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## From structure topology to chemical composition. XX. Titanium silicates: the crystal structure of hejtmanite, Ba2Mn4Ti2(Si2O7)(2)O-2(OH)(2)F-2, a Group-II TS-block mineral

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### 25 Abstract

26 The crystal structure of hejtmanite, Ba<sub>2</sub>Mn<sub>4</sub>Ti<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>, from Mbolve Hill,

- 27 Mkushi River area, Central Province, Zambia (holotype material) has been refined on a twinned
- crystal to  $R_1$  = 1.88% on the basis of 4539 [ $|F| > 4\sigma |F|$ ]. Hejtmanite is triclinic,  $C\overline{1}$ , a =
- 29 10.716(2), b = 13.795(3), c = 11.778(2) Å,  $\alpha = 90.07(3)$ ,  $\beta = 112.24(3)$ ,  $\gamma = 90.03(3)^{\circ}$ , V =
- 30 1612(2) Å<sup>3</sup>. Chemical analysis (electron microprobe) gives:  $Ta_2O_5$  0.09, Nb<sub>2</sub>O<sub>5</sub> 1.27, ZrO<sub>2</sub> 0.65,
- 31 TiO<sub>2</sub> 14.35, SiO<sub>2</sub> 23.13, BaO 26.68, SrO 0.19; FeO 11.28, MnO 15.12, Cs<sub>2</sub>O 0.05, K<sub>2</sub>O 0.33, F
- 32 3.82,  $H_2O_{calc.}$  1.63, O=F -1.61, total 97.10 wt.%, where the  $H_2O$  content was calculated from the
- 33 crystal-structure refinement, with (OH + F) = 4 a.p.f.u. The empirical formula, calculated on the

34 basis of 20 (O + F) anions, is of the form 
$$A_{2}^{P}M_{4}^{O}M_{2}^{H}(Si_{2}O_{7})_{2}(X^{O})_{4}(X^{P})_{2}$$
, Z = 4:

- $35 \quad (Ba_{1.82}K_{0.07}Sr_{0.02})_{\Sigma 1.91} (Mn_{2.33}Fe^{2+}_{1.65}Zr_{0.04}Mg_{0.03})_{\Sigma 3.95} (Ti_{1.88}Nb_{0.10}Zr_{0.02})_{\Sigma 2} (Si_{2.02}O_7)_2O_2 [(OH)_{1.89}F_{0.11}]_{\Sigma 2} (OH)_{1.89}F_{0.11}]_{\Sigma 2} ($
- 36 F<sub>2</sub>. The crystal structure is a combination of a TS (Titanium Silicate) block and an I
- 37 (intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral).
- 38 The topology of the TS block is as in Group-II TS-block minerals: Ti (+ Nb) = 2 a.p.f.u. per
- $(Si_2O_7)_2$  [as defined by Sokolova (2006)]. In the O sheet, five <sup>[6]</sup> $M^{O}$  sites are occupied mainly by
- 40 Mn, less Fe<sup>2+</sup> and minor Zr and Mg, with  $\langle M^{O}-\phi \rangle = 2.198$  Å ( $\phi = O,OH$ ), ideally giving Mn<sub>4</sub>
- 41 a.p.f.u. In the H sheet, two <sup>[6]</sup>  $M^{H}$  sites are occupied mainly by Ti, with  $\langle M^{H}-\phi \rangle = 1.962$  Å ( $\phi =$
- 42 O,F), ideally giving Ti<sub>2</sub> a.p.f.u.; four <sup>[4]</sup>Si sites are occupied by Si, with  $\langle$ Si–O $\rangle$  = 1.625 Å. The M<sup>H</sup>
- 43 octahedra and Si<sub>2</sub>O<sub>7</sub> groups constitute the H sheet. The two <sup>[12]</sup>Ba-dominant  $A^{P}(1,2)$  sites, with
- 44  $\langle A^{P}-\phi \rangle = 2.984 \text{ Å} (\phi = O, F)$ , ideally give Ba<sub>2</sub> a.p.f.u. Two  $X^{O}_{M}(1,2)$  and two  $X^{O}_{A}(1,2)$  sites are
- 45 occupied by O atoms and OH groups with minor F, respectively, ideally giving  $(X^{O})_{4} = (X^{O}_{M})_{2} +$
- 46  $(X_{A}^{O})_{2} = O_{2}(OH)_{2}$  p.f.u. Two  $X_{M}^{P}(1,2)$  sites are occupied by F, giving F<sub>2</sub> a.p.f.u. TS blocks link via
- 47 a layer of Ba atoms which constitute the I block. Simplified and endmember formulae of
- 48 hejtmanite are  $Ba_2(Mn, Fe^{2+})_4Ti_2(Si_2O_7)_2O_2(OH, F)_2F_2$  and  $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , Z = 4.
- 49 Hejtmanite is a Mn-analogue of bafertisite,  $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ .

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- 50 Keywords: hejtmanite, holotype, electron microprobe, single-crystal X-ray diffraction, crystal
- 51 structure, chemical formula, TS block, Group II.

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#### 53 Introduction

Semenov and Zhang Peishan (1959) described bafertisite,  $BaFe_2TiSi_2O_9$ , Z = 2, as a new mineral 54 55 from the Bayan Obo REE deposit, Inner Mongolia, China. The crystal structure of bafertisite from 56 the Bayan Obo deposit was determined by (1) Guan et al. (1963) and (2) Peng Zhizhong and 57 Shen Jinchuan (1963): [1] monoclinic, space group Cm, a = 10.60, b = 13.64, c = 12.47 Å,  $\beta =$ 119.5°, [2] monoclinic, space group  $P2_1/m$ , a = 10.98, b = 6.80, c = 5.36 Å,  $\beta = 94^{\circ}$ . Based on the 58 59 structure-refinement results, Guan et al. (1963) and Peng Zhizhong and Shen Jinchuan (1963) 60 gave the chemical formula of bafertisite as follows:  $BaFe_2Ti[Si_2O_7IO(OH)_2, Z = 8 and 2,$ 61 respectively. Vrána et al. (1992) described heitmanite from Mbolve Hill, Mkushi River area, 62 Central Province, Zambia, as a manganese-dominant analogue of bafertiste: monoclinic, diffraction symbol  $C^{*/*}$ , a = 10.698(4), b = 13.768(5), c = 11.748(4) Å,  $\beta = 112.27(2)^{\circ}$ , V = 1601(2)63 64 Å<sup>3</sup>,  $D_{\text{meas.}}$  = 4.02 g/cm<sup>3</sup>. Vrána *et al.* (1992) determined the chemical composition of hejtmanite by electron microprobe (Table 2) and by analogy with bafertisite (Semenov and Zhang Peishan, 65 66 1959; Guan et al., 1963; Peng Zhizhong and Shen Jinchuan, 1963), and gave simplified and 67 endmember formulae Ba(Mn,Fe)<sub>2</sub>TiO(Si<sub>2</sub>O<sub>7</sub>)(OH,F)<sub>2</sub> and BaMn<sub>2</sub>TiO(Si<sub>2</sub>O<sub>7</sub>)(OH,F)<sub>2</sub>, Z = 8. Pautov 68 (private communication, 1989; Mineraly, 1996) reported the occurrence of a Mn-analogue of 69 bafertisite in a rhodonite-tephroite-spessartine-quartz association from the Muzeinoe gorge, the 70 Inyl'chek mountain ridge, Tyan-Shan, South-Eastern Kirgizia, and gave its empirical and general formulae,  $(Ba_{0.96}Na_{0.03}Ca_{0.01}Cs_{0.002})_{\Sigma1}(Mn_{1.70}Fe^{2+}_{0.17}Mg_{0.05}Al_{0.08})_{\Sigma2}(Ti_{0.93}Sn_{0.07}Nb_{0.015})_{\Sigma1.01})_{\Sigma1.01}$ 71  $(Si_{1.97}AI_{0.02})_{\Sigma 1.99}O_7O_{2.09}(H_2O)_{0.25}$  and  $BaMn_2TiO(Si_2O_7)(OH)_2$ , respectively. All the crystals of the 72 73 material from Inyl'chek were heavily twinned, and complicated the structure work. Sokolova et al. 74 (1989) reported the unit cell for the Mn-analogue of bafertisite from the Inyl'chek mountain ridge, BaMn<sub>2</sub>TiO(Si<sub>2</sub>O<sub>7</sub>)(OH)<sub>2</sub>: triclinic, space groups P1 or  $P\overline{1}$ , a = 10.767(7), b = 13.858(9), c = 13.858(9)75 32.99(6) Å,  $\alpha = 90.3(1)$ ,  $\beta = 94.6(1)$ ,  $\gamma = 89.96(5)^{\circ}$ , V = 4906(2) Å<sup>3</sup>, Z = 24, and the structure model 76 for the monoclinic subcell: space group Pm, a = 5.374(3), b = 6.911(3), c = 32.82(1) Å,  $\beta =$ 77 94.62(4)°, V = 1214(2) Å<sup>3</sup>, R = 19.89%. They showed that the general topology of the structure of 78

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79 the Mn-analogue of bafertisite from the Invl'chek mountain ridge is identical to that of bafertisite 80 (Guan et al., 1963). Rastsvetaeva et al. (1991) collected new X-ray diffraction data using the 81 crystal of the Mn-analogue of bafertisite from the Inyl'chek mountain ridge previously studied by 82 Sokolova et al. (1989). They considered the crystal in question to be an intergrowth of two 83 monoclinic phases of the composition  $BaMn_2TiO(Si_2O_7)(OH)_2$ : (1) space group  $P2_1/m$ , a = 5.361, b = 6.908, c = 12.556 Å,  $\beta = 119.8^{\circ}$ , V = 403 Å<sup>3</sup>, Z = 2, R = 6.8%, and (2) space group Cm, a = 84 10.723, b = 13.812, c = 12.563 Å,  $\beta = 119.9^{\circ}$ , V = 1613 Å<sup>3</sup>, Z = 8, R = 8.3%; both phases are 85 86 isostructural with bafertisite [cf. P2<sub>1</sub>/m and Cm bafertisite structures of Peng Zhizhong and Shen 87 Jinchuan (1963) and Guan et al. (1963), respectively]. However, both structures of Rastsvetaeva 88 et al. (1991) have Si-O distances that are too short: (1) space group P2<sub>1</sub>/m: 1.54 Å, and (2) space 89 group Cm: 1.49 Å. These distances imply significant errors in both structures. The problems with 90 the crystal structure of heitmanite arise from the poor quality of its crystals, which is related to the 91 extensive twinning [cf. bafertisite, Cámara et al. (2015b)] and possible intergrowths with other 92 phases, a common problem with TS-block minerals. Based on the structure work of Rastsvetaeva 93 et al. (1991), Sokolova (2006) and Sokolova and Cámara (2013) considered heitmanite a TS-94 block mineral with two modifications: heitmanite-C (space group Cm) and heitmanite-P (space 95 group  $P2_1/m$ ).

96 The TS (Titanium Silicate) block is the main structural unit in the fast-growing family of 97 forty minerals: thirty-four minerals are listed in Sokolova and Cámara (2013), and information on 98 six minerals, kolskyite, emmerichite, saamite, betalomonosovite, bobshannonite and fogoite-(Y) 99 can be found in Cámara et al. (2013), Aksenov et al. (2014), Cámara et al. (2014a), Sokolova et 100 al. (2015a), Sokolova et al. (2015b) and Cámara et al. (2015a), respectively [cf. twenty-four 101 minerals (Sokolova, 2006)]. The TS block consists of a central trioctahedral (O) sheet and two 102 adjacent heteropolyhedral (H) sheets of [5-7]-coordinated polyhedra and Si<sub>2</sub>O<sub>7</sub> groups. The TS 103 block is characterized by a planar cell based on minimal lengths of translational vectors,  $t_1 \sim 5.5$ and  $t_2 \sim 7$  Å, and  $\mathbf{t_1} \wedge \mathbf{t_2} \approx 90^\circ$ . The general formula of the TS block is  $A_2^P B_2^P M_2^H M_4^O (Si_2O_7)_2 X_{4+n}$ . 104

105 where  $M_{2}^{H}$  and  $M_{4}^{O}$  = cations of the H and O sheets;  $M^{H}$  = Ti, Nb, Zr, Mn, Ca + REE, Ca;  $M^{O}$  = Ti, Zr, Nb, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mg, Mn, Ca, Na; A<sup>P</sup> and B<sup>P</sup> = cations at the peripheral (P) sites = Na, Ca + 106 REE, Ca, Ba, Sr, K; X = anions, O, OH, F, and H<sub>2</sub>O groups;  $X_{4+n} = X_{n}^{O} + X_{n}^{P}$ , n = 0, 1, 1.5, 2, 4, 107 108 where  $X_{4}^{O}$  = anions of the O sheet which do not coordinate Si atoms,  $X_{n}^{P}$  = anions at the 109 periphery of the TS block; X = O, OH, F, H<sub>2</sub>O (Sokolova and Cámara, 2013). Sokolova (2006) 110 developed general structural principles for the TS-block minerals. There are three topologically 111 distinct TS blocks based on three types of linkage of H and O sheets. In the crystal structures of 112 TS-block minerals, TS blocks either link directly or alternate with intermediate (I) blocks. The I 113 block consists of alkali and alkaline-earth cations, oxyanions (PO<sub>4</sub>), (SO<sub>4</sub>) and (CO<sub>3</sub>), and H<sub>2</sub>O 114 groups. Sokolova (2006) divided TS-block structures into four Groups, based on the topology and 115 stereochemistry of the TS block. Each group of structures has a different linkage, content and stereochemistry of Ti (+ Nb + Zr + Fe<sup>3+</sup> + Mg + Mn) per  $(Si_2O_7)_2$ . In Group I, Ti (+ Nb + Zr) = 1 116 117 a.p.f.u. (atoms per formula unit); in Group II, Ti (+ Nb) = 2 a.p.f.u.; in Group III, Ti (+ Nb + Mg +  $Fe^{3+}$ ) = 3 a.p.f.u.; in Group IV, Ti (+ Mg + Mn) = 4 a.p.f.u. In a TS-block structure, four types of 118 119 self-linkage between adjacent TS blocks occur.

120 Sokolova and Cámara (2013) introduced the concept of basic and derivative structures for 121 TS-block minerals. A basic structure has the following four characteristics: (1) There is only one 122 type of TS block; (2) The two H sheets of the TS block are identical; (3) There is only one type of I 123 block or it is absent; (4) There is only one type of self-linkage of TS blocks. Basic structures obey 124 the general structural principles laid out by Sokolova (2006). A derivative structure has one or 125 more of the three following characteristics: (1) There is more than one type of TS block; (2) There 126 is more than one type of I block; (3) There is more than one type of self-linkage of TS blocks. A 127 derivative structure is related to two or more basic structures of the same Group: it can be derived 128 by adding these structures via sharing the central O sheet of the TS blocks of adjacent structural 129 fragments which represent basic structures. There are thirty-five basic TS-block structures and 130 five derivative TS-block structures.

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131 Following our continued interest in TS-block minerals, we felt strongly that the crystal 132 structure of heitmanite must be solved and refined on the holotype material of Vrána et al. (1992). 133 We studied heitmanite from (1) Mbolve Hill, Mkushi River area, Central Province, Zambia 134 (holotype material from the collection of Leonid A. Pautov, given to Leonid by Stanislav Vrána), 135 and (2) from the Muzeinoe gorge, the Inyl'chek mountain ridge, Tyan-Shan, South-Eastern 136 Kirgizia. The current paper reports the crystal structure and structural formula of heitmanite. 137 Ba<sub>2</sub>Mn<sub>4</sub>Ti<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>F<sub>2</sub>, a TS-block mineral of Group II where Ti (+ Nb) = 2 a.p.f.u. per 138  $(Si_2O_7)_2$  (Table 1).

139

### 140 Chemical composition

141 Crystals of heitmanite were analyzed with a Cameca SX-100 electron microprobe operating in 142 wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 µm. The following standards were used: Si: diopside; Ta: 143 144 Mn(Ta<sub>1.70</sub>Nb<sub>0.30</sub>)O<sub>6</sub>; Nb, Ba: Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub>; Zr: zircon; Ti: titanite; Fe: fayalite; Mn: spessartine; 145 Mq: forsterite; Sn: cassiterite; Sr: SrTiO<sub>3</sub>; Cs: pollucite; K: orthoclase; F: fluorite. The elements 146 Na, Al, Zn, Ca, Pb, Rb and Cl were sought but not detected. The data were reduced and 147 corrected by the PAP method of Pouchou and Pichoir (1985). The H<sub>2</sub>O (presence of OH groups 148 confirmed by IR spectroscopy, Vrána et al., 1992) was calculated from the results of the crystal-149 structure analysis on the basis that F + OH = 4 a.p.f.u. Table 2 gives the chemical composition 150 of heitmanite from Zambia (holotype material) compared with its original chemical analysis 151 (Vrána et al., 1992) and hejtmanite from Inyl'chek, Kirgizia. The empirical formula was calculated on the basis of 20 (O + F) anions and is of the form  $A_2^P M_4^O M_2^H (Si_2O_7)_2 (X^O)_4 (X^P)_2$ , Z 152 153 =4: For heitmanite from Zambia (holotype), it is  $(Ba_{1.82}K_{0.07}Sr_{0.02})_{\Sigma 1.91}$ 154  $(Mn_{2.33}Fe^{2+}_{1.65}Zr_{0.04}Mg_{0.03})_{\Sigma 3.95}(Ti_{1.88}Nb_{0.10}Zr_{0.02})_{\Sigma 2}(Si_{2.02}O_7)_2O_2[(OH)_{1.89}F_{0.11}]_{\Sigma 2}F_{2,}D_{calc.} = 4.189$ g/cm<sup>3</sup> and is in accord with  $D_{meas}$  = 4.02 g/cm<sup>3</sup> (Vrána *et al.*, 1992). For hejtmanite from 155 156 Inyl'chek, Kirgizia, it is Ba<sub>1.92</sub>(Mn<sub>3.62</sub>Fe<sup>2+</sup>0.25Mg<sub>0.08</sub>Zr<sub>0.02</sub>)<sub> $\Sigma$ 3.97</sub>(Ti<sub>1.59</sub>Sn<sub>0.42</sub>)<sub> $\Sigma$ 2.01</sub>(Si<sub>2.02</sub>O<sub>7</sub>)<sub>2</sub>O<sub>2</sub>

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157	$[(OH)_{1.93}F_{0.07}]_{\Sigma 2}F_{2,}D_{calc.} = 4.189 g/cm^3$ . Hejtmanite from Inyl'chek, Kirgizia, is characterized by
158	very high MnO, significant SnO <sub>2</sub> , lower TiO <sub>2</sub> and lack of Nb <sub>2</sub> O <sub>5</sub> : 23.91, 5.95, 11.82 and 0 wt.%,
159	respectively, cf. 14.12, 0, 14.35 and 1.27 wt.%, respectively (hejtmanite from Zambia, this work)
160	(Table 2). By analogy with Sn-rich astrophyllite where $Sn^{4+}$ constitutes ~ 31% of the Ti-
161	dominant <i>D</i> site in the H sheet of the HOH block (Cámara <i>et al.</i> , 2010), we assigned all $Sn^{4+}$ to
162	the Ti-dominant $M^{H}$ site in the H sheet of the TS block (Table 2): $(Ti_{1.59}Sn_{0.42})_{\Sigma 2.01}$ a.p.f.u.
163	Simplified and endmember formulae of hejtmanite are $Ba_2(Mn,Fe^{2+})_4Ti_2(Si_2O_7)_2O_2(OH,F)_2F_2$ and
164	$Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , Z =4.

165

#### 166 Crystal structure

#### 167 Data collection and structure refinement

168 Single-crystal X-ray data for heitmanite from Zambia were collected using a Bruker 169 APEX II ULTRA three-circle diffractometer with a rotating-anode generator (Mo $K\alpha$ ), multilayer optics and an APEX II 4K CCD detector. The intensities of 9468 reflections with -15 < h < 15, -170 171 19 < k < 19, -16 < l < 16 were measured to  $60.28^{\circ} 2\theta$  using 16 s per  $0.3^{\circ}$  frame. Unit-cell 172 dimensions were determined by least-squares refinement of 9989 reflections with  $l > 10\sigma l$ , and 173 are given in Table 3, together with other miscellaneous information on data collection and 174 structure refinement. An absorption correction was done using the SADABS program (Sheldrick, 175 2008). The unit-cell dimensions of heitmanite (this work) are in good agreement with those of 176 Vrána et al. (1992) (Table 3). All calculations were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick, 2008). The crystal structure was refined in space group C1 177 178 using the atom coordinates of bafertisite (Cámara et al., 2015) and refined to  $R_1 = 1.88\%$  on a 179 twinned crystal with two components related by the twin matrix [100 010 001] and a twin ratio of 180 0.526(1):0.474(1). The (Niggli) reduced unit cell is: a = 8.732(2), b = 8.736(2), c = 11.778(2) Å,  $\alpha$ = 103.37(3),  $\beta$  = 103.48(3),  $\gamma$  = 104.32(3)°, V = 806(1) Å<sup>3</sup>, P1, Z = 2. The P1 unit cell can be 181 182 

183 unconventional space group C1 for consistency of orientation with all other thirty-nine TS-block 184 structures characterized by the planar cell based on minimal lengths of translational vectors,  $t_1 \sim$ 185 5.5 and  $t_2 \sim 7$  Å, and  $t_1 \wedge t_2 \approx 90^\circ$ , and specifically with bafertisite, the Fe<sup>2+</sup>-analogue of 186 heitmanite. Scattering curves for neutral atoms were taken from the International Tables for 187 Crystallography (Wilson, 1992). In the crystal structure of bafertisite, there are 3 groups of cation sites:  $M^{\circ}$  sites of the O sheet,  $M^{H}$  and Si sites of the H sheet, and peripheral  $A^{P}$  sites 188 189 which occur in the I block; site labeling is in accord with Sokolova (2006). Site-scattering values 190 were refined for the  $M^{0}(1-5)$  sites with the scattering curve of Mn,  $M^{H}(1,2)$  sites (scattering curve of Ti) and  $A^{P}(1,2)$  sites (scattering curve of Ba). For the H(1,2) atoms, the D (donor)–H 191 192 distances were softly constrained to 0.98 Å. Final atom coordinates and anisotropic 193 displacement parameters for hejtmanite are listed in Table 4, selected interatomic distances and 194 angles are given in Table 5, refined site-scattering values and assigned site-populations for 195 selected cation and anion sites are given in Table 6, bond-valence values for selected anions in 196 Table 7 and details of hydrogen bonding in Table 8. A table of structure factors and CIF for 197 hejtmanite have been deposited with the Principal Editor of Mineralogical Magazine and are 198 available from www.minersoc.org/pages/e journals/dep mat.html.

199

200 Topology of the structure

Hejtmanite is a TS-block mineral of Group II, Ti (+ Nb) = 2 a.p.f.u. per (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> (Sokolova, 2006).

202 The crystal structure of hejtmanite is a combination of a TS block and an I block (Fig. 1*a*). The

203 TS block consists of HOH sheets. In the O sheet, there are five Mn-dominant <sup>[6]</sup> M<sup>O</sup>(1–4) sites,

with  $\langle M^{O}-\phi \rangle = 2.198$  Å ( $\phi = O$ , OH) (Tables 5, 6, Fig. 1*b*). Five  $M^{O}$  sites ideally give Mn<sub>4</sub> a.p.f.u.

- (Table 6). In the H sheet, the two  ${}^{[6]}M^{H}(1,2)$  sites are occupied mainly by Ti and minor Nb and
- 206 Zr, ideally giving Ti<sub>2</sub> a.p.f.u., with  $\langle M^{H}-\phi \rangle = 1.962$  Å ( $\phi = O, F$ ) and four <sup>[4]</sup>Si sites are occupied
- solely by Si, with  $\langle Si-O \rangle = 1.625$  Å (Tables 5, 6). The M<sup>H</sup> octahedra and Si<sub>2</sub>O<sub>7</sub> groups
- 208 constitute the H sheet (Fig. 1c). Two H sheets and the central O sheet link via common vertices

of M<sup>H</sup> octahedra and Si<sub>2</sub>O<sub>7</sub> groups with M<sup>O</sup> octahedra to form the TS block. In Group II, the TS block exhibits linkage 2 where the Si<sub>2</sub>O<sub>7</sub> groups of two H sheets link to M<sup>O</sup> octahedra adjacent along  $\mathbf{t}_2$  (|| **b** where  $b = 2t_2$ ) in the O sheet (Fig. 1*a*) as defined by Sokolova (2006). There are two <sup>[12]</sup>Ba-dominant A<sup>P</sup>(1,2) sites, with  $\langle A^P(1)-\phi \rangle = 2.934$  Å and  $\langle A^P(2)-\phi \rangle = 3.034$  Å ( $\phi = O, F$ ). The two A<sup>P</sup> sites ideally give Ba<sub>2</sub> a.p.f.u. (Table 6). In the crystal structure of hejtmanite, TS blocks link via a layer of Ba atoms which constitute the I block (Fig. 1*a*). The topology of the hejtmanite structure is identical to that of bafertisite (Cámara *et al.*, 2015).

216

## 217 Anion considerations

218 The O(1–14) atoms coordinate Si atoms of Si<sub>2</sub>O<sub>7</sub> groups, giving  $(Si_2O_7)_2$  p.f.u. Two X<sup>O</sup><sub>M</sub>(1,2)

anions are bonded to one  $M^{H}$  (Ti) cation and three  $M^{O}$  (Mn) cations, receive 1.84 and 1.85 vu

(valence units) and hence they are O atoms, giving  $O_2$  a.p.f.u. (Tables 5–7). Two  $X_{M}^{P}(1,2)$ 

anions are bonded to one  $M^{H}$  (Ti) cation and three  $A^{P}$  (Ba) cations (Fig. 1*d*), they receive 0.84

and 0.82 vu (Table 7). We conclude that the  $X_{M}^{P}(1,2)$  anions are monovalent. The two  $X_{M}^{P}$  sites

are coordinated by four cations and hence there is no space to accommodate the H atom of an

224 OH group and a hydrogen bond at those sites. Therefore we assign F to the  $X_{M}^{P}(1,2)$  sites, and

they give  $F_2$  a.p.f.u. (Table 6). Two  $X^{O}_{A}(1,2)$  anions are bonded to three  $M^{O}$  (Mn) cations, with

incident valence sums of 1.18 and 1.22 vu (Table 7), hence they are monovalent anions.

227 Chemical analysis gives 2.11 F a.p.f.u. for hejtmanite (Table 2) and we assign 1.89 OH + [2.11

228  $-2.00(X_{M}^{P})_{2} = ] 0.11 \text{ F to the } X_{A}^{O}(1,2) \text{ sites, ideally (OH)}_{2} \text{ a.p.f.u. (Table 6). The H(1,2) atoms}$ 

are involved in weak hydrogen bonding with O atoms that belong to the H sheets (Table 8).

230

231 Endmember formula

We write the endmember formula of hejtmanite as the sum of the groups of cation and anion

233 sites: Ba<sub>2</sub> ( $A^{P}_{2}$ ) + Mn<sub>4</sub> ( $M^{O}_{4}$ ) + Ti<sub>2</sub> ( $M^{H}_{2}$ ) + (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> + O<sub>2</sub> [( $X^{O}_{M}$ )<sub>2</sub>] + (OH)<sub>2</sub> [( $X^{O}_{A}$ )<sub>2</sub>] + F<sub>2</sub> [( $X^{P}_{M}$ )<sub>2</sub>] =

234  $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , Z =4.

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236

# In the crystal structure of hejtmanite, (1) there is only one type of TS block of composition $[Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2]^{4-}$ ; (2) the two H sheets of the TS block are identical; (3) there is only one type of I block of composition $[Ba_2]^{4+}$ ; and (4) there is only one type of self-linkage of TS blocks, via a layer of Ba atoms in the of I block. Points (1)–(4) are in accord with the definition of a basic structure by Sokolova and Cámara (2013). The crystal structure of hejtmanite is of the B2(GII) structure type in accord with Sokolova and Cámara (2013).

243

## 244 **On F in the Group-II TS-block structures**

Basic TS-block structure

245 Ideal structural formulae for Group-II minerals heitmanite and bafertisite (the bafertisite structure 246 type, B2); bobshannonite, perraultite and jinshajiangite (the perraultite structure type, B1), 247 cámaraite (the D1 cámaraite structure type related to the bafertisite and perraultite structure 248 types), yoshimuraite (B3) and bussenite (B4) are presented in Table 1. All minerals have basic 249 structures except for cámaraite. In perraultite, jinshajiangite and bobshannonite, TS blocks connect via  $M^{H}$ -  $X^{P}_{M}$ - $M^{H}$  bridges as in the astrophyllite-group minerals (Cámara *et al.*, 2010) and 250 251 related nafertisite, Na<sub>3</sub>Fe<sup>2+</sup><sub>10</sub>Ti<sub>2</sub>(Si<sub>6</sub>O<sub>17</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>6</sub>F(H<sub>2</sub>O)<sub>2</sub> (Cámara *et al.*, 2014*b*). The 252 composition of an  $X_{M}^{P}$  anion correlates with the composition of the M<sup>H</sup> cations: where  $M^{H}$  sites 253 are locally occupied by Nb (as in bobshannonite), the bridging anion is an O atom; where  $M^{H}$ 254 sites are locally occupied by Ti (as in perraultite and jinshajiangite), the bridging anion is a F 255 atom (Table 1). A similar phenomenon was noted for astrophyllite-group minerals (cf. niobophyllite, Cámara *et al.*, 2010). In most astrophyllite-group minerals, the  $X^{P}_{M}$  anion is 256 257 coordinated by six cations: two Ti or Nb (at the  $M^{H}$  site), two K (at the A site) and two Na (at the *B* site) and an OH group cannot/does not occur at the  $X_{M}^{P}$  site as there is no room to 258 259 accommodate an H atom and a hydrogen bond; where there is a vacancy at the A or B sites. OH groups occur at the  $X_{M}^{P}$  site (Sokolova, 2012). In bafertisite and hejtmanite, TS blocks 260

connect via a layer of Ba atoms in the I block. F ( $X_{M}^{P}$  site) atoms are apical anions of the M<sup>H</sup> (=Ti) cations and they are coordinated by four cations: Ti ( $M^{H}$  site) and three Ba [ $A^{P}(1,2)$  sites]. In bafertisite and hejtmanite, an OH group cannot occur at the  $X_{M}^{P}$  site as there is no room to accommodate an H atom and a hydrogen bond. Hence F atoms and OH groups are ordered at the  $X_{M}^{P}$  and  $X_{A}^{O}$  sites, respectively.

Hejtmanite is related to cámaraite, ideally NaBa<sub>3</sub>Fe<sup>2+</sup> $_{8}$ Ti<sub>4</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>4</sub>O<sub>4</sub>(OH)<sub>4</sub>F<sub>3</sub>. The derivative structure of cámaraite has one type of TS block, two types of I block, and TS blocks link to each other in two different ways. The structure of cámaraite can be built of structural fragments of minerals of the same group, jinshajiangite and bafertisite. The *bafertisite* component of the cámaraite structure is topologically identical to the hejtmanite structure. The general and ideal structural formulae of cámaraite are written as sums of the corresponding formulae of bafertisite and jinshajiangite (Table 1).

273

## 274 Summary

- (1) Hejtmanite, ideally  $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , is a Group-II TS-block mineral (Ti + Nb = 2
- a.p.f.u.) in accord with Sokolova (2006). The crystal structure of bafertisite [a = 10.716(2), b =

277 13.795(3), c = 11.778(2) Å,  $\alpha = 90.07(3)$ ,  $\beta = 112.24(3)$ ,  $\gamma = 90.03(3)^{\circ}$ , V = 1612(2) Å<sup>3</sup>, space

- group C1 is of basic type [B2(GII)] and is an alternation of TS and I blocks of the composition
- [ $Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ ]<sup>4-</sup> and [ $Ba_2$ ]<sup>4+</sup>, respectively. The crystal structure of hejtmanite is of the
- same topology as that of baferisite,  $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ .
- (2) In the crystal structure of hejtmanite, OH groups and F atoms are ordered at the  $X^{O}_{A}$  sites in
- 282 the O sheet and  $X^{P}_{M}$  sites on the periphery of the TS block.
- 283 (3) The endmember formula of hejtmanite is of the form  $A_2^P M_4^O M_2^H (Si_2O_7)_2 (X^O)_4 (X^P)_2$ :
- 284  $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ , Z =4 where  $Ba_2 A_2^P = Ba_2$ ,  $M_4^O = Mn_4$ ,  $M_2^H = Ti_2$ ,  $(X_3^O)_4 = (X_3^O)_2 + (X_3^$
- 285  $(X^{O}_{A})_{2} = O_{2}(OH)_{2}, (X^{P}_{M})_{2} = F_{2}.$
- 286

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## 378 **Figure captions**

379

- 380 Fig. 1. A general view of the crystal structure of hejtmanite which consists of TS and I blocks (*a*)
- 381 and the details of the structure: the close-packed O sheet of Mn-dominant M<sup>O</sup> octahedra (*b*), the
- 382 H sheet of Ti-dominant M<sup>H</sup> octahedra and Si<sub>2</sub>O<sub>7</sub> groups (c), the F atom at the  $X^{P}_{M}$  site
- 383 coordinated by the four cations (*d*). SiO<sub>4</sub> tetrahedra are orange, Ti-dominant and Mn-dominant
- octahedra are yellow and magenta, respectively; Ba atoms at the  $A^{P}$  sites in the I block are
- 385 shown as raspberry spheres; O and H atoms of OH groups at the  $X^{O}_{A}$  sites are shown as
- turquoise and small white spheres; F atoms at the  $X^{P_{M}}$  sites are shown as yellow spheres. Unit
- 387 cell is shown by thin black lines.

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Mineral					Formu	ıla					<i>a</i> (Å)	b (Å)	<i>c</i> (Å)	-		
Structure type*	*	A <sup>P</sup> <sub>1-2</sub>	B <sup>P</sup> <sub>0-2</sub>	M <sup>H</sup> 2	M <sup>0</sup> <sub>4</sub>	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>		(X <sup>0</sup> <sub>M</sub> ) <sub>2</sub>	(X <sup>0</sup> <sub>A</sub> ) <sub>2</sub>	(X <sup>P</sup> <sub>M</sub> ) <sub>0-2</sub>	α (°)	β (°)	γ (°)	Sp. gr.	Ζ	Ref.
hejtmanite B2(GII)		Ba <sub>2</sub>		Ti <sub>2</sub>	Mn₄	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>		<b>O</b> <sub>2</sub>	(OH) <sub>2</sub>	F <sub>2</sub>	10.716 90.07	13.795 112.24	11.778 90.03	CĪ	4	(1)
bafertisite B2(GII)		Ba <sub>2</sub>		Ti₂	Fe <sup>2+</sup> <sub>4</sub>	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>		<b>O</b> <sub>2</sub>	(OH) <sub>2</sub>	F <sub>2</sub>	10.677 90.11	13.767 112.28	11.737 90.02	CĪ	4	(2)
cámaraite <sup>1</sup> D1(GII)		Ba₃	Na	Ti₄	Fe <sup>2+</sup> 8	(Si <sub>2</sub> O <sub>7</sub> ) <sub>4</sub>		<b>O</b> <sub>4</sub>	(OH) <sub>4</sub>	F <sub>3</sub>	10.6965 99.345	13.7861 92.315	21.478 89.993	$C\overline{1}$	4	(3)
jinshajiangite B1(GII)		Ва	Na	Ti₂	Fe <sup>2+</sup> <sub>4</sub>	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>		<b>O</b> <sub>2</sub>	(OH) <sub>2</sub>	F	10.7059 90.008	13.7992 94.972	20.760 89.984	$C\overline{1}$	8	(4)
perraultite B1(GII)		Ва	Na	Ti₂	Mn₄	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>		<b>O</b> <sub>2</sub>	(OH) <sub>2</sub>	F	10.731 90	13.841 95.06	20.845 90	C2	8	(5)
bobshannonite B1(GII)	1	Ba K	Na <sub>2</sub>	(Nb,Ti) <sub>4</sub>	(Mn,Na)	<sub>8</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>4</sub>		<b>O</b> <sub>4</sub>	(OH)₄	(O,F) <sub>2</sub>	10.839 89.99	13.912 95.02	20.98 89.998	$C\overline{1}$	4	(6)
yoshimuraite <sup>2</sup> B3(GII)		Ba <sub>2</sub>	Ba <sub>2</sub>	<sup>[5]</sup> Ti <sub>2</sub>	Mn₄	(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (	(PO <sub>4</sub> ) <sub>2</sub>	<b>O</b> <sub>2</sub>	(OH) <sub>2</sub>		5.386 95.50	6.999 93.62	14.748 89.98	P1	2	(7)
bussenite <sup>3</sup> B4(GII)	(Na□) <sub>2</sub>	Ba <sub>2</sub>	Ba <sub>2</sub>	Ti <sub>2</sub>	(M <sup>2+</sup> Na) <sub>2</sub>	2 (Si <sub>2</sub> O <sub>7</sub> )2 (	(CO <sub>3</sub> ) <sub>2</sub>	<b>O</b> <sub>2</sub>	(OH) <sub>2</sub>	(H <sub>2</sub> O) <sub>2</sub> F <sub>2</sub>	5.399 102.44	7.016 93.18	16.254 90.10	$P\overline{1}$	2	(8)

TABLE 1. Ideal structural formulae\* and unit-cell parameters for Group-II TS-block minerals, Ti + Nb = 2 a.p.f.u. per (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>.

\* The general structural formula of the TS block is  $A_2^P B_2^P M_2^H M_2^O (Si_2O_7)_2 X_{4+n}$ , where  $M_2^H$  and  $M_4^O = cations of the H and O sheets$ ;  $A^P$  and  $B^P = cations at the peripheral ($ *P* $) sites; X = anions; X_{4+n} = X_4^O + X_n^P$ , n = 0, 1, 1.5, 2, 4 (Sokolova and Cámara, 2013).  $X_4^O = (X_M^O)_2 + (X_A^O)_2$ ;  $X_M^O = anions at common vertices of 3M^O and M^H polyhedra and <math>X_A^O = anions$  at common vertices of 3M^O and A^P polyhedra (where  $A^P - X_A^O < 3A$ );  $X_M^P = anical anions of M^H cations at the periphery of the TS block. The stoichiometry of the core part of the TS block, <math>M_2^H M_4^O (Si_2O_7)_2 X_4^O$ , is invariant in all structures (shown in bold). In Group II,  $A^P$  and  $B^P$  cations, plus (PO\_4)<sub>2</sub> (in yoshimuraite) and (Na $\Box$ )<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>F<sub>2</sub> (in bussenite) constitute the I block.

\*\* Bn(GII) and Dn(GII) denote B for basic and D for derivative structures of Group II (Sokolova and Cámara, 2013).

For yoshimuraite and bussenite, ideal structural formulae are from Sokolova (2006). Surkhobite (Rastsvetaeva *et al.*, 2008) is not listed here as there are problems with its crystal structure.

<sup>1</sup> the formulae for cámaraite and bobshannonite are per double minimal cell based on 2t<sub>1</sub> and 2t<sub>2</sub> translations [(Si<sub>2</sub>O<sub>7</sub>)<sub>4</sub>];

<sup>2</sup> there are misprints in McDonald *et al.* (2000):  $\alpha$  = 89.98,  $\gamma$  = 95.50°;

<sup>3</sup> M<sup>2+</sup>= Fe<sup>2+</sup>, Mn;

References (the most recent reference on the structure): (1) this work; (2) Cámara *et al.* (2015*b*); (3) Cámara *et al.* (2009); (4) Cámara *et al.* (in preparation) and Sokolova *et al.* (2009); (5) Yamnova *et al.* (1998); (6) Sokolova *et al.* (2015*b*); (7) McDonald *et al.* (2000); (8) Zhou *et al.* (2002).

Componen	t	wt.%				Formula unit (a.p	o.f.u.)
	← (	Zambia (holotype) →	Inyl'chek, Kirgizia		~	Zambia (holotype) →	Inyl'chek, Kirgizia
	This work	Vrána <i>et al.</i> (1992)	This work		This work	Vrána <i>et al.</i> (1992)	This work
Ta <sub>2</sub> O <sub>5</sub>	0.09	n.d.	n.d.	Si	4.04	4.11	4.03
$Nb_2O_5$	1.27	1.4	n.d.				
SnO <sub>2</sub>	n.d.	n.d.	5.95	Mn	2.23	2.09	3.62
ZrO <sub>2</sub>	0.65	n.d.	0.22	Fe <sup>2+</sup>	1.65	1.65	0.25
TiO <sub>2</sub>	14.35	13.27	11.82	Zr	0.04	0	0.02
SiO <sub>2</sub>	23.13	23.52	22.53	Mg	0.03	0.03	0.08
$AI_2O_3$	n.d.	0.37	n.d.	Na	0	0.02	0
BaO	26.68	30.20	27.41	Σ4M <sup>0</sup>	3.95	3.79	3.97
SrO	0.19	n.d.	n.d.				
FeO	11.28	11.29	1.65	Ti	1.88	1.75	1.59
MnO	15.12	14.12	23.91	Sn	0	0	0.42
CaO	n.d.	n.d.	0.04	Nb	0.10	0.11	0
MgO	0.12	0.13	0.30	Zr	0.02	0	0
Cs <sub>2</sub> O	0.05	n.d.	0.04	AI	0	0.08	0
K <sub>2</sub> O	0.33	0.30	n.d.	Σ2M <sup>H</sup>	2.00	1.94	2.01
Na <sub>2</sub> O	n.d.	0.06	n.d.				
H <sub>2</sub> O**	1.63	1.86	1.62	Ba	1.82	2.07	1.92
F	3.82	3.30	3.66	Sr	0.02	0	0
CI	n.d.	<0.1	n.d.	K	0.07	0.07	0
$-O=F_2,Cl_2$	1.61	1.39	1.54	$\Sigma 2A^{P}$	1.91	2.14	1.92
Total	97.10	98.43	97.61				
				Σcations	11.90	11.98	11.94
				F	2.11	1.82	2.07
				ОН	1.89	2.18	1.93
				$\Sigma 2X^{P}_{M} + 2X^{O}$	<sup>0</sup> <sub>A</sub> 4.00	4.00	4.00

TABLE 2. Chemical composition and unit formula\* for hejtmanite.

n.d. - not detected;

\* calculated on anion basis: O + F = 20 a.p.f.u.;

\*\* calculated from structure solution and refinement (this work) and by crystallochemical calculations (Vrána *et al.*, 1992): OH + F = 4 a.p.f.u.

	This work	Vrána <i>et al</i> . (1992)
a (Å)	10.716(2)	10.698(4)
b	13.795(3)	13.768(5)
С	11.778(2)	11.748(4)
α (°)	90.07(3)	90
β	112.24(3)	112.27(2)
γ	90.03(3)	90
V (Å <sup>3</sup> )	1612(2)	1601(2)
Space group	CĪ	C*/* (diffraction symbol)
Ζ	4	4
Absorption coefficient (mm <sup>-1</sup> )	9.00	
<i>F</i> (000)	1885.8	
$D_{\text{calc.}}$ (g/cm <sup>3</sup> )	4.189	4.29
Crystal size (mm)	0.004 x 0.025 x 0.040	
Second component*	0.474(1)	
Radiation/monochromator	MoKα/graphite	
2θ-range for data collection (°)	60.28	
<i>R</i> (int) (%)	1.32	
Reflections collected	9468	
Independent reflections $F_{o} > 4\sigma F$	4748 4539	
Refinement method	Full-matrix least square fixed weights proportion	es on $F^2$ , nal to $1/\sigma F_o^2$
No. of refined parameters	308	
Final R indices (%)		
$R_1 (F_o > 4\sigma F)$	1.88	
$R_1$	2.05	
wR <sub>2</sub>	5.11	
Goodness of fit on $F^2$	1.090	

TABLE 3. Miscellaneous refinement data for hejtmanite.

\*Second component of the crystal is related to the first component by the twin matrix [100  $0\overline{10}$  001].

TABLE 4. Atom coordinates and anisotropic displacement parameters (Å<sup>2</sup>) for hejtmanite.

Atom	x	у	Z	U <sub>11</sub>	U <sub>22</sub>	<i>U</i> <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	<i>U</i> <sub>12</sub>	$U_{ m eq}$
M <sup>υ</sup> (1)	0	0	0	0.0071(5)	0.0103(5)	0.0145(5)	-0.0002(4)	0.0048(4)	0.0008(4)	0.0104(3)
M <sup>0</sup> (2)	0.24447(4)	0.12358(6)	-0.01128(4)	0.0082(2)	0.0102(2)	0.0121(2)	0.0003(4)	0.00394(15)	-0.0001(3)	0.01016(12)
M <sup>0</sup> (3)	0.25626(4)	0.87317(6)	0.00822(4)	0.0087(2)	0.0104(2)	0.0114(2)	-0.0002(4)	0.00396(14)	0.0001(4)	0.01009(12)
M <sup>0</sup> (4)	0.99575(5)	0.75166(3)	0.99334(5)	0.0084(5)	0.0123(4)	0.0164(5)	0.0036(3)	0.0026(3)	-0.0001(3)	0.0130(3)
M <sup>0</sup> (5)	1/2	0	0	0.0064(5)	0.0193(6)	0.0255(7)	-0.0109(5)	0.0023(4)	0.0023(4)	0.0182(3)
M <sup>H</sup> (1)	0.46397(5)	0.60457(4)	0.71450(5)	0.0039(2)	0.0085(3)	0.0059(2)	0.00001(17)	0.00229(17)	0.00015(17)	0.00598(16)
М <sup>н</sup> (2)	0.53708(5)	0.85658(4)	0.28856(5)	0.0038(2)	0.0094(4)	0.0061(2)	0.00073(18)	0.00235(17)	0.00029(18)	0.00627(17)
Si(1)	0.28264(14)	0.01493(9)	0.24821(13)	0.0077(5)	0.0061(5)	0.0072(5)	-0.0002(4)	0.0018(4)	0.0010(4)	0.0073(3)
Si(2)	0.71633(14)	0.76433(9)	0.75030(13)	0.0064(5)	0.0085(5)	0.0069(5)	0.0004(4)	0.0031(4)	0.0003(4)	0.0071(2)
Si(3)	0.74114(14)	0.48385(9)	0.74999(13)	0.0069(5)	0.0066(5)	0.0069(5)	-0.0002(4)	0.0028(4)	-0.0004(4)	0.0067(2)
Si(4)	0.26032(14)	0.73678(9)	0.24969(13)	0.0085(5)	0.0077(5)	0.0073(5)	0.0008(4)	0.0029(4)	-0.0001(4)	0.0079(3)
$A^{P}(1)$	0.61130(2)	0.62440(2)	0.46823(1)	0.00851(8)	0.01261(9)	0.00841(8)	0.00013(16)	0.00315(6)	0.00035(16)	0.00986(5)
A <sup>P</sup> (2)	0.38948(2)	0.87832(3)	0.53561(2)	0.00985(9)	0.03465(14)	0.01072(10)	-0.0004(2)	0.00416(7)	-0.0019(2)	0.01833(7)
O(1)	0.4168(3)	0.95191(19)	0.3214(2)	0.0104(11)	0.0170(13)	0.0123(12)	0.0018(10)	0.0052(9)	0.0042(10)	0.0130(5)
O(2)	0.6702(3)	0.5008(2)	0.3061(2)	0.0123(12)	0.0140(13)	0.0152(12)	-0.0008(11)	0.0102(10)	-0.0020(10)	0.0123(5)
O(3)	0.2192(4)	1.0000(3)	0.1006(3)	0.0085(14)	0.0152(15)	0.0039(15)	-0.0002(12)	-0.0001(11)	0.0003(11)	0.0099(7)
O(4)	0.6560(19)	0.87436(18)	0.72513(17)	0.0107(8)	0.0095(9)	0.0104(9)	0.0000(10)	0.0031(7)	-0.0011(10)	0.0105(4)
O(5)	0.6724(3)	0.7532(2)	0.3096(3)	0.0108(12)	0.0162(13)	0.0144(12)	0.0066(11)	0.0064(9)	0.0040(11)	0.0133(5)
O(6)	0.7838(4)	0.7504(2)	0.8986(4)	0.0099(14)	0.0083(14)	0.0107(16)	0.0006(12)	0.0048(12)	0.0006(11)	0.0094(7)
O(7)	0.5829(3)	0.69880(18)	0.6825(2)	0.0136(12)	0.0127(12)	0.0129(12)	-0.0016(10)	0.0069(9)	-0.0033(10)	0.0126(5)
O(8)	0.8186(3)	0.54787(18)	0.6829(3)	0.0112(12)	0.0147(13)	0.0145(12)	0.0000(11)	0.0062(9)	-0.0025(10)	0.0131(5)
O(9)	0.5806(2)	0.50058(19)	0.6939(2)	0.0077(11)	0.0156(13)	0.0137(12)	-0.0021(10)	0.0032(9)	0.0020(9)	0.0126(5)
O(10)	0.7975(4)	0.4969(3)	0.8984(3)	0.0106(15)	0.0143(15)	0.0053(15)	-0.0016(12)	0.0013(12)	0.0005(11)	0.0106(7)
O(11)	0.27786(19)	0.87280(19)	0.72202(17)	0.0112(8)	0.0086(9)	0.0118(9)	0.0007(10)	0.0049(7)	0.0002(10)	0.0104(4)
O(12)	0.2056(4)	0.7507(2)	0.101(4)	0.0096(15)	0.0090(14)	0.0103(16)	0.0003(12)	0.0051(12)	0.0001(11)	0.0092(7)
O(13)	0.4205(2)	0.75272(19)	0.3126(2)	0.0086(11)	0.0148(13)	0.0150(12)	0.0038(11)	0.0032(9)	-0.0000(10)	0.0132(5)
O(14)	0.3162(3)	0.69775(18)	0.6804(2)	0.0105(12)	0.0141(12)	0.01248	-0.0021(10)	0.0046(9)	0.0026(10)	0.0123(5)
X <sup>0</sup> <sub>M</sub> (1)	0.5347(2)	0.6161(3)	0.87959(19)	0.0094(9)	0.0158(14)	0.0096(9)	-0.0004(12)	0.0047(7)	-0.0016(11)	0.0113(5)
X <sup>0</sup> <sub>M</sub> (2)	0.4650(2)	0.8656(3)	0.12430(19)	0.0100(9)	0.0163(4)	0.0109(9)	-0.0020(12)	0.0040(7)	0.0000(12)	0.0123(5)
X <sup>0</sup> <sub>A</sub> (1)	-0.0432(2)	0.1243(3)	0.08664(18)	0.0135(9)	0.0118(10)	0.0106(9)	0.0008(15)	0.0043(7)	0.0013(16)	0.0120(4)
X <sup>0</sup> <sub>A</sub> (2)	0.45556(19)	0.1270(3)	0.07877(18)	0.0101(9)	0.0134(10)	0.0093(9)	-0.0002(16)	0.0031(7)	0.0003(16)	0.0111(4)
X <sup>P</sup> <sub>M</sub> (1)	0.61734(19)	0.40573(16)	0.47686(18)	0.0122(9)	0.0277(11)	0.0089(9)	-0.0012(7)	0.0040(7)	0.0004(8)	0.0162(4)
X <sup>P</sup> <sub>M</sub> (2)	0.61551(19)	0.85348(19)	0.48003(17)	0.0134(9)	0.0449(17)	0.0079(9)	0.0002(9)	0.0038(7)	0.0009(9)	0.0221(6)
H(1)	-0.003(3)	0.142(3)	0.1730(14)	0.01445*						
H(2)	0.494(3)	0.146(3)	0.1652(14)	0.01334*						

TABLE 5. Selected interatomic distances (Å) and angles (°) in hejtmanite.

				( )	<b>v</b> (	, ,	
M <sup>o</sup> (1)–X <sup>o</sup> <sub>A</sub> (1) M <sup>o</sup> (1)–O(3)a M <sup>o</sup> (1)–X <sup>o</sup> <sub>M</sub> (1)b <m<sup>o(1)–φ&gt;</m<sup>	2.133(4) x2 2.194(4) x2 2.262(3) x2 2.196	2 2 2	$\begin{array}{l} M^{O}(2) - X^{O}_{A}(2) \\ M^{O}(2) - X^{O}_{M}(1)b \\ M^{O}(2) - O(6)b \\ M^{O}(2) - O(10)b \\ M^{O}(2) - O(3)a \\ M^{O}(2) - O(6)c \\ < M^{O}(2) - \phi > \end{array}$	2.104(2) 2.128(2) 2.170(4) 2.228(4) 2.234(4) <u>2.275(4)</u> 2.190	_	$\begin{array}{l} M^{\rm O}(3) - X^{\rm O}_{\rm A}(1)d \\ M^{\rm O}(3) - X^{\rm O}_{\rm M}(2) \\ M^{\rm O}(3) - O(3) \\ M^{\rm O}(3) - O(12) \\ M^{\rm O}(3) - O(12)e \\ M^{\rm O}(3) - O(10)f \\ M^{\rm O}(3) - \phi > \end{array}$	2.129(2) 2.137(2) 2.174(4) 2.192(4) 2.270(4) <u>2.284(4)</u> 2.198
$\begin{array}{l} M^{O}(4) - X^{O}_{A}(1)c \\ M^{O}(4) - X^{O}_{A}(2)g \\ M^{O}(4) - O(6) \\ M^{O}(4) - O(12)h \\ M^{O}(4) - X^{O}_{M}(2)j \\ M^{O}(4) - X^{O}_{M}(1)i \\ < M^{O}(4) - \phi > \end{array}$	2.107(4) 2.118(4) 2.118(4) 2.123(4) 2.270(3) <u>2.458(3)</u> 2.199		M <sup>O</sup> (5)–O(10)b M <sup>O</sup> (5)–X <sup>O</sup> <sub>A</sub> (2) M <sup>O</sup> (5)–X <sup>O</sup> <sub>M</sub> (2)a <m<sup>O(5)–φ&gt;</m<sup>	2.044(4) 2.119(4) 2.479(3) 2.214	x2 x2 x2		
$\begin{array}{l} M^{H}(1) - X^{O}_{M}(1) \\ M^{H}(1) - O(7) \\ M^{H}(1) - O(14) \\ M^{H}(1) - O(9) \\ M^{H}(1) - O(2)c \\ M^{H}(1) - X^{\mathcal{P}}_{M}(1)c \\ < M^{H}(1) - \varphi \\ \end{array}$	1.807(2) 1.954(3) 1.960(3) 1.977(3) 1.994(3) 2.091(5) 1.964		$\begin{array}{l} M^{H}(2) - X^{O}_{M}(2) \\ M^{H}(2) - O(8)j \\ M^{H}(2) - O(1) \\ M^{H}(2) - O(5) \\ M^{H}(2) - O(13) \\ M^{H}(2) - X^{P}_{M}(2) \\ < M^{H}(2) - \phi > \end{array}$	1.796(2) 1.961(3) 1.980(3) 1.982(3) 1.990(3) 2.088(2) 1.960	_	Si(1)–O(2)k Si(1)–O(1)a Si(1)–O(3)a Si(1)–O(4)c <si(1)–o></si(1)–o>	1.605(3) 1.622(3) 1.622(4) <u>1.645(3)</u> 1.624
Si(2)–O(5)j Si(2)–O(7) Si(2)–O(6) Si(2)–O(4) <si(2)–o></si(2)–o>	1.617(3) 1.623(3) 1.629(4) <u>1.633(3)</u> 1.626		Si(3)–O(9)k Si(3)–O(8)r Si(3)–O(10) Si(3)–O(11)l <si(3)–o></si(3)–o>	1.609(3) 1.610(3) 1.628(4) <u>1.645(3)</u> 1.623	_	Si(4)–O(13) Si(4)–O(12) Si(4)–O(11)m Si(4)–O(14)m <si(4)–o></si(4)–o>	1.607(3) 1.630(4) 1.633(3) <u>1.636(3)</u> 1.627
$\begin{array}{l} A^{P}(1) - X^{P}_{M}(2)j \\ A^{V}(1) - X^{V}_{M}(1)c \\ A^{P}(1) - O(13) \\ A^{P}(1) - O(2) \\ A^{P}(1) - O(2) \\ A^{P}(1) - O(9)c \\ A^{P}(1) - O(5) \\ A^{P}(1) - O(7) \\ A^{$	2.772(2) 2.792(2) 2.801(3) 2.803(3) 2.804(3) 2.830(3) 2.844(3) 2.864(3) 3.018(2) 3.163(3) 3.235(3) 3.280(3) 2.934		$\begin{array}{l} A^{P}(2)-X^{P}_{M}(1)n\\ A^{P}(2)-X^{P}_{M}(2)l\\ A^{P}(2)-O(1)\\ A^{P}(2)-O(14)m\\ A^{P}(2)-O(11)\\ A^{P}(2)-O(4)\\ A^{P}(2)-O(4)\\ A^{P}(2)-O(1)o\\ A^{P}(2)-O(13)\\ A^{P}(2)-O(13)\\ A^{P}(2)-O(14)\\ A^{P}(2)-O(14)\\ A^{P}(2)-O(2)n\\ $	2.757(2) 2.759(2) 2.836(3) 2.860(3) 2.871(2) 2.884(2) 3.158(3) 3.170(3) 3.265(3) 3.274(3) 3.279(3) 3.300(3) 3.034	_	Si(1)c-O(4)-Si(2) Si(3)n-O(11)-Si(4)n <si-o-si></si-o-si>	136.6(1) 136.4(1) 136.5

a: x, y–1, z; b: x–1/2, y–1/2, z–1; c: –x+1, –y+1, –z+1; d: –x, –y+1, –z; e: –x+1/2, –y+3/2, –z; f: x–1/2, y+1/2, z–1; g: x+1/2, y+1/2, z+1; h: x+1, y, z+1; i: –x+3/2, –y+3/2, –z+2; j: –x+3/2, –y+3/2, –z+1; k: x–1/2, y–1/2, z; l: x+1/2, y–1/2, z; m: –x+1/2, –y+3/2, –z+1; n: x–1/2, y+1/2, z; o: –x+1, –y+2, –z+1

Site *	Refined site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	<Χ-φ> <sub>obs</sub> .** (Å)	Ideal composition (a.p.f.u.)
		Cations			
<i>M</i> <sup>0</sup> (1)	12.70(6)			2.196	Mn <sub>0.5</sub>
<i>M</i> <sup>O</sup> (2)	25.94(7)	24		2.190	Mn
<i>M</i> <sup>O</sup> (3)	25.85(7)	2.23 Mn + 1.65 Fe <sup>2+</sup> + 0.04 Zn + 0.03 Mg + 0.05 □	I	2.198	Mn
<i>M</i> <sup>O</sup> (4)	26.05(10)			2.199	Mn
M <sup>O</sup> (5)	12.96(6)			2.214	Mn <sub>0.5</sub>
Σ <i>Μ</i> <sup>0</sup> (1-5)	103.50	2.23 Mn + 1.65 Fe <sup>2+</sup> + 0.04 Zn + 0.03 Mg + 0.05 □	100.61		Mn <sub>4</sub>
<i>M</i> <sup>H</sup> (1)	22.62(7)			1.964	Ti
<i>M</i> <sup>H</sup> (2)	22.56(6)	1.88 Ti + 0.10 Nb + 0.02 Zr		1.960	Ti
Σ <i>M</i> <sup>H</sup> (1,2)	45.18	1.88 Ti + 0.10 Nb + 0.02 Zr	46.26		Ti <sub>2</sub>
<sup>[12]</sup> <i>A<sup>P</sup></i> (1)	55.21(10)	0.93 Ba + 0.02 Sr + 0.05 □	52.84	2.934	Ва
<sup>[12]</sup> <i>A<sup>P</sup></i> (2)	53.48(10)	0.89 Ba + 0.07 K + 0.04 □	51.17	3.034	Ва
Σ <i>A<sup>P</sup></i> (1,2)	108.69	1.82 Ba + 0.07 K + 0.02 Sr + 0.09 □	104.01		Ba <sub>2</sub>
		Anions			
$\Sigma X^{O}{}_{M}(1,2)$		2.00 O			O <sub>2</sub>
$\Sigma X^{O}_{A}(1,2)$		1.89 OH + 0.11 F			(OH) <sub>2</sub>
Σ <i>X</i> <sup>P</sup> <sub>M</sub> (1,2)		2.00 F			F <sub>2</sub>

TABLE 6. Refined site-scattering values and assigned site-populations for hejtmanite.

\* coordination number is given only for non-[6]-coordinated sites; \*\* X = cation,  $\phi$  = O, OH, F;

Atom	M <sup>0</sup> (1)	M <sup>0</sup> (2)	M <sup>0</sup> (3)	M <sup>0</sup> (4)	M <sup>0</sup> (5)	М <sup>н</sup> (1)	M <sup>H</sup> (2)	A <sup>P</sup> (1)	A <sup>P</sup> (2)	Σ
Х <sup>о</sup> <sub>м</sub> (1)	0.28	0.39		0.17		1.00				1.84
X <sup>0</sup> <sub>M</sub> (2)			0.38	0.27	0.17		1.03			1.85
<sup>[3]</sup> X <sup>O</sup> <sub>A</sub> (1)	0.38		0.39	0.41						1.18
<sup>[3]</sup> X <sup>O</sup> <sub>A</sub> (2)		0.42		0.40	0.40					1.22
X <sup>P</sup> <sub>M</sub> (1)						0.34		0.18 0.13	0.19	0.84
X <sup>P</sup> <sub>M</sub> (2)						0.34		0.19 0.10	0.19	0.82

TABLE 7. Bond-valence values\* for selected anions in heitmanite.

\* Bond-valence parameters (vu) are from Brown (1981); bond-valence values calculated for  $M^{O} = Mn$ ;  $M^{H} = Ti$ ;  $A^{P} = Ba$ ; coordination numbers are shown for non-4-coordinated anions.

		•		
D–HA	D–H (Å)	HA (Å)	DA (Å)	∠ DHA (°)
X <sup>0</sup> <sub>A</sub> (1)OH–H(1)…O(5)a	0.98(1)	2.48(3)	3.285(4)	140(3)
X <sup>O</sup> <sub>A</sub> (1)OH–H(1)O(9)a	0.98(1)	2.59(3)	3.339(4)	133(3)
X <sup>0</sup> <sub>A</sub> (2)OH–H(2)O(11)b	0.98(1)	2.31(3)	2.931(3)	120(3)
X <sup>O</sup> <sub>A</sub> (2)OH–H(2)O(4)b	0.98(1)	2.43(3)	2.976(3)	115(3)

TABLE 8. Hydrogen bonding in hejtmanite.

a: x-1/2, y-1/2, z; b: -x+1, -y+1, -z+1.



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