-------------------------|--------------------------------|
| Lamprophyllite-2 <i>M</i>  | (SrNa)Ti,Na,Ti(Si,O <sub>7</sub> ),O <sub>2</sub> (OH),   | 19.215                                | 7.061                         | 5.3719                           | C2/m                                    | 2                                       | 06                        | 96.797                 | 90                      | (1)                            |
| Lamprophyllite-20  | $(SrNa)Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$  | 19.128                                | 7.0799                        | 5.3824                           | Pmm                                     | 0                                       | 90                        | 90                     | 90                      | (1)                            |
| Nabalamprophyllite-2M  | BaNaTi2Na3Ti(Si2O7)2O2(OH)2   | 19.741                                | 7.105                         | 5.408                            | P2/m                                    | 2                                       | 90                        | 96.67                  | 90                      | (2)                            |
| Nabalamprophyllite-20  | $(BaNa)Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$  | 19.564                                | 7.1173                        | 5.414                            | Pnmn                                    | 2                                       | 90                        | 90                     | 90                      | (3)                            |
| Barytolamprophyllite   | (BaK)Ti <sub>2</sub> Na <sub>3</sub> Ti(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> O <sub>2</sub> (OH) <sub>2</sub>  | 19.8971                               | 7.1165                        | 5.4108                           | C2/m                                    | 2                                       | 90                        | 96.676                 | 90                      | (4)                            |
| Innelite   | Ba <sub>2</sub> Ba <sub>2</sub> Ti <sub>2</sub> Na <sub>2</sub> CaTi(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> O <sub>4</sub> | 14.76                                 | 7.14                          | 5.38                             | P1                                      | 1                                       | 90.00                     | 95.00                  | 99.00                   | (5)                            |
| Epistolite   | $(Na\Box)Nb_2Na_3Ti(Si_3O_7)_2O_2(OH)_2(H_2O)_4$  | 5.460                                 | 7.170                         | 12.041                           | $P\overline{1}$                         | 1                                       | 103.63                    | 96.01                  | 89.98                   | (9)                            |
| Vuonnemite   | $Na_6Na_2Nb_2Na_3Ti(Si_2O_7)_2(PO_4)_2O_3F$   | 5.4984                                | 7.161                         | 14.450                           | $P\overline{1}$                         | 1                                       | 92.60                     | 95.30                  | 90.60                   |                                |
| Bornemanite  | $Na_3BaNbTiNa_3Ti(Si_2O_7)_2(PO_4)O_2(OH)F$   | 5.4587                                | 7.1421                        | 24.528                           | $P\overline{1}$                         | 2                                       | 96.790                    | 96.927                 | 90.326                  | (8)                            |
| * For all minerals (except<br>The invariant core of the T          | bornemanite, this work), ideal structural formuls<br>S block, $M_2^HM_4^Q(Si_2O_7)_2X_4^Q$ , is shown in bold: $M^1$  | te are from {<br>= cations of         | Sokolova<br>f the H sh        | (2006).<br>eet; M <sup>O</sup> = | cations of                              | the O sh                                | eet; $X_4^0 = a$          | inions sha             | red betwe               | en O and                       |
| H sneets.<br>References: (1) Krivovich<br>and Chukanov (1999); (3) | ev <i>et al.</i> (2003); Rastsvetaeva and Dorfman (1995<br>Sokolova and Hawthorne (2008 <i>b</i> ); (4) Sokolova  | ); Rastsvetae<br>and Cámara           | va <i>et al.</i><br>1 (2008); | (1990); Si<br>Rastsveta          | if yanov <i>et</i><br>eva <i>et al.</i> | <i>al.</i> (198<br>(1995); <sup>]</sup> | (3); Woodr<br>Peng et al. | ow (1964)<br>(1984); ( | ); (2) Ras<br>(5) Chern | tsvetaeva<br>ov <i>et al</i> . |
| (1971); (6) Sokolova and<br>The latest reference on th             | Hawthorne (2004); (7) Ercit $et al.$ (1998); Drozd e structure is the first entry in the numbered list  | ov <i>et al.</i> (19<br>of references | 74); (8) 1<br>;               | his work.                        |   |   |                           |                        |                         |                                |

# CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY OF BORNEMANITE

|   | k l  | 0 8                          | $\overline{1}$ $\overline{6}$ | $\frac{1}{1}$            | 1 7               | 1 5        | $\overline{2}$    | 2 0                           | 2 0               | 1 7        | 2<br>2            | $\overline{1}$ 6 | 2                      | 1 8                      | 2<br>2   | 2               | 2<br>3   | 5<br>9           | 4               | 31<br>31    | 0 7       | ĪĪ              | 0                | 2          | 0 2                            | 0 0              | $1\overline{8}$ | 6 0         | 0           | 1 8              | 0 1         | 2<br>4                        | 2                    | $1 \overline{9}$         | 2<br>2    |
|---|--|------------------------------|-------------------------------|--------------------------|-------------------|------------|-------------------|-------------------------------|-------------------|------------|-------------------|------------------|------------------------|--------------------------|----------|-----------------|----------|------------------|-----------------|-------------|-----------|-----------------|------------------|------------|--------------------------------|------------------|-----------------|-------------|-------------|------------------|-------------|-------------------------------|----------------------|--------------------------|-----------|
| *   | Ч  | 0                            | -                             | -                        | 0                 | 1          | -                 | 1                             | 1                 |            | 1                 | -                | 0                      | 0                        | 1        | -               | 1        | 0                | -               | 1           | 1         | 1               | 0                | -          | 0                              | 0                | 1               | 0           | 2           | 0                | 0           | 1                             | -                    | 0                        | -         |
| his work**  | $D_{\mathrm{calc}}$  | 3.022                        | 2.992                         | 2.978                    | 2.968             | 2.960      | 2.960             | 2.960                         | 2.940             | 2.936      | 2.930             | 2.920            | 2.910                  | 2.908                    | 2.884    | 2.862           | 2.838    | 2.835            | 2.834           | 2.777       | 2.763     | 2.737           | 2.729            | 2.720      | 2.715                          | 2.709            | 2.688           | 2.686       | 2.668       | 2.667            | 2.657       | 2.648                         | 2.625                | 2.618                    | 7 587     |
| <br>  | $I_{\rm calc}$   | 25                           | Э                             | 1                        | б                 | 10         | 1                 | 8                             | 8                 | 7          | 11                | 7                | S,                     | 4                        | 10       | 4               | 2        | 7                | 17              | 40          | 9         | 2               | 2                | 24         | 16                             | 25               | 7               | 6           | 1           | 4                | 8           | 2                             | 14                   | 5                        | v         |
| s et al.<br>1)**  | $d_{\rm obs}$  | 3.016                        |                               |                          |                   |            |                   | 2.951                         |                   |            |                   |                  | 2.909                  |                          |          |                 | 2.833    |                  |                 | 2.772       |           |                 |                  |            |                                | 2.705            |                 | 2.683       |             |                  |             |                               |                      | 2.619                    |           |
| Ferraris<br>(200  | $I_{\text{calc}}$  | 94                           |                               |                          |                   |            |                   | 10                            |                   |            |                   |                  | 10                     |                          |          |                 | 12       |                  |                 | 13          |           |                 |                  |            |                                | 24               |                 | 41          |             |                  |             |                               |                      | 6                        |           |
| ov <i>et al.</i><br>5)*                                     | $d_{\rm obs}$  | 3.02                         |                               |                          |                   |            |                   |                               |                   |            |                   |                  |                        |                          |          |                 | 2.832    |                  |                 |             | 2.758     |                 |                  |            |                                |                  |                 | 2.682       |             |                  |             |                               |                      |                          | 202 L     |
| Men'shik<br>(197  | $I_{\rm obs}$  | 10                           |                               |                          |                   |            |                   |                               |                   |            |                   |                  |                        |                          |          |                 | 1        |                  |                 |             | 1         |                 |                  |            |                                |                  |                 | 8           |             |                  |             |                               |                      |                          | -         |
|   | 1  | -                            | 0                             | m                        | 0                 | 1          | n<br>Cl           | 4                             | 0                 | 5          | З                 | 4                | ŝ                      | З                        | 0        | 4               |          |                  | 0               | З           | -         | 5               | 1                | 0          | 9                              | ŝ                | ŝ               | 2           | 4           | 4                | S           | З                             | 9                    | 4                        | ı         |
|   |  |                              |                               |                          |                   |            |                   |                               |                   |            |                   |                  |                        |                          | 0        | _               | _        |                  | _               |             |           | -               | _                |            | _                              |                  |                 |             |             |                  |             |                               |                      |                          |           |
|   | k  | 0                            | 0                             | 0                        | 1                 | -          | -                 | 0                             | -                 | 0          | -                 | 1                | 0                      | <u> </u>                 |          |                 |          |                  |                 | <u> </u>    |           |                 | -                |            | 0                              | -                | 0               | -           | 0           | -                | 1           |                               | 1                    |                          | C         |
| *   | h k  | 0 0                          | 0 0                           | 0 0                      | 0 1               | 0 1        | 0 1               | 0 0                           | 0 1               | 1 0        | 0 1               | 0 1              | 0                      | -                        | -        | 0               | -        | 1                |                 | 1           | 1         | 1               | 1                | 1          | 0                              | $1 \overline{1}$ | 1               | 1           | 1 0         | 1 1              | 0 1         | $1 \overline{1}$              | 0 1                  | $1 \overline{1}$         | с<br>0    |
| This work***  | $D_{\text{calc}}$ h k  | 24.17 0 0                    | 12.09 0 0                     | 8.06 0 0                 | 7.09 0 1          | 6.59 0 1   | 6.47 0 1          | 6.04 0 0                      | 5.82 0 1          | 5.19 1 0   | 5.03 0 1          | 4.90 0 1         | 4.83 0 (               | 4.77 Ī (                 | 4.73 1   | 4.35 0          | 4.33 1   | 4.30 1           | 4.264 1         | 4.262 1 (   | 4.261 1   | 4.25 1          | 4.08 1           | 4.06 1 1   | 4.03 0 0                       | 3.866 1 I        | 3.848 1 0       | 3.824 1 1   | 3.810 1 0   | 3.798 1 1        | 3.789 0 1   | $3.788 1 \overline{1}$        | 3.698 0 1            | $3.571  1  \overline{1}$ | 2 570 0 7 |
| — This work <sup>***</sup> —                                | $I_{\text{calc}}$ $D_{\text{calc}}$ $h$ $k$                                    | 100 24.17 0 0                | 2 12.09 0 0                   | 31 8.06 0 0              | 2 7.09 0 1        | 1 6.59 0 1 | 6 6.47 0 1        | <1 6.04 0 0                   | 9 5.82 0 1        | 2 5.19 1 0 | 8 5.03 0 1        | 3 4.90 0 1       | 2 4.83 0 (             | $6$ 4.77 $\bar{1}$ (     | 1 4.73 1 | 1 4.35 0        | 1 4.33 1 | 15 4.30 1        | 10 4.264 1      | 1 4.262 1 ( | 2 4.261 1 | 7 4.25 1        | 12 4.08 1 1      | 4 4.06 1 1 | 3 4.03 0 0                     | 3 3.866 1 1      | 2 3.848 1 0     | 8 3.824 1 1 | 5 3.810 1 0 | 5 3.798 1 1      | 3 3.789 0 1 | $14$ 3.788 $1$ $\overline{1}$ | 12 3.698 0 1         | 12 3.571 1 1             |           |
| et al. This work***)**                                      | $\int d_{\rm obs} = I_{\rm calc} = D_{\rm calc} - h - k$                       | 23.80 100 24.17 0 0          | 12.00 2 12.09 0 0             | 8.02 31 8.06 0 0         | 7.05 2 7.09 0 1   | 1 6.59 0 1 | 6.51 6 6.47 0 1   | $6.02 < <1 \\ 6.04 \\ 0 \\ 0$ | 5.80 9 5.82 0 1   | 2 5.19 1 0 | 5.01 8 5.03 0 1   | 3 4.90 0 1       | 4.82 2 4.83 0 (        | 4.76 6 4.77 <u>1</u> (   | 1 4.73 1 | 4.34 1 4.35 0   | 1 4.33 1 | 4.29 15 4.30 1   | 10 4.264 1      | 1 4.262 1 ( | 2 4.261 1 | 4.25 7 4.25 1   | 4.08 12 4.08 1   | 4 4.06 1 1 | 4.02 3 $4.03$ 0 0              | 3 3.866 1 1      | 2 3.848 1 0     | 8 3.824 1 1 | 5 3.810 1 0 | 5 3.798 1 1      | 3 3.789 0 1 | 3.786 14 3.788 1 <u>1</u>     | 3.695 12 3.698 0 1   | 3.568 12 3.571 1 1       |           |
| Ferraris <i>et al.</i> — This work*** — (2001)**            | $I_{\text{calc}}$ $d_{\text{obs}}$ $I_{\text{calc}}$ $D_{\text{calc}}$ $h$ $k$ | 100 23.80 100 24.17 0 0      | 2.5 12.00 2 12.09 0 0         | 92 8.02 31 8.06 0 0      | 1 7.05 2 7.09 0 1 | 1 6.59 0 1 | 2 6.51 6 6.47 0 1 | 1 $6.02$ <1 $6.04$ 0 0        | 2 5.80 9 5.82 0 1 | 2 5.19 1 0 | 3 5.01 8 5.03 0 1 | 3 4.90 0 1       | 8 4.82 2 4.83 0 (      | 2 4.76 6 4.77 Ī (        | 1 4.73 1 | 3 4.34 1 4.35 0 | 1 4.33 1 | 6 4.29 15 4.30 1 | 10 4.264 1      | 1 4.262 1 ( | 2 4.261 1 | 6 4.25 7 4.25 1 | 4 4.08 12 4.08 1 | 4 4.06 1 1 | 13 4.02 3 4.03 0 $\frac{1}{2}$ | 3 3.866 1 1      | 2 3.848 1 0     | 8 3.824 1 1 | 5 3.810 1 0 | 5 3.798 1 1      | 3 3.789 0 1 | 8 3.786 14 3.788 1 <u>1</u>   | 7 3.695 12 3.698 0 1 | 7 3.568 12 3.571 1 1     |           |
| ikov et al. Ferraris et al. — This work*** — 775)* (2001)** | $d_{obs}$ $I_{calc}$ $d_{obs}$ $I_{calc}$ $D_{calc}$ $h$ $k$                   | 24.1 100 23.80 100 24.17 0 0 | 12.0 2.5 12.00 2 12.09 0 0    | 8.04 92 8.02 31 8.06 0 0 | 1 7.05 2 7.09 0 1 | 1 6.59 0 1 | 2 6.51 6 6.47 0 1 | 1 $6.02$ <1 $6.04$ 0 0        | 2 5.80 9 5.82 0 1 | 2 5.19 1 0 | 3 5.01 8 5.03 0 1 | 3 4.90 0 1       | 4.82 8 4.82 2 4.83 0 ( | 2 4.76 6 4.77 <u>1</u> ( | 1 4.73 1 | 3 4.34 1 4.35 0 | 1 4.33 1 | 6 4.29 15 4.30 1 | 4.26 10 4.264 1 | 1 4.262 1 ( | 2 4.261 1 | 6 4.25 7 4.25 1 | 4 4.08 12 4.08 1 | 4 4.06 1 1 | 4.02 13 $4.02$ 3 $4.03$ 0 $0$  | 3 3.866 1 1      | 2 3.848 1 0     | 8 3.824 1 1 | 5 3.810 1 0 | 3.80 5 3.798 1 1 | 3 3.789 0 1 | 8 3.786 14 3.788 1 1          | 7 3.695 12 3.698 0 1 | 7 3.568 12 3.571 1 1     |           |

TABLE 8. Powder XRD pattern for bornemanite.

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| 6     | 2     | ŝ     |       | 6     | 10    | 2     | ŝ     | $\overline{10}$ | 0     | 1     | ŝ     | i x     | 10    | 1     | 4     | 2     | $\overline{10}$ | 6     | 11    | 9       | 4     | S     | 12    | 12    | ŝ     | 9     | 6     | 1     | <u>11</u> | ī     | 12    |        |
|-------|-------|-------|-------|-------|-------|-------|-------|-----------------|-------|-------|-------|---------|-------|-------|-------|-------|-----------------|-------|-------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|-------|-------|--------|
| 0     | -     | 0     |       | -     | 0     | -     | -     | -               | ŝ     | З     |       | n<br>Cl |       | ŝ     | 2     | 0     | 0               | 0     | -     | 0       | 5     | З     | 0     | -     | З     | -     | 1     | -     |           | З     | 0     |        |
| 1     | 1     | 0     |       | 0     | 0     | 0     | Ч     | 0               | 0     | 0     | Ч     | 1       | 1     | 0     | Ч     | Ч     | 1               | 0     | 0     | Ч       | Ч     | 0     | 0     | 0     | 1     | 0     | 0     | Ч     | -         | 0     | -     |        |
| 2.533 | 2.487 | 2.478 |       | 2.418 | 2.417 | 2.388 | 2.388 | 2.377           | 2.364 | 2.325 | 2.324 | 2.092   | 2.091 | 2.069 | 2.062 | 2.042 | 2.040           | 2.036 | 2.031 | 2.031   | 2.030 | 2.030 | 2.015 | 2.002 | 2.001 | 1.998 | 1.997 | 1.983 | 1.981     | 1.980 | 1.968 |        |
| 9     | б     | 9     |       | б     | б     | 2     | 1     | 1               | 1     | 2     | 1     | 4       | 1     | б     | 5     | 2     | б               | 5     | б     | 5       | 2     | б     | 7     | ŝ     | 7     | б     | 1     | б     | 2         | ę     | 9     |        |
| 2.527 |       | 2.475 | 2.445 | 2.410 |       |       |       |                 |       |       |       |         | 2.088 |       |       |       |                 | 2.027 |       |         |       |       | 2.013 |       |       |       |       |       |           |       |       |        |
| 4     |       | 3     | 2     | 17    |       |       |       |                 |       |       |       |         | с     |       |       |       |                 | 8     |       |         |       |       | 11    |       |       |       |       |       |           |       |       |        |
|       |       |       |       | 2.413 |       |       |       |                 |       |       |       |         |       |       |       |       |                 |       |       |         |       |       | 2.012 |       |       |       |       |       |           |       | 1.970 |        |
|       |       |       |       | 9     |       |       |       |                 |       |       |       |         |       |       |       |       |                 |       |       |         |       |       | 5     |       |       |       |       |       |           |       | с     |        |
| З     | 5     | ŝ     | 2     | S     | 9     | 0     | 4     | 4               | ŝ     | Ē     | 9     | 9       | 6     | ŝ     | 5     | 0     | 11              |       | 6     | -       |       | ŝ     | 5     | З     | 0     | 0     | 4     | 5     | 5         | 4     | 10    | _      |
| -     | 0     | 1     | 0     | 0     | 1     | 0     | -     | 5               |       | 0     | 0     | 1       | 0     | 0     | 1     | ŝ     | 1               | 5     | 0     | n<br>Cl | 0     | 0     | 5     | ŝ     | 0     | 5     | 2     | ŝ     |           | З     | 0     | r<br>N |
| -     | 0     | 1     | 0     | -     | 0     | 0     | -     | 0               | 1     | 1     | 1     | 0       | 1     | 0     | 0     | -     | 0               | 0     | 1     | 0       | 0     | 0     | 0     | -     | 0     | 0     | 0     | -     | 0         | 0     |       | -      |
| 3.531 | 3.518 | 3.503 | 3.453 | 3.407 | 3.336 | 3.297 | 3.237 | 3.232           | 3.194 | 3.089 | 3.059 | 2.300   | 2.297 | 2.249 | 2.202 | 2.183 | 2.174           | 2.170 | 2.170 | 2.160   | 2.156 | 2.152 | 2.149 | 2.140 | 2.132 | 2.130 | 2.126 | 2.125 | 2.124     | 2.117 | 2.114 | 2.113  |
| 2     | с     | 6     | 14    | 7     | 5     | 9     | 4     | 9               | 12    | 4     | 1     | 1       | 7     | 7     | 1     | 2     | 1               | 9     | 1     | С       | 2     | 9     | 7     | 7     | ŝ     | с     | 7     | 1     | 2         | 2     | 7     | -      |
|       |       | 3.509 | 3.447 |       | 3.326 | 3.285 |       | 3.230           | 3.188 | 3.080 |       |         | 2.294 | 2.245 |       |       |                 |       |       |         |       | 2.153 |       |       |       |       |       |       |           |       |       |        |
|       |       | 7     | 63    |       | 4     | 4     |       | 5               | 9     | 7     |       |         | 7     | 1     |       |       |                 |       |       |         |       | 9     |       |       |       |       |       |       |           |       |       |        |
|       |       | 3.52  | 3.44  |       |       |       |       |                 |       | 3.08  |       |         |       |       |       |       |                 |       |       |         |       | 2.152 |       |       |       |       |       |       |           |       |       |        |
|       |       | 1     | 10    |       |       |       |       |                 |       | 2     |       |         |       |       |       |       |                 |       |       |         |       | З     |       |       |       |       |       |       |           |       |       |        |

\*\*\* Calculated from atom coordinates of the crystal structure of bornemanite, Fe- $K\alpha$ ,  $\lambda = 1.93604$  Å<sup>-1</sup>, with Lazy Pulverix (Yvon *et al.* 1977).

\* Fe-K $\alpha$ , no filter, D = 57.3 mm; there are 16 more reflections up to d = 1.0077 Å.

\*\* Cu-Ka, graphite monochromator.

#### CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY OF BORNEMANITE

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TS block (Figs. 2c and 2b). In vuonnemite and barytolamprophyllite, two H sheets of the TS block are identical and are related by the inversion centre. In bornemanite, two H sheets differ in the  $M^H$  and  $A^P$  sites and are not identical. Hence, inversion centre cannot occur in the O sheet of the TS block. In the bornemanite structure, the inversion centre occurs within the I blocks (Fig. 2a).

### On the symmetry of bornemanite

Men'shikov et al. (1975) reported orthorhombic symmetry for bornemanite, a = 5.48, b = 7.10, c =48.2 Å, V = 1875.4 Å<sup>3</sup>, with possible space groups Imma and Ima2. Ferraris et al. (2001) reported monoclinic symmetry, a = 5.498, b =7.120, c = 47.95 Å,  $\gamma = 88.1^{\circ}$ , V = 1876 Å<sup>3</sup>, space group I11b. Our work indicates the triclinic symmetry, a = 5.4587, b = 7.1421, c = 24.528Å,  $\alpha = 96.790$ ,  $\beta = 96.927$ ,  $\gamma = 90.326^{\circ}$ , V = 942.4 $Å^3$ , space group  $P\overline{1}$ . We know that that this symmetry is correct due to the following evidence. We merged the single-crystal XRD data for bornemanite on three unit cells of different symmetry: orthorhombic, monoclinic and triclinic, with values for R<sub>int</sub> of 56.0, 29.8 and 2.82%, respectively. The latter value clearly indicates that the triclinic symmetry is correct.

Our triclinic primitive unit cell ( $V = 942.4 \text{ Å}^3$ ) can be related to an *I*-centred cell with a double volume, a = 5.459, b = 7.142, c = 48.367 Å,  $\alpha =$ 91.55,  $\beta = 90.59$ ,  $\gamma = 89.67^{\circ}$ ,  $V_{\rm I} = 1884.8 \text{ Å}^3$ , space group *I* by the transformation matrix [-1 0 0, 0 1 0, -1-1-2],  $V:V_{\rm I} = 1:2$ . The latter *I*-centred cell corresponds to the orthorhombic (Men'shikov *et al.*, 1975) and monoclinic (Ferraris *et al.*, 2001) *I*-centred cells previously reported for bornemanite. Note that all three angles in the triclinic *I* cell are close to but not equal to 90°.

We calculated the powder pattern from the atom coordinates of the crystal structure of bornemanite presented here and compared it with the experimental powder XRD patterns of Men'shikov *et al.* (1975) and Ferraris *et al.* (2001) in Table 8. The calculated powder pattern fits the experimental powder patterns very well. However, note that due to preferred orientation (bornemanite has perfect cleavage on (001)), basal reflections of the type (00*l*) have a greater intensity in the experimental powder patterns.

Our conclusion is that the true symmetry of bornemanite is triclinic, with space group  $P\overline{1}$ .

### Conclusions

(1) In this work, we report the crystal structure of bornemanite, ideally Na<sub>6</sub>BaTi<sub>2</sub>Nb(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> (PO<sub>4</sub>)O<sub>2</sub>(OH)F, triclinic, a = 5.4587, b = 7.1421, c = 24.528 Å,  $\alpha = 96.790$ ,  $\beta = 96.927$ ,  $\gamma = 90.326^{\circ}$ , V = 942.4 Å<sup>3</sup>, space group  $P\overline{1}$ , Z = 2,  $D_{calc.} = 3.342$  g cm<sup>-3</sup>.

(2) The structure of bornemanite is as predicted by Sokolova (2006). In bornemanite, the TS block exhibits linkage 1 and stereochemistry typical of Group III TS-block minerals: two H sheets connect to the O sheet such that two ( $Si_2O_7$ ) groups link to the *trans* edges of a Ti octahedron of the O sheet. The O sheet cations give Na<sub>3</sub>Ti (4 a.p.f.u.) in accordance with Group III.

(3) There are two H sheets in bornemanite,  $H_1$  and  $H_2$ , and their topology is identical except for coordination of the  $M^{\rm H}$  sites,  $M^{\rm H}(1) = {}^{[5]}{\rm Ti}$  and  $M^{\rm H}(2) = {}^{[6]}{\rm Nb}$ . In the  $H_1$  and  $H_2$  sheets, the peripheral  $A^P$  sites are occupied by Ba and Na, respectively.

(4) In bornemanite, TS blocks do not link directly through apical vertices of polyhedra of the H sheets, but alternate with (intermediate) I blocks. A layer of Ba atoms forms the first  $I_1$  block, with the second ( $I_2$  block) consisting of [4]- and [6]-coordinated Na polyhedra and (PO<sub>4</sub>) tetrahedra.

(5) TS and I blocks alternate along the c axis to form the crystal structure of bornemanite, with two TS blocks and two I blocks per c cell-parameter. The two TS blocks are related by an inversion centre and are identical.

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