

# From structure topology to chemical composition. XX. Titanium silicates: the crystal structure of hejtmanite, $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ , a Group-II TS-block mineral

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## ABSTRACT

The crystal structure of hejtmanite,  $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ , from Mbolve Hill, 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  $[|F| > 4\sigma(F)]$  reflections. Hejtmanite is triclinic,  $C1$ ,  $a = 10.716(2)$ ,  $b = 13.795(3)$ ,  $c = 11.778(2)$  Å,  $\alpha = 90.07(3)$ ,  $\beta = 112.24(3)$ ,  $\gamma = 90.03(3)^\circ$ ,  $V = 1612(2)$  Å<sup>3</sup>. Chemical analysis (electron microprobe) gives: Ta<sub>2</sub>O<sub>5</sub> 0.09, Nb<sub>2</sub>O<sub>5</sub> 1.27, ZrO<sub>2</sub> 0.65, 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 3.82, H<sub>2</sub>O<sub>calc.</sub> 1.63, O = F – 1.61, total 97.10 wt.%, where the H<sub>2</sub>O content was calculated from the crystal-structure refinement, with (OH + F) = 4 apfu. The empirical formula, calculated on the basis of 20 (O + F) anions, is of the form  $A_2^p M_4^o M^h (\text{Si}_2\text{O}_7)_2 (\text{X}^o)_4 (\text{X}^p)_2$ ,  $Z = 4$ :  $(\text{Ba}_{1.82}\text{K}_{0.07}\text{Sr}_{0.02})_{\Sigma 1.91}(\text{Mn}_{2.33}\text{Fe}_{1.65}^{2+}\text{Zr}_{0.04}\text{Mg}_{0.03})_{\Sigma 3.95}(\text{Ti}_{1.88}\text{Nb}_{0.10}\text{Zr}_{0.02})_{\Sigma 2}(\text{Si}_{2.02}\text{O}_7)_2\text{O}_2[(\text{OH})_{1.89}\text{F}_{0.11}]_{\Sigma 2}\text{F}_2$ . The crystal structure 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 topology of the TS block is as in Group-II TS-block minerals: Ti (+ Nb) = 2 apfu per  $(\text{Si}_2\text{O}_7)_2$  [as defined by Sokolova (2006)]. In the O sheet, five  $^{[6]}M^O$  sites are occupied mainly by Mn, less Fe<sup>2+</sup> and minor Zr and Mg, with  $\langle M^O-\varphi \rangle = 2.198$  Å ( $\varphi = \text{O}, \text{OH}$ ), ideally giving Mn<sub>4</sub> apfu. In the H sheet, two  $^{[6]}M^H$  sites are occupied mainly by Ti, with  $\langle M^H-\varphi \rangle = 1.962$  Å ( $\varphi = \text{O}, \text{F}$ ), ideally giving Ti<sub>2</sub> apfu; four  $^{[4]}Si$  sites are occupied by Si, with  $\langle \text{Si}-\text{O} \rangle = 1.625$  Å. The M<sup>H</sup> octahedra and Si<sub>2</sub>O<sub>7</sub> groups constitute the H sheet. The two  $^{[12]}Ba$ -dominant  $A^P(1,2)$  sites, with  $\langle A^P-\varphi \rangle = 2.984$  Å ( $\varphi = \text{O}, \text{F}$ ), ideally give Ba<sub>2</sub> apfu. Two  $X_M^O(1,2)$  and two  $X_A^O(1,2)$  sites are occupied by O atoms and OH groups with minor F, respectively, ideally giving  $(X^O)_4 = (X_M^O)_2 + (X_A^O)_2 = \text{O}_2(\text{OH})_2$  pfu. Two  $X_M^P(1,2)$  sites are occupied by F, giving F<sub>2</sub> apfu. TS blocks link via a layer of Ba atoms which constitute the I block. Simplified and end-member formulae of hejtmanite are  $\text{Ba}_2(\text{Mn}, \text{Fe}^{2+})_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH}, \text{F})_2\text{F}_2$  and  $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ ,  $Z = 4$ . Hejtmanite is a Mn-analogue of bafertsite,  $\text{Ba}_2\text{Fe}_4^{2+}\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ .

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

## Introduction

SEMENOV and Zhang Peishan (1959) described bafertsite,  $\text{BaFe}_2\text{TiSi}_2\text{O}_9$ ,  $Z = 2$ , as a new mineral from the Bayan Obo rare-earth element (REE) deposit, Inner Mongolia, China. The crystal

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structure of bafertisite from the Bayan Obo deposit was determined by (1) Guan *et al.* (1963) and (2) Peng Zhizhong and Shen Jinchuan (1963): [1] monoclinic, space group  $Cm$ ,  $a = 10.60$ ,  $b = 13.64$ ,  $c = 12.47$  Å,  $\beta = 119.5^\circ$ , [2] monoclinic, space group  $P2_1/m$ ,  $a = 10.98$ ,  $b = 6.80$ ,  $c = 5.36$  Å,  $\beta = 94^\circ$ . Based on the structure-refinement results, Guan *et al.* (1963) and Peng Zhizhong and Shen Jinchuan (1963) gave the chemical formula of bafertisite as follows:  $BaFe_2Ti[Si_2O_7]O(OH)_2$ ,  $Z = 8$  and 2, respectively. Vrána *et al.* (1992) described hejtmanite from Mbolve Hill, Mkushi River area, Central Province, Zambia, as a manganese-dominant analogue of bafertisite: monoclinic, diffraction symbol  $C^*/*$ ,  $a = 10.698(4)$ ,  $b = 13.768(5)$ ,  $c = 11.748(4)$  Å,  $\beta = 112.27(2)^\circ$ ,  $V = 1601(2)$  Å<sup>3</sup>,  $D_{meas.} = 4.02$  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, 1959; Guan *et al.*, 1963; Peng Zhizhong and Shen Jinchuan, 1963), gave simplified and endmember formulae  $Ba(Mn,Fe)_2TiO(Si_2O_7)(OH, F)_2$  and  $BaMn_2TiO(Si_2O_7)(OH, F)_2$ ,  $Z = 8$ . Pautov (pers comm., 1989; in Minerals. Handbook. Silicates, 1996) reported the occurrence of a Mn-analogue of bafertisite in a rhodonite-tephroite-spessartine-quartz association from the Muzeinoe gorge, the Inyl'chek mountain ridge, Tyan-Shan, South-Eastern Kirgizia, and gave its empirical and general formulae,  $(Ba_{0.96}Na_{0.03}Ca_{0.01}Cs_{0.002})_{\Sigma 1}(Mn_{1.70}Fe_{0.17}Mg_{0.05}Al_{0.08})_{\Sigma 2}(Ti_{0.93}Sn_{0.07}Nb_{0.015})_{\Sigma 1.01}(Si_{1.97}Al_{0.02})_{\Sigma 1.99}O_7O_{2.09}(H_2O)_{0.25}$  and  $BaMn_2TiO(Si_2O_7)(OH)_2$ , respectively. All the crystals of the material from Inyl'chek were extensively twinned, and complicated the structure work. Sokolova *et al.* (1989) reported the unit cell for the Mn-analogue of bafertisite from the Inyl'chek mountain ridge,  $BaMn_2TiO(Si_2O_7)(OH)_2$ : triclinic, space groups  $P1$  or  $P\bar{1}$ ,  $a = 10.767(7)$ ,  $b = 13.858(9)$ ,  $c = 32.99(6)$  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 for the monoclinic subcell: space group  $Pm$ ,  $a = 5.374(3)$ ,  $b = 6.911(3)$ ,  $c = 32.82(1)$  Å,  $\beta = 94.62(4)^\circ$ ,  $V = 1214(2)$  Å<sup>3</sup>,  $R = 19.89\%$ . They showed that the general topology of the structure of the Mn-analogue of bafertisite from the Inyl'chek mountain ridge is identical to that of bafertisite (Guan *et al.*, 1963). Rastsvetaeva *et al.* (1991) collected new X-ray diffraction data using the crystal of the Mn-analogue of bafertisite from the Inyl'chek mountain ridge previously studied by Sokolova *et al.* (1989). They considered the crystal in question to be an intergrowth of two 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  $Cm$ ,  $a = 10.723$ ,  $b = 13.812$ ,  $c = 12.563$  Å,  $\beta = 119.9^\circ$ ,  $V = 1613$  Å<sup>3</sup>,  $Z = 8$ ,  $R = 8.3\%$ ; both phases are isostructural with bafertisite [cf.  $P2_1/m$  and  $Cm$  bafertisite structures of Peng Zhizhong and Shen Jinchuan (1963) and Guan *et al.* (1963), respectively]. However, both structures of Rastsvetaeva *et al.* (1991) have Si–O distances that are too short: (1) space group  $P2_1/m$ : 1.54 Å; and (2) space group  $Cm$ : 1.49 Å. These distances imply significant errors in both structures. The problems with the crystal structure of hejtmanite arise from the poor quality of its crystals, which is related to the extensive twinning [cf. bafertisite, Cámara *et al.* (2015b)] and possible intergrowths with other phases, a common problem with TS-block minerals. Based on the structure work of Rastsvetaeva *et al.* (1991), Sokolova (2006) and Sokolova and Cámara (2013) considered hejtmanite a TS-block mineral with two modifications: hejtmanite-C (space group  $Cm$ ) and hejtmanite-P (space group  $P2_1/m$ ).

The TS (Titanium Silicate) block is the main structural unit in the fast-growing family of 40 minerals: 34 minerals are listed in Sokolova and Cámara (2013), and information on six minerals, kolskyite, emmerichite, saamite, betalomonosovite, bobshannonite and fogoite-(Y) can be found in Cámara *et al.* (2013), Aksenov *et al.* (2014), Cámara *et al.* (2014a), Sokolova *et al.* (2015a, b) and Cámara *et al.* (2015a), respectively [cf. 24 minerals (Sokolova, 2006)]. The TS block consists of a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5–7]-coordinated polyhedra and  $Si_2O_7$  groups. The TS block is characterized by a planar cell based on minimal lengths of translational vectors,  $t_1 \approx 5.5$  and  $t_2 \approx 7$  Å, and  $t_1 \wedge t_2 \approx 90^\circ$ . The general formula of the TS block is  $A_2^P B_2^P M_2^H M_4^O (Si_2O_7)_2 X_{4+n}$ , where  $M_2^H$  and  $M_4^O$  = cations of the H and O sheets;  $M^H = Ti, Nb, Zr, Y, Mn, Ca + REE, Ca$ ;  $M^O = Ti, Zr, Nb, Fe^{2+}, Fe^{3+}, Mg, Mn, Ca, Na$ ;  $A^P$  and  $B^P$  = cations at the peripheral (P) sites = Na, Ca + REE, Ca, Ba, Sr, K; X = anions, O, OH, F and H<sub>2</sub>O groups;  $X_{4+n} = X_4^O + X_n^P$ ,  $n = 0, 1, 1.5, 2, 4$ , where  $X_4^O$  = anions of the O sheet which do not coordinate Si atoms,  $X_n^P$  = anions at the periphery of the TS block; X = O, OH, F, H<sub>2</sub>O (Sokolova and Cámara, 2013). Sokolova (2006) developed general structural principles for the TS-block minerals. There are three topologically distinct TS blocks based on three types of linkage of H and O sheets. In the crystal structures of TS-block minerals, TS blocks either link directly

or alternate with intermediate (**I**) blocks. The **I** block consists of alkali and alkaline-earth cations, oxyanions ( $\text{PO}_4$ ), ( $\text{SO}_4$ ) and ( $\text{CO}_3$ ) and  $\text{H}_2\text{O}$  groups. Sokolova (2006) divided TS-block structures into four Groups, based on the topology and stereochemistry of the TS block. Each group of structures has a different linkage, content and stereochemistry of Ti (+ Nb + Zr +  $\text{Fe}^{3+}$  + Mg + Mn) per  $(\text{Si}_2\text{O}_7)_2$ . In Group I, Ti (+ Nb + Zr) = 1 atom per formula unit (apfu); in Group II, Ti (+ Nb) = 2 apfu; in Group III, Ti (+ Nb + Mg +  $\text{Fe}^{3+}$ ) = 3 apfu; in Group IV, Ti (+ Mg + Mn) = 4 apfu. In a TS-block structure, four types of self-linkage between adjacent TS blocks occur.

Sokolova and Cámara (2013) introduced the concept of ‘basic’ and ‘derivative structures’ for TS-block minerals. A basic structure has the following four characteristics: (1) there is only one type of TS block; (2) the two H sheets of the TS block are identical; (3) there is only one type of **I** block or it is absent; (4) there is only one type of self-linkage of TS blocks. Basic structures obey the general structural principles laid out by Sokolova (2006). A derivative structure has one or more of the three following characteristics: (1) there is more than one type of TS block; (2) there is more than one type of **I** block; (3) there is more than one type of self-linkage of TS blocks. A derivative structure is related to two or more basic structures of the same Group: it can be derived by adding these structures via sharing the central O sheet of the TS blocks of adjacent structural fragments which represent basic structures. There are 35 basic TS-block structures and five derivative TS-block structures.

Following our continued interest in TS-block minerals, we felt strongly that the crystal structure of hejtmanite must be solved and refined on the holotype material of Vrána *et al.* (1992). We studied hejtmanite from: (1) Mbolve Hill, Mkushi River area, Central Province, Zambia (holotype material from the collection of Leonid A. Pautov, given to Leonid by Stanislav Vrána); and (2) from the Muzeinoe gorge, the Inyl’chek mountain ridge, Tyan-Shan, South-Eastern Kirgizia. The current paper reports the crystal structure and structural formula of hejtmanite,  $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ , a TS-block mineral of Group II where Ti (+ Nb) = 2 apfu per  $(\text{Si}_2\text{O}_7)_2$  (Table 1).

## Chemical composition

Crystals of hejtmanite were analysed with a Cameca SX-100 electron microprobe operating in

wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA and a beam diameter of 10  $\mu\text{m}$ . The following standards were used: Si: diopside; Ta:  $\text{Mn}(\text{Ta}_{1.70}\text{Nb}_{0.30})\text{O}_6$ ; Nb, Ba:  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ ; Zr: zircon; Ti: titanite; Fe: fayalite; Mn: spessartine; Mg: forsterite; Sn: cassiterite; Sr:  $\text{SrTiO}_3$ ; Cs: pollucite; K: orthoclase; F: fluorite. The elements Na, Al, Zn, Ca, Pb, Rb and Cl were sought but not detected. The data were reduced and corrected by the *PAP* method of Pouchou and Pichoir (1985). The  $\text{H}_2\text{O}$  (presence of OH groups confirmed by IR spectroscopy, Vrána *et al.*, 1992) was calculated from the results of the crystal-structure analysis on the basis that  $\text{F} + \text{OH} = 4$  apfu. Table 2 gives the chemical composition of hejtmanite from Zambia (holotype material) compared with its original chemical analysis (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  $\text{A}_2^p\text{M}_4^q\text{M}_2^h(\text{Si}_2\text{O}_7)_2(\text{X}^o)_4(\text{X}^p)_2$ ,  $Z = 4$ . For hejtmanite from Zambia (holotype), it is  $(\text{Ba}_{1.82}\text{K}_{0.07}\text{Sr}_{0.02})_{\Sigma 1.91}(\text{Mn}_{2.33}\text{Fe}_{1.65}^{2+}\text{Zr}_{0.04}\text{Mg}_{0.03})_{\Sigma 3.95}(\text{Ti}_{1.88}\text{Nb}_{0.10}\text{Zr}_{0.02})_{\Sigma 2}(\text{Si}_{2.02}\text{O}_7)_2\text{O}_2[(\text{OH})_{1.89}\text{F}_{0.11}]_{\Sigma 2}\text{F}_2$ ,  $D_{\text{calc.}} = 4.189 \text{ g/cm}^3$  and is in accord with  $D_{\text{meas.}} = 4.02 \text{ g/cm}^3$  (Vrána *et al.*, 1992). For hejtmanite from Inyl’chek, Kirgizia, it is  $\text{Ba}_{1.92}(\text{Mn}_{3.62}\text{Fe}_{0.25}^{2+}\text{Mg}_{0.08}\text{Zr}_{0.02})_{\Sigma 3.97}(\text{Ti}_{1.59}\text{Sn}_{0.42})_{\Sigma 2.01}(\text{Si}_{2.02}\text{O}_7)_2\text{O}_2[(\text{OH})_{1.93}\text{F}_{0.07}]_{\Sigma 2}\text{F}_2$ ,  $D_{\text{calc.}} = 4.189 \text{ g/cm}^3$ . Hejtmanite from Inyl’chek, Kirgizia, is characterized by very high MnO, significant  $\text{SnO}_2$ , lower  $\text{TiO}_2$  and lack of  $\text{Nb}_2\text{O}_5$ : 23.91, 5.95, 11.82 and 0 wt.%, respectively, *cf.* 14.12, 0, 14.35 and 1.27 wt.%, respectively (hejtmanite from Zambia, this work) (Table 2). By analogy with Sn-rich astrophyllite where  $\text{Sn}^{4+}$  constitutes ~ 31% of the Ti-dominant *D* site in the H sheet of the HOH block (Cámara *et al.*, 2010), we assigned all  $\text{Sn}^{4+}$  to the Ti-dominant *M*<sup>H</sup> site in the H sheet of the TS block (Table 2):  $(\text{Ti}_{1.59}\text{Sn}_{0.42})_{\Sigma 2.01}$  apfu. Simplified and end-member formulae of hejtmanite are  $\text{Ba}_2(\text{Mn}, \text{Fe}^{2+})_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH}, \text{F})_2\text{F}_2$  and  $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ ,  $Z = 4$ .

## Crystal structure

### Data collection and structure refinement

Single-crystal X-ray data for hejtmanite from Zambia were collected using a Bruker APEX II ULTRA three-circle diffractometer with a rotating-anode generator ( $\text{MoK}\alpha$ ), multilayer optics and an APEX II 4 K CCD detector. The intensities of 4539 [ $|F| > 4\sigma |F|$ ] reflections with  $-15 < h < 15$ ,

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

Mineral	Formula								<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Sp. gr.	<i>Z</i>	Ref.
	<i>A</i> <sup><i>P</i></sup> <sub>1-2</sub>	<i>B</i> <sup><i>P</i></sup> <sub>0-2</sub>	<b>M<sup>O</sup></b>	<b>M<sup>H</sup></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	<b>(X<sub>M</sub><sup>O</sup>)<sub>2</sub></b>	<b>(X<sub>A</sub><sup>O</sup>)<sub>2</sub></b>	(X <sup><i>P</i></sup> <sub>M</sub> ) <sub>0-2</sub>	<i>α</i> (°)	<i>β</i> (°)	<i>γ</i> (°)			
hejtmanite B2(GII)	Ba <sub>2</sub>		<b>Mn<sub>4</sub></b>	<b>Ti<sub>2</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>(OH)<sub>2</sub></b>	F <sub>2</sub>	10.716 90.07	13.795 112.24	11.778 90.03	C $\bar{1}$	4	(1)
bafertisite B2(GII)	Ba <sub>2</sub>		<b>Fe<sub>4</sub><sup>2+</sup></b>	<b>Ti<sub>2</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>(OH)<sub>2</sub></b>	F <sub>2</sub>	10.677 90.11	13.767 112.28	11.737 90.02	C $\bar{1}$	4	(2)
cámaraite <sup>1</sup> D1(GII)	Ba <sub>3</sub>	Na	<b>Fe<sub>8</sub><sup>2+</sup></b>	<b>Ti<sub>4</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>4</sub></b>	<b>O<sub>4</sub></b>	<b>(OH)<sub>4</sub></b>	F <sub>3</sub>	10.6965 99.345	13.7861 92.315	21.478 89.993	C $\bar{1}$	4	(3)
jinshajiangite B1(GII)	Ba	Na	<b>Fe<sub>4</sub><sup>2+</sup></b>	<b>Ti<sub>2</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>(OH)<sub>2</sub></b>	F	10.7059 90.008	13.7992 94.972	20.760 89.984	C $\bar{1}$	8	(4)
perraultite B1(GII)	Ba	Na	<b>Mn<sub>4</sub></b>	<b>Ti<sub>2</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	<b>O<sub>2</sub></b>	<b>(OH)<sub>2</sub></b>	F	10.731 90	13.841 95.06	20.845 90	C2	8	(5)
bobshannonite <sup>1</sup> B1(GII)	Ba K	Na <sub>2</sub>	<b>(Mn,Na)<sub>8</sub></b>	<b>(Nb,Ti)<sub>4</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>4</sub></b>	<b>O<sub>4</sub></b>	<b>(OH)<sub>4</sub></b>	(O,F) <sub>2</sub>	10.839 89.99	13.912 95.02	20.98 89.998	C $\bar{1}$	4	(6)
yoshimuraite <sup>2</sup> B3(GII)	Ba <sub>2</sub>	Ba <sub>2</sub>	<b>Mn<sub>4</sub></b>	<sup>15</sup> <b>Ti<sub>2</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	(PO <sub>4</sub> ) <sub>2</sub>	<b>O<sub>2</sub></b>	<b>(OH)<sub>2</sub></b>	5.386 95.50	6.999 93.62	14.748 89.98	P $\bar{1}$	2	(7)
bussenite <sup>3</sup> B4(GII)	(Na□) <sub>2</sub>	Ba <sub>2</sub>	Ba <sub>2</sub>	<b>(M<sup>2+</sup>Na)<sub>2</sub></b>	<b>Ti<sub>2</sub></b>	<b>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub></b>	(CO <sub>3</sub> ) <sub>2</sub>	<b>O<sub>2</sub></b>	5.399 102.44	7.016 93.18	16.254 90.10	P $\bar{1}$	2	(8)

\*The general structural formula of the TS block is  $A_2^P B_2^P M_4^O M_2^H (Si_2O_7)_2 X_{4+n}$ , 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<sup>O</sup> and M<sup>H</sup> polyhedra and  $X_A^O$  = anions at common vertices of 3M<sup>O</sup> and A<sup>P</sup> polyhedra (where  $A^P - X_A^O < 3$  Å);  $X_M^P$  = apical anions of M<sup>H</sup> cations at the periphery of the TS block. The stoichiometry of the core part of the TS block,  $M_4^O M_2^H (Si_2O_7)_2 X_4^O$ , is invariant in all structures (shown in bold). In Group II, A<sup>P</sup> and B<sup>P</sup> cations, plus (PO<sub>4</sub>)<sub>2</sub> (in yoshimuraite) and (Na□)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>F<sub>2</sub> (in busenite) 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 busenite, 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 2*t*<sub>1</sub> and 2*t*<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):  $\alpha = 89.98$ ,  $\gamma = 95.50^\circ$ ;

<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.* (2015b); (3) Cámara *et al.* (2009); (4) Cámara *et al.* (2016); (5) Yamnova *et al.* (1998); (6) Sokolova *et al.* (2015b); (7) McDonald *et al.* (2000); (8) Zhou *et al.* (2002).

## THE CRYSTAL STRUCTURE OF HEJTMANITE

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

Component	wt. %			Formula unit (apfu)			
	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 <sub>2</sub> O <sub>5</sub>	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
Al <sub>2</sub> O <sub>3</sub>	n.d.	0.37	n.d.	Na	0	0.02	0
BaO	26.68	30.20	27.41	Σ4M <sup>O</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	Al	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
Cl	n.d.	<0.1	n.d.	K	0.07	0.07	0
–O=F <sub>2</sub> Cl <sub>2</sub>	1.61	1.39	1.54	Σ2A <sup>P</sup>	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
				OH	1.89	2.18	1.93
				Σ2X <sub>M</sub> <sup>P</sup> + 2X <sub>A</sub> <sup>O</sup>	4.00	4.00	4.00

n.d. – not detected.

\*Calculated on anion basis: O + F = 20 apfu.

\*\*Calculated from structure solution and refinement (this work) and by crystallochemical calculations (Vrána *et al.*, 1992): OH + F = 4 apfu.

$-19 < k < 19$ ,  $-16 < l < 16$  were measured to  $60.28^\circ$   $2\theta$  using 16 s per  $0.3^\circ$  frame. Unit-cell dimensions were determined by least-squares refinement of 9989 reflections with  $I > 10\sigma I$ , and are given in Table 3, together with other miscellaneous information on data collection and structure refinement. An absorption correction was undertaken using the *SADABS* program (Sheldrick, 2008). The unit-cell dimensions of hejtmánite (this work) are in good agreement with those of Vrána *et al.* (1992) (Table 3). All calculations were carried out with the Bruker *SHELXTL* version 5.1 system of programs (Sheldrick, 2008). The crystal structure was refined in space group  $C\bar{1}$  using the atom coordinates of bafertisite (Cámara *et al.*, 2015b) and

refined to  $R_1 = 1.88\%$  on a twinned crystal with two components related by the twin matrix  $[100\ 0\bar{1}0\ 001]$  and a twin ratio of 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,  $\alpha = 103.37(3)$ ,  $\beta = 103.48(3)$ ,  $\gamma = 104.32(3)^\circ$ ,  $V = 806(1)$  Å<sup>3</sup>,  $P\bar{1}$ ,  $Z = 2$ . The  $P\bar{1}$  unit cell can be derived from the  $C\bar{1}$  unit cell via the transformation matrix  $[\frac{1}{2}\ \frac{1}{2}\ 0\ \frac{1}{2}\ \frac{1}{2}\ 0\ 00\bar{1}]$ . We chose the unconventional space group  $C\bar{1}$  for consistency of orientation with all other thirty-nine TS-block structures characterized by the planar cell based on minimal lengths of translational vectors,  $t_1 \approx 5.5$  and  $t_2 \approx 7$  Å, and  $\mathbf{t}_1 \approx \mathbf{t}_2 \approx 90^\circ$ , and specifically with bafertisite, the Fe<sup>2+</sup>-analogue of hejtmánite. Scattering curves for neutral atoms were taken from

TABLE 3. Miscellaneous refinement data for hejtmanite.

	This work	Vrána <i>et al.</i> (1992)
<i>a</i> (Å)	10.716(2)	10.698(4)
<i>b</i>	13.795(3)	13.768(5)
<i>c</i>	11.778(2)	11.748(4)
$\alpha$ (°)	90.07(3)	90
$\beta$	112.24(3)	112.27(2)
$\gamma$	90.03(3)	90
<i>V</i> (Å <sup>3</sup> )	1612(2)	1601(2)
Space group	<i>C</i> 1	<i>C</i> */*
<i>Z</i>	4	4
Absorption coefficient (mm <sup>-1</sup> )	9.00	
<i>F</i> (000)	1885.8	
<i>D</i> <sub>calc.</sub> (g/cm <sup>3</sup> )	4.189	4.29
Crystal size (mm)	0.004 × 0.025 × 0.040	
Second component*	0.474(1)	
Radiation/monochromator	MoK $\alpha$ /graphite	
2 $\theta$ range for data collection (°)	60.28	
<i>R</i> (int) (%)	1.32	
Reflections collected	9468	
Independent reflections		
<i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i>	4539	4748
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup> , fixed weights proportional to 1/ $\sigma$ <i>F</i> <sub>o</sub> <sup>2</sup>	
No. of refined parameters	308	
Final <i>R</i> indices (%)		
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i> )	1.88	
<i>R</i> <sub>1</sub>	2.05	
<i>wR</i> <sub>2</sub>	5.11	
Goodness of fit on <i>F</i> <sup>2</sup>	1.090	

\*Second component of the crystal is related to the first component by the twin matrix [100 010 001].

the *International Tables for Crystallography* (Wilson, 1992). In the crystal structure of hejtmanite, there are 3 groups of cation sites: *M*<sup>O</sup> sites of the O sheet, *M*<sup>H</sup> and *Si* sites of the H sheet, and peripheral *A*<sup>P</sup> sites which occur in the **I** block; site labelling is in accord with Sokolova (2006). Site-scattering values were refined for the *M*<sup>O</sup>(1–5) sites with the scattering curve of Mn, *M*<sup>H</sup>(1,2) sites (scattering curve of Ti) and *A*<sup>P</sup>(1,2) sites (scattering curve of Ba). For the H(1,2) atoms, the D (donor)–H distances were softly constrained to 0.98 Å. Final atom coordinates and anisotropic displacement parameters for hejtmanite are listed in Table 4, selected interatomic distances and angles are given in Table 5, refined site-scattering values and assigned site-populations for selected cation and anion sites are given in Table 6, bond-valence values for selected anions in Table 7 and details of hydrogen bonding in Table 8. A table of structure factors and CIF for hejtmanite have been deposited

with the Principal Editor of *Mineralogical Magazine* and are available from [www.minersoc.org/pages/e\\_journals/dep\\_mat.html](http://www.minersoc.org/pages/e_journals/dep_mat.html).

### Topology of the structure

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

The crystal structure of hejtmanite is a combination of a TS block and an **I** block (Fig. 1a). The TS block consists of HOH sheets. In the O sheet, there are five Mn-dominant <sup>6</sup>*M*<sup>O</sup>(1–5) sites, with  $\langle M^O - \varphi \rangle = 2.198$  Å ( $\varphi = O, OH$ ) (Tables 5, 6, Fig. 1b). Five *M*<sup>O</sup> sites ideally give Mn<sub>4</sub> apfu (Table 6). In the H sheet, the two <sup>6</sup>*M*<sup>H</sup>(1,2) sites are occupied mainly by Ti and minor Nb and Zr, ideally giving Ti<sub>2</sub> apfu, with  $\langle M^H - \varphi \rangle = 1.962$  Å ( $\varphi = O, F$ ) 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

TABLE 4. Atom coordinates and anisotropic displacement parameters ( $\text{\AA}^2$ ) for hejtmantite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$	$U_{\text{eq}}$
M <sup>O</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>O</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>O</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>O</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>O</sup> (5)	½	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)
M <sup>H</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 <sup>P</sup> (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 <sub>M</sub> <sup>O</sup> (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 <sub>M</sub> <sup>O</sup> (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 <sub>A</sub> <sup>O</sup> (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 <sub>A</sub> <sup>O</sup> (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 <sub>M</sub> <sup>P</sup> (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 <sub>M</sub> <sup>P</sup> (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*						

\* $U_{\text{iso}}$ .

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

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

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:  $-x+1, -y+2, -z+1$ .

Si<sub>2</sub>O<sub>7</sub> groups 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  $\mathbf{t}_2$  ( $\parallel \mathbf{b}$  where  $b = 2t_2$ ) in the O sheet (Fig. 1a) as defined by Sokolova (2006). There are two

[12]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> apfu (Table 6). In the crystal structure of hejtmanite, TS blocks link via a layer of Ba atoms which constitute the I block (Fig. 1a). The topology of the hejtmanite structure is identical to that of bafertisitite (Cámara *et al.*, 2015b).



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

Site*	Refined site-scattering (epfu)	Assigned site-population (apfu)	Calculated site-scattering (epfu)	$\langle X-\varphi \rangle_{\text{obs}}$ ** (Å)	Ideal composition (apfu)
Cations					
$M^O(1)$	12.70(6)	2.23 Mn + 1.65 Fe <sup>2+</sup>		2.196	Mn <sub>0.5</sub>
$M^O(2)$	25.94(7)	+ 0.04 Zn + 0.03 Mg + 0.05 □		2.190	Mn
$M^O(3)$	25.85(7)			2.198	Mn
$M^O(4)$	26.05(10)			2.199	Mn
$M^O(5)$	12.96(6)			2.214	Mn <sub>0.5</sub>
$\Sigma M^O(1-5)$	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>
$M^H(1)$	22.62(7)	1.88 Ti + 0.10 Nb + 0.02 Zr		1.964	Ti
$M^H(2)$	22.56(6)			1.960	Ti
$\Sigma M^H(1,2)$	45.18	1.88 Ti + 0.10 Nb + 0.02 Zr	46.26		Ti <sub>2</sub>
$^{121}A^P(1)$	55.21(10)	0.93 Ba + 0.02 Sr + 0.05 □	52.84	2.934	Ba
$^{121}A^P(2)$	53.48(10)	0.89 Ba + 0.07 K + 0.04 □	51.17	3.034	Ba
$\Sigma A^P(1,2)$	108.69	1.82 Ba + 0.07 K + 0.02 Sr + 0.09 □	104.01		Ba <sub>2</sub>
Anions					
$\Sigma X_M^O(1,2)$	2.00 O				O <sub>2</sub>
$\Sigma X_A^O(1,2)$	1.89 OH + 0.11 F				(OH) <sub>2</sub>
$\Sigma X_M^P(1,2)$	2.00 F				F <sub>2</sub>

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

\*\*X = cation,  $\varphi$  = O, OH, F.

epfu – electrons per formula unit.

### Anion considerations

The O(1–14) atoms coordinate Si atoms of Si<sub>2</sub>O<sub>7</sub> groups, giving (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> pfu. Two X<sub>M</sub><sup>O</sup>(1,2) anions are bonded to one M<sup>H</sup> (Ti) cation and three M<sup>O</sup> (Mn) cations, receive 1.84 and 1.85 vu (valence units) and hence they are O atoms, giving O<sub>2</sub> apfu

(Tables 5–7). Two X<sub>M</sub><sup>P</sup>(1,2) anions are bonded to one M<sup>H</sup> (Ti) cation and three A<sup>P</sup> (Ba) cations (Fig. 1d), they receive 0.84 and 0.82 vu (Table 7). We conclude that the X<sub>M</sub><sup>P</sup>(1,2) anions are monovalent. The two X<sub>M</sub><sup>P</sup> sites are coordinated by four cations and hence there is no space to accommodate

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

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

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

TABLE 8. Hydrogen bonding in hejtmanite.

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

a:  $x^{-1/2}, y^{-1/2}, z$ ; b:  $-x + 1, -y + 1, -z + 1$ .

the H atom of an 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<sub>2</sub> apfu (Table 6). Two  $X_A^O(1,2)$  anions are bonded to three M<sup>O</sup> (Mn) cations, with incident valence sums of 1.18 and 1.22 vu (Table 7), hence they are monovalent anions. Chemical analysis gives 2.11 F apfu for hejtmanite (Table 2) and we assign 1.89 OH + [2.11–2.00 ( $X_M^P$ )<sub>2</sub> = ] 0.11 F to the  $X_A^O(1,2)$  sites, ideally (OH)<sub>2</sub> apfu (Table 6). The H(1,2) atoms are involved in weak hydrogen bonding with O atoms that belong to the H sheets (Table 8).

### End-member formula

We write the end-member formula of hejtmanite as the sum of the groups of cation and anion sites: Ba<sub>2</sub>(A<sub>2</sub><sup>P</sup>) + Mn<sub>4</sub> (M<sub>4</sub><sup>O</sup>) + Ti<sub>2</sub> (M<sub>2</sub><sup>H</sup>) + (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> + O<sub>2</sub> [(X<sub>M</sub><sup>P</sup>)<sub>2</sub>] + (OH)<sub>2</sub> [(X<sub>A</sub><sup>O</sup>)<sub>2</sub>] + F<sub>2</sub> [(X<sub>M</sub><sup>P</sup>)<sub>2</sub>] = 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>, Z = 4.

### Basic TS-block structure

In the crystal structure of hejtmanite, (1) there is only one type of TS block of composition [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>]<sup>4+</sup>; (2) the two H sheets of the TS block are identical; (3) there is only one type of **I** block of composition [Ba<sub>2</sub>]<sup>4+</sup>; 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).

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

Ideal structural formulae for Group-II minerals hejtmanite and bafertisite (the bafertisite structure

type, B2); bobshannonite, perraultite and jinshajiangite (the perraultite structure type, B1), cámaraita (the D1 cámaraita structure type related to the bafertisite and perraultite structure types), yoshimuraite (B3) and busenite (B4) are presented in Table 1. All minerals have basic structures except for cámaraita. In perraultite, jinshajiangite and bobshannonite, TS blocks connect via M<sup>H</sup>–X<sub>M</sub><sup>P</sup>–M<sup>H</sup> bridges as in the astrophyllite-group minerals (Cámara *et al.*, 2010) and related nafertisite, Na<sub>3</sub>Fe<sub>10</sub><sup>2+</sup>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.*, 2014b). The composition of an X<sub>M</sub><sup>P</sup> anion correlates with the composition of the M<sup>H</sup> cations: where M<sup>H</sup> sites are locally occupied by Nb (as in bobshannonite), the bridging anion is an O atom; where M<sup>H</sup> sites are occupied locally by Ti (as in perraultite and jinshajiangite), the bridging anion is a F 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<sub>M</sub><sup>P</sup> anion is coordinated by six cations: two Ti or Nb (at the D 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<sub>M</sub><sup>P</sup> site as there is no room to 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<sub>M</sub><sup>P</sup> site (Sokolova, 2012). In bafertisite and hejtmanite, TS blocks connect via a layer of Ba atoms in the **I** block. The F (X<sub>M</sub><sup>P</sup> site) atoms are apical anions of the M<sup>H</sup> (= Ti) cations and they are coordinated by four cations: Ti (M<sup>H</sup> site) and three Ba [A<sup>P</sup>(1,2) sites]. In bafertisite and hejtmanite, an OH group cannot occur at the X<sub>M</sub><sup>P</sup> 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<sub>M</sub><sup>P</sup> and X<sub>A</sub><sup>O</sup> sites, respectively.

Hejtmanite is related to cámaraita, ideally NaBa<sub>3</sub>Fe<sub>8</sub><sup>2+</sup>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 cámaraita has one type of TS block, two types of **I** block, and TS blocks link to each other in

## THE CRYSTAL STRUCTURE OF HEJTMANITE

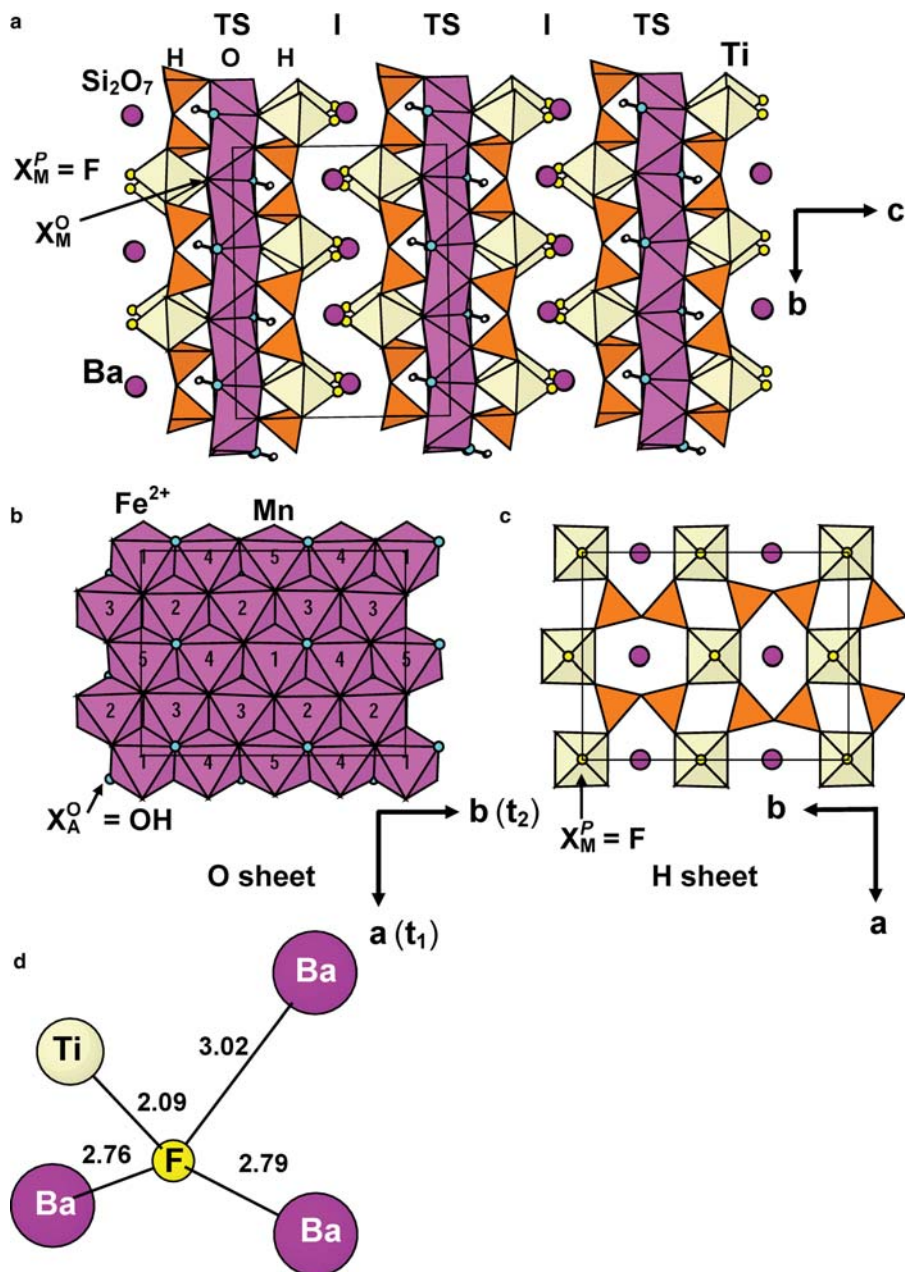


FIG. 1. A general view of the crystal structure of hejtmannite which consists of TS and I blocks (a) and the details of the structure: the close-packed O sheet of Mn-dominant  $M^O$  octahedra (b), the H sheet of Ti-dominant  $M^H$  octahedra and  $\text{Si}_2\text{O}_7$  groups (c), the F atom at the  $X_M^P$  site coordinated by the four cations (d).  $\text{SiO}_4$  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 shown as raspberry spheres; O and H atoms of OH groups at the  $X_A^O$  sites are shown as turquoise and small white spheres; F atoms at the  $X_M^P$  sites are shown as yellow spheres. The unit cell is shown by thin black lines.

two different ways. The structure of cámaraité can be built of structural fragments of minerals of the same group, jinshajiangite and bafertisite. The bafertisite component of the cámaraité structure is topologically identical to the hejtmanite structure. The general and ideal structural formulae of cámaraité are written as sums of the corresponding formulae of bafertisite and jinshajiangite (Table 1).

## Summary

(1) Hejtmanite, ideally  $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ , is a Group-II TS-block mineral ( $\text{Ti} + \text{Nb} = 2$  apfu) in accord with Sokolova (2006). The crystal structure of hejtmanite [ $a = 10.716(2)$ ,  $b = 13.795(3)$ ,  $c = 11.778(2)$  Å,  $\alpha = 90.07(3)$ ,  $\beta = 112.24(3)$ ,  $\gamma = 90.03(3)^\circ$ ,  $V = 1612(2)$  Å<sup>3</sup>, space group  $C\bar{1}$ ] is of basic type [B2(GII)] and is an alternation of TS and I blocks of the composition  $[\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2]^{4+}$  and  $[\text{Ba}_2]^{4+}$ , respectively. The crystal structure of hejtmanite is of the same topology as that of bafertisite,  $\text{Ba}_2\text{Fe}_4^{2+}\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ .

(2) In the crystal structure of hejtmanite, OH groups and F atoms are ordered at the  $X_A^O$  sites in the O sheet and  $X_M^P$  sites on the periphery of the TS block.

(3) The end-member formula of hejtmanite is of the form  $A_2^P M_4^O M_2^H (\text{Si}_2\text{O}_7)_2 (X^O)_4 (X^P)_2$ :  $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$ ,  $Z = 4$  where  $A_2^P = \text{Ba}_2$ ,  $M_4^O = \text{Mn}_4$ ,  $M_2^H = \text{Ti}_2$ ,  $(X^O)_4 = (X_M^O)_2 + (X_A^O)_2 = \text{O}_2(\text{OH})_2$ ,  $(X_M^P)_2 = \text{F}_2$ .

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