

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

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

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1557069> since 2016-06-08T10:04:07Z

Published version:

DOI:10.1180/minmag.2016.080.026

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

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

E. Sokolova^{1*}, F. Cámara^{2,3}, F.C. Hawthorne¹, and L.A. Pautov⁴

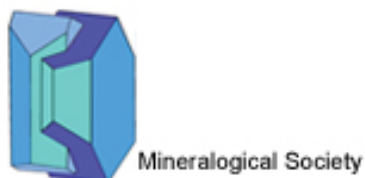
¹ Department of Geological Sciences, University of Manitoba, Winnipeg, MB, R3T 2N2, Canada

² Dipartimento di Scienze della Terra, Università di Torino, I-10125, Torino, Italy

³ CrisDi - Interdepartmental Center for Crystallography, via Giuria 7, 10126, Torino, Italy

⁴ A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Prospekt 18-2, Moscow 117071, Russia

* E-mail: elena_sokolova@umanitoba.ca



25 **Abstract**

26 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,
27 Mkushi River area, Central Province, Zambia (holotype material) has been refined on a twinned
28 crystal to $R_1 = 1.88\%$ on the basis of 4539 $[|F| > 4\sigma|F|]$. Hejtmanite is triclinic, $C\bar{1}$, $a =$
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 $1612(2)$ Å³. Chemical analysis (electron microprobe) gives: Ta_2O_5 0.09, Nb_2O_5 1.27, ZrO_2 0.65,
31 TiO_2 14.35, SiO_2 23.13, BaO 26.68, SrO 0.19; FeO 11.28, MnO 15.12, Cs_2O 0.05, K_2O 0.33, F
32 3.82, $\text{H}_2\text{O}_{\text{calc.}}$ 1.63, $\text{O}=\text{F} -1.61$, total 97.10 wt.%, where the H_2O content was calculated from the
33 crystal-structure refinement, with $(\text{OH} + \text{F}) = 4$ a.p.f.u. The empirical formula, calculated on the
34 basis of 20 (O + F) anions, is of the form $A^P_2M^O_4M^H_2(\text{Si}_2\text{O}_7)_2(X^O)_4(X^P)_2$, $Z = 4$:
35 $(\text{Ba}_{1.82}\text{K}_{0.07}\text{Sr}_{0.02})_{\Sigma 1.91}(\text{Mn}_{2.33}\text{Fe}^{2+}_{1.65}\text{Zr}_{0.04}\text{Mg}_{0.03})_{\Sigma 3.95}(\text{Ti}_{1.88}\text{Nb}_{0.10}\text{Zr}_{0.02})_{\Sigma 2}(\text{Si}_{2.02}\text{O}_7)_2\text{O}_2[(\text{OH})_{1.89}\text{F}_{0.11}]_{\Sigma 2}$
36 F_2 . 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: $\text{Ti} (+ \text{Nb}) = 2$ a.p.f.u. per
39 $(\text{Si}_2\text{O}_7)_2$ [as defined by Sokolova (2006)]. In the O sheet, five $^{[6]}M^O$ sites are occupied mainly by
40 Mn, less Fe^{2+} and minor Zr and Mg, with $\langle M^O-\varphi \rangle = 2.198$ Å ($\varphi = \text{O}, \text{OH}$), ideally giving Mn_4
41 a.p.f.u. In the H sheet, two $^{[6]}M^H$ sites are occupied mainly by Ti, with $\langle M^H-\varphi \rangle = 1.962$ Å ($\varphi =$
42 O, F), ideally giving Ti_2 a.p.f.u.; four $^{[4]}Si$ sites are occupied by Si, with $\langle \text{Si}-\text{O} \rangle = 1.625$ Å. The M^H
43 octahedra and Si_2O_7 groups constitute the H sheet. The two $^{[12]}Ba$ -dominant $A^P(1,2)$ sites, with
44 $\langle A^P-\varphi \rangle = 2.984$ Å ($\varphi = \text{O}, \text{F}$), ideally give Ba_2 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 $(X^O_A)_2 = \text{O}_2(\text{OH})_2$ p.f.u. Two $X^P_M(1,2)$ sites are occupied by F, giving F_2 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 $\text{Ba}_2(\text{Mn}, \text{Fe}^{2+})_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH}, \text{F})_2\text{F}_2$ and $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$, $Z = 4$.
49 Hejtmanite is a Mn-analogue of bafertisite, $\text{Ba}_2\text{Fe}^{2+}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$.

50 **Keywords:** hejtmanite, holotype, electron microprobe, single-crystal X-ray diffraction, crystal
51 structure, chemical formula, TS block, Group II.
52

53 Introduction

54 Semenov and Zhang Peishan (1959) described bafertisite, $\text{BaFe}_2\text{TiSi}_2\text{O}_9$, $Z = 2$, as a new mineral
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, $\beta =$
58 119.5° , [2] monoclinic, space group $P2_1/m$, $a = 10.98$, $b = 6.80$, $c = 5.36$ Å, $\beta = 94^\circ$. Based on the
59 structure-refinement results, Guan *et al.* (1963) and Peng Zhizhong and Shen Jinchuan (1963)
60 gave the chemical formula of bafertisite as follows: $\text{BaFe}_2\text{Ti}[\text{Si}_2\text{O}_7]\text{O}(\text{OH})_2$, $Z = 8$ and 2 ,
61 respectively. Vrána *et al.* (1992) described hejtmanite from Mbolve Hill, Mkushi River area,
62 Central Province, Zambia, as a manganese-dominant analogue of bafertisite: monoclinic,
63 diffraction symbol $C^*/*$, $a = 10.698(4)$, $b = 13.768(5)$, $c = 11.748(4)$ Å, $\beta = 112.27(2)^\circ$, $V = 1601(2)$
64 Å³, $D_{\text{meas.}} = 4.02$ g/cm³. Vrána *et al.* (1992) determined the chemical composition of hejtmanite by
65 electron microprobe (Table 2) and by analogy with bafertisite (Semenov and Zhang Peishan,
66 1959; Guan *et al.*, 1963; Peng Zhizhong and Shen Jinchuan, 1963), and gave simplified and
67 endmember formulae $\text{Ba}(\text{Mn,Fe})_2\text{TiO}(\text{Si}_2\text{O}_7)(\text{OH,F})_2$ and $\text{BaMn}_2\text{TiO}(\text{Si}_2\text{O}_7)(\text{OH,F})_2$, $Z = 8$. 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
71 formulae, $(\text{Ba}_{0.96}\text{Na}_{0.03}\text{Ca}_{0.01}\text{Cs}_{0.002})_{\Sigma 1}(\text{Mn}_{1.70}\text{Fe}^{2+}_{0.17}\text{Mg}_{0.05}\text{Al}_{0.08})_{\Sigma 2}(\text{Ti}_{0.93}\text{Sn}_{0.07}\text{Nb}_{0.015})_{\Sigma 1.01}$
72 $(\text{Si}_{1.97}\text{Al}_{0.02})_{\Sigma 1.99}\text{O}_7\text{O}_{2.09}(\text{H}_2\text{O})_{0.25}$ and $\text{BaMn}_2\text{TiO}(\text{Si}_2\text{O}_7)(\text{OH})_2$, respectively. All the crystals of the
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,
75 $\text{BaMn}_2\text{TiO}(\text{Si}_2\text{O}_7)(\text{OH})_2$: triclinic, space groups $P1$ or $P\bar{1}$, $a = 10.767(7)$, $b = 13.858(9)$, $c =$
76 $32.99(6)$ Å, $\alpha = 90.3(1)$, $\beta = 94.6(1)$, $\gamma = 89.96(5)^\circ$, $V = 4906(2)$ Å³, $Z = 24$, and the structure model
77 for the monoclinic subcell: space group Pm , $a = 5.374(3)$, $b = 6.911(3)$, $c = 32.82(1)$ Å, $\beta =$
78 $94.62(4)^\circ$, $V = 1214(2)$ Å³, $R = 19.89\%$. They showed that the general topology of the structure of

79 the Mn-analogue of bafertisite from the Inyl'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 $\text{BaMn}_2\text{TiO}(\text{Si}_2\text{O}_7)(\text{OH})_2$: (1) space group $P2_1/m$, $a = 5.361$,
84 $b = 6.908$, $c = 12.556 \text{ \AA}$, $\beta = 119.8^\circ$, $V = 403 \text{ \AA}^3$, $Z = 2$, $R = 6.8\%$, and (2) space group Cm , $a =$
85 10.723 , $b = 13.812$, $c = 12.563 \text{ \AA}$, $\beta = 119.9^\circ$, $V = 1613 \text{ \AA}^3$, $Z = 8$, $R = 8.3\%$; both phases are
86 isostructural with bafertisite [*cf.* $P2_1/m$ 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 $P2_1/m$: 1.54 \AA , and (2) space
89 group Cm : 1.49 \AA . These distances imply significant errors in both structures. The problems with
90 the crystal structure of hejtmanite 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 hejtmanite a TS-
94 block mineral with two modifications: hejtmanite-C (space group Cm) and hejtmanite-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_2O_7 groups. The TS
103 block is characterized by a planar cell based on minimal lengths of translational vectors, $t_1 \sim 5.5$
104 and $t_2 \sim 7 \text{ \AA}$, and $t_1 \wedge t_2 \approx 90^\circ$. The general formula of the TS block is $A^P_2B^P_2M^H_2M^O_4(\text{Si}_2\text{O}_7)_2X_{4+n}$,

105 where M^H_2 and M^O_4 = cations of the H and O sheets; M^H = Ti, Nb, Zr, Mn, Ca + REE, Ca; M^O = Ti,
106 Zr, Nb, Fe^{2+} , Fe^{3+} , Mg, Mn, Ca, Na; A^P and B^P = cations at the peripheral (*P*) sites = Na, Ca +
107 REE, Ca, Ba, Sr, K; X = anions, O, OH, F, and H₂O groups; $X_{4+n} = X^O_4 + X^P_n$, n = 0, 1, 1.5, 2, 4,
108 where X^O_4 = anions of the O sheet which do not coordinate Si atoms, X^P_n = anions at the
109 periphery of the TS block; X = O, OH, F, H₂O (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 (PO₄), (SO₄) and (CO₃), and H₂O
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
116 stereochemistry of Ti (+ Nb + Zr + Fe^{3+} + Mg + Mn) per (Si₂O₇)₂. In Group I, Ti (+ Nb + Zr) = 1
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 +
118 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
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.

131 Following our continued interest in TS-block minerals, we felt strongly that the crystal
132 structure of hejtmanite must be solved and refined on the holotype material of Vrána *et al.* (1992).
133 We studied hejtmanite 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 hejtmanite,
137 $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$, a TS-block mineral of Group II where Ti (+ Nb) = 2 a.p.f.u. per
138 $(\text{Si}_2\text{O}_7)_2$ (Table 1).

139

140 **Chemical composition**

141 Crystals of hejtmanite 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
143 nA, and a beam diameter of 10 μm . The following standards were used: Si: diopside; Ta:
144 $\text{Mn}(\text{Ta}_{1.70}\text{Nb}_{0.30})\text{O}_6$; Nb, Ba: $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$; Zr: zircon; Ti: titanite; Fe: fayalite; Mn: spessartine;
145 Mg: forsterite; Sn: cassiterite; Sr: SrTiO_3 ; 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_2O (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 $\text{F} + \text{OH} = 4$ a.p.f.u. Table 2 gives the chemical composition
150 of hejtmanite 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
152 calculated on the basis of 20 (O + F) anions and is of the form $\text{A}^P_2\text{M}^{\text{O}}_4\text{M}^{\text{H}}_2(\text{Si}_2\text{O}_7)_2(\text{X}^{\text{O}})_4(\text{X}^{\text{P}})_2$, Z
153 =4: For hejtmanite from Zambia (holotype), it is $(\text{Ba}_{1.82}\text{K}_{0.07}\text{Sr}_{0.02})_{\Sigma 1.91}$
154 $(\text{Mn}_{2.33}\text{Fe}^{2+}_{1.65}\text{Zr}_{0.04}\text{Mg}_{0.03})_{\Sigma 3.95}(\text{Ti}_{1.88}\text{Nb}_{0.10}\text{Zr}_{0.02})_{\Sigma 2}(\text{Si}_{2.02}\text{O}_7)_2\text{O}_2[(\text{OH})_{1.89}\text{F}_{0.11}]_{\Sigma 2}\text{F}_2$, $D_{\text{calc.}} = 4.189$
155 g/cm^3 and is in accord with $D_{\text{meas.}} = 4.02 \text{ g}/\text{cm}^3$ (Vrána *et al.*, 1992). For hejtmanite from
156 Inyl'chek, Kirgizia, it is $\text{Ba}_{1.92}(\text{Mn}_{3.62}\text{Fe}^{2+}_{0.25}\text{Mg}_{0.08}\text{Zr}_{0.02})_{\Sigma 3.97}(\text{Ti}_{1.59}\text{Sn}_{0.42})_{\Sigma 2.01}(\text{Si}_{2.02}\text{O}_7)_2\text{O}_2$

157 $[(\text{OH})_{1.93}\text{F}_{0.07}]_{\Sigma 2}\text{F}_2$, $D_{\text{calc.}} = 4.189 \text{ g/cm}^3$. Hejtmanite from Inyl'chek, Kirgizia, is characterized by
158 very high MnO, significant SnO₂, lower TiO₂ and lack of Nb₂O₅: 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 Sn⁴⁺ constitutes ~ 31% of the Ti-
161 dominant *D* site in the H sheet of the HOH block (Cámara *et al.*, 2010), we assigned all Sn⁴⁺ to
162 the Ti-dominant *M*^H site in the H sheet of the TS block (Table 2): $(\text{Ti}_{1.59}\text{Sn}_{0.42})_{\Sigma 2.01} \text{ a.p.f.u.}$
163 Simplified and endmember formulae of hejtmanite are $\text{Ba}_2(\text{Mn,Fe}^{2+})_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH,F})_2\text{F}_2$ and
164 $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$, $Z = 4$.

165

166 **Crystal structure**

167 *Data collection and structure refinement*

168 Single-crystal X-ray data for hejtmanite from Zambia were collected using a Bruker
169 APEX II ULTRA three-circle diffractometer with a rotating-anode generator (MoK α), multilayer
170 optics and an APEX II 4K CCD detector. The intensities of 9468 reflections with $-15 < h < 15$, $-$
171 $19 < k < 19$, $-16 < l < 16$ were measured to $60.28^\circ 2\theta$ using 16 s per 0.3° frame. Unit-cell
172 dimensions were determined by least-squares refinement of 9989 reflections with $I > 10\sigma I$, 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 hejtmanite (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
177 system of programs (Sheldrick, 2008). The crystal structure was refined in space group $C\bar{1}$
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 $[100 \ 0\bar{1}0 \ 001]$ and a twin ratio of
180 0.526(1):0.474(1). The (Niggli) reduced unit cell is: $a = 8.732(2)$, $b = 8.736(2)$, $c = 11.778(2) \text{ \AA}$, α
181 $= 103.37(3)$, $\beta = 103.48(3)$, $\gamma = 104.32(3)^\circ$, $V = 806(1) \text{ \AA}^3$, $P\bar{1}$, $Z = 2$. The $P\bar{1}$ unit cell can be
182 derived from the $C\bar{1}$ unit cell via the transformation matrix $[-\frac{1}{2} \ -\frac{1}{2} \ 0 \ -\frac{1}{2} \ \frac{1}{2} \ 0 \ 0 \ 0 \ -1]$. We chose the

183 unconventional space group $C\bar{1}$ 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 $t_2 \sim 7 \text{ \AA}$, and $t_1 \wedge t_2 \approx 90^\circ$, and specifically with bafertisite, the Fe^{2+} -analogue of
186 hejtmanite. 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
188 cation sites: M^O sites of the O sheet, M^H and Si sites of the H sheet, and peripheral A^P sites
189 which occur in the I block; site labeling is in accord with Sokolova (2006). Site-scattering values
190 were refined for the $M^O(1-5)$ sites with the scattering curve of Mn, $M^H(1,2)$ sites (scattering
191 curve of Ti) and $A^P(1,2)$ sites (scattering curve of Ba). For the H(1,2) atoms, the D (donor)–H
192 distances were softly constrained to 0.98 \AA . 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*

201 Hejtmanite is a TS-block mineral of Group II, $\text{Ti (+ Nb)} = 2 \text{ a.p.f.u. per } (\text{Si}_2\text{O}_7)_2$ (Sokolova, 2006).
202 The crystal structure of hejtmanite is a combination of a TS block and an I block (Fig. 1a). The
203 TS block consists of HOH sheets. In the O sheet, there are five Mn-dominant $^{[6]}M^O(1-4)$ sites,
204 with $\langle M^O-\varphi \rangle = 2.198 \text{ \AA}$ ($\varphi = \text{O, OH}$) (Tables 5, 6, Fig. 1b). Five M^O sites ideally give $\text{Mn}_4 \text{ a.p.f.u.}$
205 (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 $\text{Ti}_2 \text{ a.p.f.u.}$, with $\langle M^H-\varphi \rangle = 1.962 \text{ \AA}$ ($\varphi = \text{O, F}$) and four $^{[4]}Si$ sites are occupied
207 solely by Si, with $\langle \text{Si-O} \rangle = 1.625 \text{ \AA}$ (Tables 5, 6). The M^H octahedra and Si_2O_7 groups
208 constitute the H sheet (Fig. 1c). Two H sheets and the central O sheet link via common vertices

209 of M^H octahedra and Si_2O_7 groups with M^O octahedra to form the TS block. In Group II, the TS
 210 block exhibits linkage 2 where the Si_2O_7 groups of two H sheets link to M^O octahedra adjacent
 211 along t_2 ($\parallel b$ where $b = 2t_2$) in the O sheet (Fig. 1a) as defined by Sokolova (2006). There are
 212 two ^{12}Ba -dominant $A^P(1,2)$ sites, with $\langle A^P(1)-\varphi \rangle = 2.934 \text{ \AA}$ and $\langle A^P(2)-\varphi \rangle = 3.034 \text{ \AA}$ ($\varphi = O, F$).
 213 The two A^P sites ideally give Ba_2 a.p.f.u. (Table 6). In the crystal structure of hejtmanite, TS
 214 blocks link via a layer of Ba atoms which constitute the I block (Fig. 1a). The topology of the
 215 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_2O_7 groups, giving $(Si_2O_7)_2$ p.f.u. Two $X^O_M(1,2)$
 219 anions are bonded to one M^H (Ti) cation and three M^O (Mn) cations, receive 1.84 and 1.85 vu
 220 (valence units) and hence they are O atoms, giving O_2 a.p.f.u. (Tables 5–7). Two $X^P_M(1,2)$
 221 anions are bonded to one M^H (Ti) cation and three A^P (Ba) cations (Fig. 1d), they receive 0.84
 222 and 0.82 vu (Table 7). We conclude that the $X^P_M(1,2)$ anions are monovalent. The two X^P_M sites
 223 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 $X^P_M(1,2)$ sites, and
 225 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
 226 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 $1.89 \text{ OH} + [2.11$
 228 $- 2.00(X^P_M)_2 =] 0.11 \text{ F}$ to the $X^O_A(1,2)$ sites, ideally $(OH)_2$ a.p.f.u. (Table 6). The H(1,2) atoms
 229 are involved in weak hydrogen bonding with O atoms that belong to the H sheets (Table 8).

230

231 *Endmember formula*

232 We write the endmember formula of hejtmanite as the sum of the groups of cation and anion
 233 sites: $Ba_2 (A^P_2) + Mn_4 (M^O_4) + Ti_2 (M^H_2) + (Si_2O_7)_2 + O_2 [(X^O_M)_2] + (OH)_2 [(X^O_A)_2] + F_2 [(X^P_M)_2] =$
 234 $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2, Z = 4.$

235

236 *Basic TS-block structure*

237 In the crystal structure of hejtmanite, (1) there is only one type of TS block of composition
238 $[\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2]^{4-}$; (2) the two H sheets of the TS block are identical; (3) there is only
239 one type of I block of composition $[\text{Ba}_2]^{4+}$; and (4) there is only one type of self-linkage of TS
240 blocks, via a layer of Ba atoms in the of I block. Points (1)–(4) are in accord with the definition of
241 a basic structure by Sokolova and Cámara (2013). The crystal structure of hejtmanite is of the
242 B2(GII) structure type in accord with Sokolova and Cámara (2013).

243

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

245 Ideal structural formulae for Group-II minerals hejtmanite 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
250 connect via $M^H-X_M^P-M^H$ bridges as in the astrophyllite-group minerals (Cámara *et al.*, 2010) and
251 related nafertisite, $\text{Na}_3\text{Fe}^{2+}_{10}\text{Ti}_2(\text{Si}_6\text{O}_{17})_2\text{O}_2(\text{OH})_6\text{F}(\text{H}_2\text{O})_2$ (Cámara *et al.*, 2014b). The
252 composition of an X_M^P anion correlates with the composition of the M^H 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.*
256 niobophyllite, Cámara *et al.*, 2010). In most astrophyllite-group minerals, the X_M^P anion is
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
258 B site) and an OH group cannot/does not occur at the X_M^P site as there is no room to
259 accommodate an H atom and a hydrogen bond; where there is a vacancy at the A or B sites,
260 OH groups occur at the X_M^P site (Sokolova, 2012). In bafertisite and hejtmanite, TS blocks

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

266 Hejtmanite is related to cámaraitite, ideally $\text{NaBa}_3\text{Fe}^{2+}_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4\text{F}_3$. The
 267 derivative structure of cámaraitite has one type of TS block, two types of I block, and TS blocks
 268 link to each other in two different ways. The structure of cámaraitite can be built of structural
 269 fragments of minerals of the same group, jinshajiangite and bafertisite. The *bafertisite*
 270 component of the cámaraitite structure is topologically identical to the hejtmanite structure. The
 271 general and ideal structural formulae of cámaraitite are written as sums of the corresponding
 272 formulae of bafertisite and jinshajiangite (Table 1).

273

274 **Summary**

275 (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 (Ti + Nb = 2
 276 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, $\alpha = 90.07(3)$, $\beta = 112.24(3)$, $\gamma = 90.03(3)^\circ$, $V = 1612(2)$ Å³, space
 278 group $C\bar{1}$] is of basic type [B2(GII)] and is an alternation of TS and I blocks of the composition
 279 $[\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2]^{4-}$ and $[\text{Ba}_2]^{4+}$, respectively. The crystal structure of hejtmanite is of the
 280 same topology as that of bafertisite, $\text{Ba}_2\text{Fe}^{2+}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$.

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

283 (3) The endmember formula of hejtmanite is of the form $A^P_2M^O_4M^H_2(\text{Si}_2\text{O}_7)_2(X^O)_4(X^P)_2$:

284 $\text{Ba}_2\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$, Z = 4 where $\text{Ba}_2 A^P_2 = \text{Ba}_2$, $M^O_4 = \text{Mn}_4$, $M^H_2 = \text{Ti}_2$, $(X^O)_4 = (X^O_M)_2 +$
 285 $(X^O_A)_2 = \text{O}_2(\text{OH})_2$, $(X^P_M)_2 = \text{F}_2$.

286

287 **Acknowledgements**

288 We thank Mark Cooper for collecting single-crystal X-ray data for hejtmanite. LAP
289 acknowledges financial support by the grant 12-05-00911-a from the Russian Foundation for
290 Basic Research; FC acknowledges financial support by the grant Ricerca Locale 2014,
291 Università di Torino; FC and ES were supported by a Canada Research Chair in
292 Crystallography and Mineralogy and by a Discovery grant from the Natural Sciences and
293 Engineering Research Council of Canada and by Innovation Grants from the Canada
294 Foundation for Innovation to FCH.

295 **References**

- 296 Aksenov, S.M., Rastsvetaeva, R.K. and Chukanov, N.V. (2014) The crystal structure of
297 emmerichite $\text{Ba}_2\text{Na}_3\text{Fe}^{3+}\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, a new lamprophyllite-group mineral. *Zeitschrift*
298 *für Kristallographie*, **229**(1), 1-7.
- 299 Brown, I.D. (1981) The bond valence method: an empirical approach to chemical structure and
300 bonding. Pp. 1–30 in: *Structure and Bonding in Crystals II* (M. O'Keeffe and A.
301 Navrotsky, editors). Academic Press, New York, N.Y.
- 302 Cámara, F., Sokolova, E. and Nieto, F. (2009) Cámaraite, $\text{Ba}_3\text{NaTi}_4(\text{Fe}^{2+}, \text{Mn})_8(\text{Si}_2\text{O}_7)_4\text{O}_4$
303 $(\text{OH}, \text{F})_7$. II. The crystal structure and crystal chemistry of a new group-II Ti-disilicate
304 mineral. *Mineralogical Magazine*, **73**, 855–870.
- 305 Cámara, F., Sokolova, E., Abdu, Y. and Hawthorne, F.C. (2010): The crystal structures of
306 niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite; revisions to the crystal chemistry
307 of the astrophyllite-group minerals. *The Canadian Mineralogist*, **48**, 1–16.
- 308 Cámara, F., Sokolova, E., Abdu, Y.A., Hawthorne, F.C. and Khomyakov, A.P. (2013) Kolskyite,
309 $(\text{Ca}\square)\text{Na}_2\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4(\text{H}_2\text{O})_7$, a Group-IV Ti-disilicate mineral from the Khibiny alkaline
310 massif, Kola Peninsula, Russia: description and crystal structure. *The Canadian*
311 *Mineralogist*, **51**(6), 921-936.
- 312 Cámara, F., Sokolova, E., Abdu, Y.A. and Hawthorne, F.C. (2014a) Saamite,
313 $\text{Ba}\square\text{TiNbNa}_3\text{Ti}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_2$, a Group-III Ti-disilicate mineral from the Khibiny
314 alkaline massif, Kola Peninsula, Russia: description and crystal structure. *The Canadian*
315 *Mineralogist*, **52**, 745-761.
- 316 Cámara, F., Sokolova, E., Abdu, Y.A. and Hawthorne, F.C. (2014b) Nafertisite,
317 $\text{Na}_3\text{Fe}^{2+}_{10}\text{Ti}_2(\text{Si}_6\text{O}_{17})_2\text{O}_2(\text{OH})_6\text{F}(\text{H}_2\text{O})_2$, from Mt. Kukisvumchorr, Khibiny alkaline massif,
318 Kola peninsula, Russia: Refinement of the crystal structure and revision of the chemical
319 formula. *European Journal of Mineralogy*, **26**, 689-700.
- 320

321
322 Cámara, F., Sokolova, E., Abdu, Y.A., Hawthorne, F.C., Charrier, T., Dorcet, V. and Carpentier,
323 J.-F. (2015a) Fogoite-(Y), IMA 2014-098. *Mineralogical Magazine*, **79**, 247-251.
324 Cámara, F., Sokolova, E., Abdu, Y.A. and Pautov, L.A. (2015b) From structure topology to
325 chemical composition. XIX. Titanium silicates: revision of the crystal structure and
326 chemical formula of bafertisite, $\text{Ba}_2\text{Fe}^{2+}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}_2$, a Group-II TS-block
327 mineral. *The Canadian Mineralogist* (submitted).
328 Guan, Ya. S., Simonov, V.I. and Belov, N.V. (1963) Crystal structure of bafertisite,
329 $\text{BaFe}_2\text{TiO}[\text{Si}_2\text{O}_7](\text{OH})_2$. *Doklady Akademii Nauk SSSR*, **149**, 1416–1419 (in Russian).
330 *Mineraly. Handbook. Silicates* (1996) **IV**(3) (additions to volumes **III** and **IV**), p. 132, Nauka:
331 Moscow (in Russian).
332 Peng Zhizhong and Shen Jinchuan (1963) Crystal structure of bafertisite. *Kexue Tongbao*,
333 **14**(1), 66-68 (in Chinese).
334 Pouchou, J.L. and Pichoir, F. (1985) "PAP" ($\phi\rho Z$) procedure for improved quantitative
335 microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San
336 Francisco Press, San Francisco, California, U.S.A.
337 Rastsvetaeva, R.K., Tamazyán, R.A., Sokolova, E.V. and Belakovskii, D.I. (1991): Crystal
338 structures of two modifications of natural Ba, Mn-titanosilicate. *Soviet Physics*
339 *Crystallography*, **36**, 186-189.
340 Rastsvetaeva, R.K., Eskova, E.M., Dusmatov, V.D., Chukanov, N.V. and Schneider, F. (2008)
341 Surkhobite: revalidation and redefinition with the new formula, $(\text{Ba,K})_2\text{CaNa}$
342 $(\text{Mn,Fe}^{2+},\text{Fe}^{3+})_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{F,OH,O})_6$. *European Journal of Mineralogy*, **20**, 289–295.
343 Semenov, E.I. and Zhang Peishan (1959) New Mineral - bafertisite. *Science Record. New Ser.*
344 *Mineralogy III*(12), 652-655 (in Russian).
345 Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.

- 346 Sokolova, E. (2006) From structure topology to chemical composition. I. Structural hierarchy
347 and stereochemistry in titanium disilicate minerals. *The Canadian Mineralogist*, **44**,
348 1273–1330.
- 349 Sokolova, E. (2012) Further developments in the structure topology of the astrophyllite-group
350 minerals. *Mineralogical Magazine*, **76**, 863-882.
- 351 Sokolova, E. and Cámara, F. (2013) From structure topology to chemical composition. XVI. New
352 developments in the crystal chemistry and prediction of new structure topologies for
353 titanium disilicate minerals with the TS block. *The Canadian Mineralogist*, **51**, 861–891.
- 354 Sokolova, E.V., Egorov-Tismenko, Yu.K., Pautov, L.A. and Belakovskii, D.I. (1989) On the
355 crystal structure of a new Ba-titanosilicate, $\text{BaMn}_2\text{TiO}[\text{Si}_2\text{O}_7](\text{OH})_2$ – a member of the
356 homologous series seidozerite – nacaphite. *Zapiski Vsesoyuznogo Mineralogicheskogo*
357 *Obshchestva*, **118**(4), 81-84 (in Russian).
- 358 Sokolova, E., Cámara, F., Hawthorne, F.C. and Abdu, Y. (2009) From structure topology to
359 chemical composition. VII. Titanium silicates: the crystal structure and crystal chemistry
360 of jinshajiangite. *European Journal of Mineralogy*, **21**, 871–883.
- 361 Sokolova, E., Abdu, Y.A., Hawthorne, F.C., Genovese, A., Cámara, F. and Khomyakov, A.P.
362 (2015a) From structure topology to chemical composition. XVIII. Titanium silicates:
363 revision of the crystal structure and chemical formula of betalomonosovite, a Group-IV
364 TS-block mineral from the Lovozero alkaline massif, Kola Peninsula, Russia. *The*
365 *Canadian Mineralogist*, **53**(3).
- 366 Sokolova, E., Cámara, F., Abdu, Y.A., Hawthorne, F.C., Horváth, L. and Pfenninger- Horváth, E.
367 (2015b) Bobshannonite, $\text{Na}_2\text{KBa}(\text{Mn},\text{Na})_8(\text{Nb},\text{Ti})_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4(\text{O},\text{F})_2$, a new TS-block
368 mineral from Mont Saint-Hilaire, Québec, Canada: Description and crystal structure.
369 *Mineralogical Magazine* (accepted).
- 370 Vrána, S., Rieder, M. and Gunter, M.E. (1992) Hejtmanite, a manganese-dominant analogue of
371 bafertisite, a new mineral. *European Journal of Mineralogy*, **4**, 35-43.

- 372 Wilson, A.J.C. (editor) (1992) International Tables for Crystallography. Volume C: Mathematical,
373 physical and chemical tables. Kluwer Academic Publishers, Dordrecht, The Netherlands.
374 Yamnova, N.A., Egorov-Tismenko, Yu.K. and Pekov, I.V. (1998) Crystal structure of perraultite
375 from the coastal region of the Sea of Azov. *Crystallography Reports*, **43**, 401–410.
376
377

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^O octahedra (b), the
382 H sheet of Ti-dominant M^H octahedra and Si_2O_7 groups (c), the F atom at the X_M^P site
383 coordinated by the four cations (d). SiO_4 tetrahedra are orange, Ti-dominant and Mn-dominant
384 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_A^O sites are shown as
386 turquoise and small white spheres; F atoms at the X_M^P sites are shown as yellow spheres. Unit
387 cell is shown by thin black lines.

388

TABLE 1. Ideal structural formulae* and unit-cell parameters for Group-II TS-block minerals, Ti + Nb = 2 a.p.f.u. per (Si₂O₇)₂.

Mineral	Formula							a (Å)	b (Å)	c (Å)	Sp. gr.	Z	Ref.	
	Structure type**	A ^P ₁₋₂	B ^P ₀₋₂	M ^H ₂	M ^O ₄	(Si ₂ O ₇) ₂	(X ^O _M) ₂	(X ^O _A) ₂	(X ^P _M) ₀₋₂	α (°)				β (°)
hejtmanite B2(GII)	Ba ₂		Ti ₂	Mn ₄	(Si ₂ O ₇) ₂	O ₂	(OH) ₂	F ₂	10.716 90.07	13.795 112.24	11.778 90.03	C $\bar{1}$	4	(1)
bafertisite B2(GII)	Ba ₂		Ti ₂	Fe ²⁺ ₄	(Si ₂ O ₇) ₂	O ₂	(OH) ₂	F ₂	10.677 90.11	13.767 112.28	11.737 90.02	C $\bar{1}$	4	(2)
cámaraite ¹ D1(GII)	Ba ₃	Na	Ti ₄	Fe ²⁺ ₈	(Si ₂ O ₇) ₄	O ₄	(OH) ₄	F ₃	10.6965 99.345	13.7861 92.315	21.478 89.993	C $\bar{1}$	4	(3)
jinshajiangite B1(GII)	Ba	Na	Ti ₂	Fe ²⁺ ₄	(Si ₂ O ₇) ₂	O ₂	(OH) ₂	F	10.7059 90.008	13.7992 94.972	20.760 89.984	C $\bar{1}$	8	(4)
perraultite B1(GII)	Ba	Na	Ti ₂	Mn ₄	(Si ₂ O ₇) ₂	O ₂	(OH) ₂	F	10.731 90	13.841 95.06	20.845 90	C2	8	(5)
bobshannonite ¹ B1(GII)	Ba K	Na ₂	(Nb,Ti) ₄	(Mn,Na) ₈	(Si ₂ O ₇) ₄	O ₄	(OH) ₄	(O,F) ₂	10.839 89.99	13.912 95.02	20.98 89.998	C $\bar{1}$	4	(6)
yoshimuraite ² B3(GII)	Ba ₂	Ba ₂	⁵¹ Ti ₂	Mn ₄	(Si ₂ O ₇) ₂	(PO ₄) ₂	O ₂	(OH) ₂	5.386 95.50	6.999 93.62	14.748 89.98	P $\bar{1}$	2	(7)
bussenite ³ B4(GII)	(Na□) ₂	Ba ₂	Ba ₂	Ti ₂	(M ²⁺ Na) ₂	(Si ₂ O ₇) ₂	(CO ₃) ₂	O ₂	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^P₂B^P₂M^H₂M^O₄(Si₂O₇)₂X_{4+n}, where M^H₂ and M^O₄ = cations of the H and O sheets; A^P and B^P = cations at the peripheral (P) sites; X = anions; X_{4+n} = X^O₄ + X^P_n, n = 0, 1, 1.5, 2, 4 (Sokolova and Cámara, 2013). X^O₄ = (X^O_M)₂ + (X^O_A)₂; X^O_M = anions at common vertices of 3M^O and M^H polyhedra and X^O_A = anions at common vertices of 3M^O and A^P polyhedra (where A^P-X^O_A < 3 Å); X^P_M = apical anions of M^H cations at the periphery of the TS block. The stoichiometry of the core part of the TS block, M^H₂M^O₄(Si₂O₇)₂X^O₄, is invariant in all structures (shown in bold). In Group II, A^P and B^P cations, plus (PO₄)₂ (in yoshimuraite) and (Na□)₂(CO₃)₂F₂ (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.

¹ the formulae for cámaraite and bobshannonite are per double minimal cell based on 2t₁ and 2t₂ translations [(Si₂O₇)₄];

² there are misprints in McDonald *et al.* (2000): α = 89.98, γ = 95.50°;

³ M²⁺ = Fe²⁺, 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.* (in preparation) and Sokolova *et al.* (2009); (5) Yamnova *et al.* (1998); (6) Sokolova *et al.* (2015b); (7) McDonald *et al.* (2000); (8) Zhou *et al.* (2002).

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

Component	wt. %			Formula unit (a.p.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 ₂ O ₅	0.09	n.d.	n.d.	Si	4.04	4.11	4.03
Nb ₂ O ₅	1.27	1.4	n.d.				
SnO ₂	n.d.	n.d.	5.95	Mn	2.23	2.09	3.62
ZrO ₂	0.65	n.d.	0.22	Fe ²⁺	1.65	1.65	0.25
TiO ₂	14.35	13.27	11.82	Zr	0.04	0	0.02
SiO ₂	23.13	23.52	22.53	Mg	0.03	0.03	0.08
Al ₂ O ₃	n.d.	0.37	n.d.	Na	0	0.02	0
BaO	26.68	30.20	27.41	Σ4M ^O	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 ₂ O	0.05	n.d.	0.04	Al	0	0.08	0
K ₂ O	0.33	0.30	n.d.	Σ2M ^H	2.00	1.94	2.01
Na ₂ O	n.d.	0.06	n.d.				
H ₂ 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 ₂ ,Cl ₂	1.61	1.39	1.54	Σ2A ^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
				OH	1.89	2.18	1.93
				Σ2X ^P _M + 2X ^O _A	4.00	4.00	4.00

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.

TABLE 3. Miscellaneous refinement data for hejtmanite.

	This work	Vrána <i>et al.</i> (1992)
a (Å)	10.716(2)	10.698(4)
b	13.795(3)	13.768(5)
c	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 ³)	1612(2)	1601(2)
Space group	$C\bar{1}$	$C^*/*$ (diffraction symbol)
Z	4	4
Absorption coefficient (mm ⁻¹)	9.00	
$F(000)$	1885.8	
$D_{\text{calc.}}$ (g/cm ³)	4.189	4.29
Crystal size (mm)	0.004 x 0.025 x 0.040	
Second component*	0.474(1)	
Radiation/monochromator	MoK α /graphite	
2 θ -range for data collection (°)	60.28	
$R(\text{int})$ (%)	1.32	
Reflections collected	9468	
Independent reflections	4748	
$F_o > 4\sigma F$	4539	
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional 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_2	5.11	
Goodness of fit on F^2	1.090	

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

TABLE 4. Atom coordinates and anisotropic displacement parameters (\AA^2) for hejzmanite.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M ^O (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 ^O (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 ^O (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 ^O (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 ^O (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 ^H (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 ^H (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 ^P (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 ^O _M (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 ^O _M (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 ^O _A (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 ^O _A (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 ^P _M (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 ^P _M (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_{iso}

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

$M^O(1)-X^O_A(1)$	2.133(4) x2	$M^O(2)-X^O_A(2)$	2.104(2)	$M^O(3)-X^O_A(1)d$	2.129(2)
$M^O(1)-O(3)a$	2.194(4) x2	$M^O(2)-X^O_M(1)b$	2.128(2)	$M^O(3)-X^O_M(2)$	2.137(2)
$M^O(1)-X^O_M(1)b$	2.262(3) x2	$M^O(2)-O(6)b$	2.170(4)	$M^O(3)-O(3)$	2.174(4)
$\langle M^O(1)-\varphi \rangle$	2.196	$M^O(2)-O(10)b$	2.228(4)	$M^O(3)-O(12)$	2.192(4)
		$M^O(2)-O(3)a$	2.234(4)	$M^O(3)-O(12)e$	2.270(4)
		$M^O(2)-O(6)c$	2.275(4)	$M^O(3)-O(10)f$	2.284(4)
		$\langle M^O(2)-\varphi \rangle$	2.190	$M^O(3)-\varphi \rangle$	2.198
$M^U(4)-X^U_A(1)c$	2.107(4)	$M^U(5)-O(10)b$	2.044(4) x2		
$M^O(4)-X^O_A(2)g$	2.118(4)	$M^O(5)-X^O_A(2)$	2.119(4) x2		
$M^O(4)-O(6)$	2.118(4)	$M^O(5)-X^O_M(2)a$	2.479(3) x2		
$M^O(4)-O(12)h$	2.123(4)	$\langle M^O(5)-\varphi \rangle$	2.214		
$M^O(4)-X^O_M(2)j$	2.270(3)				
$M^U(4)-X^U_M(1)i$	2.458(3)				
$\langle M^O(4)-\varphi \rangle$	2.199				
$M^H(1)-X^O_M(1)$	1.807(2)	$M^H(2)-X^O_M(2)$	1.796(2)	$Si(1)-O(2)k$	1.605(3)
$M^H(1)-O(7)$	1.954(3)	$M^H(2)-O(8)j$	1.961(3)	$Si(1)-O(1)a$	1.622(3)
$M^H(1)-O(14)$	1.960(3)	$M^H(2)-O(1)$	1.980(3)	$Si(1)-O(3)a$	1.622(4)
$M^H(1)-O(9)$	1.977(3)	$M^H(2)-O(5)$	1.982(3)	$Si(1)-O(4)c$	1.645(3)
$M^H(1)-O(2)c$	1.994(3)	$M^H(2)-O(13)$	1.990(3)	$\langle Si(1)-O \rangle$	1.624
$M^H(1)-X^P_M(1)c$	2.091(5)	$M^H(2)-X^P_M(2)$	2.088(2)		
$\langle M^H(1)-\varphi \rangle$	1.964	$\langle M^H(2)-\varphi \rangle$	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)
$\langle Si(2)-O \rangle$	1.626	$\langle Si(3)-O \rangle$	1.623	$\langle Si(4)-O \rangle$	1.627
$A^P(1)-X^P_M(2)j$	2.772(2)	$A^P(2)-X^P_M(1)n$	2.757(2)	$Si(1)c-O(4)-Si(2)$	136.6(1)
$A^P(1)-X^P_M(1)c$	2.792(2)	$A^P(2)-X^P_M(2)l$	2.759(2)	$Si(3)n-O(11)-Si(4)n$	136.4(1)
$A^P(1)-O(13)$	2.801(3)	$A^P(2)-O(1)$	2.836(3)	$\langle Si-O-Si \rangle$	136.5
$A^P(1)-O(2)$	2.803(3)	$A^P(2)-O(14)m$	2.860(3)		
$A^P(1)-O(9)c$	2.804(3)	$A^P(2)-O(11)$	2.871(2)		
$A^P(1)-O(5)$	2.830(3)	$A^P(2)-O(4)$	2.884(2)		
$A^P(1)-O(7)$	2.844(3)	$A^P(2)-O(1)o$	3.158(3)		
$A^P(1)-O(8)$	2.864(3)	$A^P(2)-O(8)n$	3.170(3)		
$A^P(1)-X^P_M(1)$	3.018(2)	$A^P(2)-O(13)$	3.265(3)		
$A^P(1)-X^P_M(2)$	3.163(3)	$A^P(2)-O(7)$	3.274(3)		
$A^P(1)-O(5)jj$	3.235(3)	$A^P(2)-O(14)$	3.279(3)		
$A^P(1)-O(9)$	3.280(3)	$A^P(2)-O(2)n$	3.300(3)		
$\langle A^P(1)-\varphi \rangle$	2.934	$\langle A^P(2)-\varphi \rangle$	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

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

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

* coordination number is given only for non-[6]-coordinated sites;

** X = cation, φ = O, OH, F;

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

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

* 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.

TABLE 8. Hydrogen bonding in hejtmanite.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠ DHA (°)
$X_A^O(1)OH-H(1)...O(5)a$	0.98(1)	2.48(3)	3.285(4)	140(3)
$X_A^O(1)OH-H(1)...O(9)a$	0.98(1)	2.59(3)	3.339(4)	133(3)
$X_A^O(2)OH-H(2)...O(11)b$	0.98(1)	2.31(3)	2.931(3)	120(3)
$X_A^O(2)OH-H(2)...O(4)b$	0.98(1)	2.43(3)	2.976(3)	115(3)

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

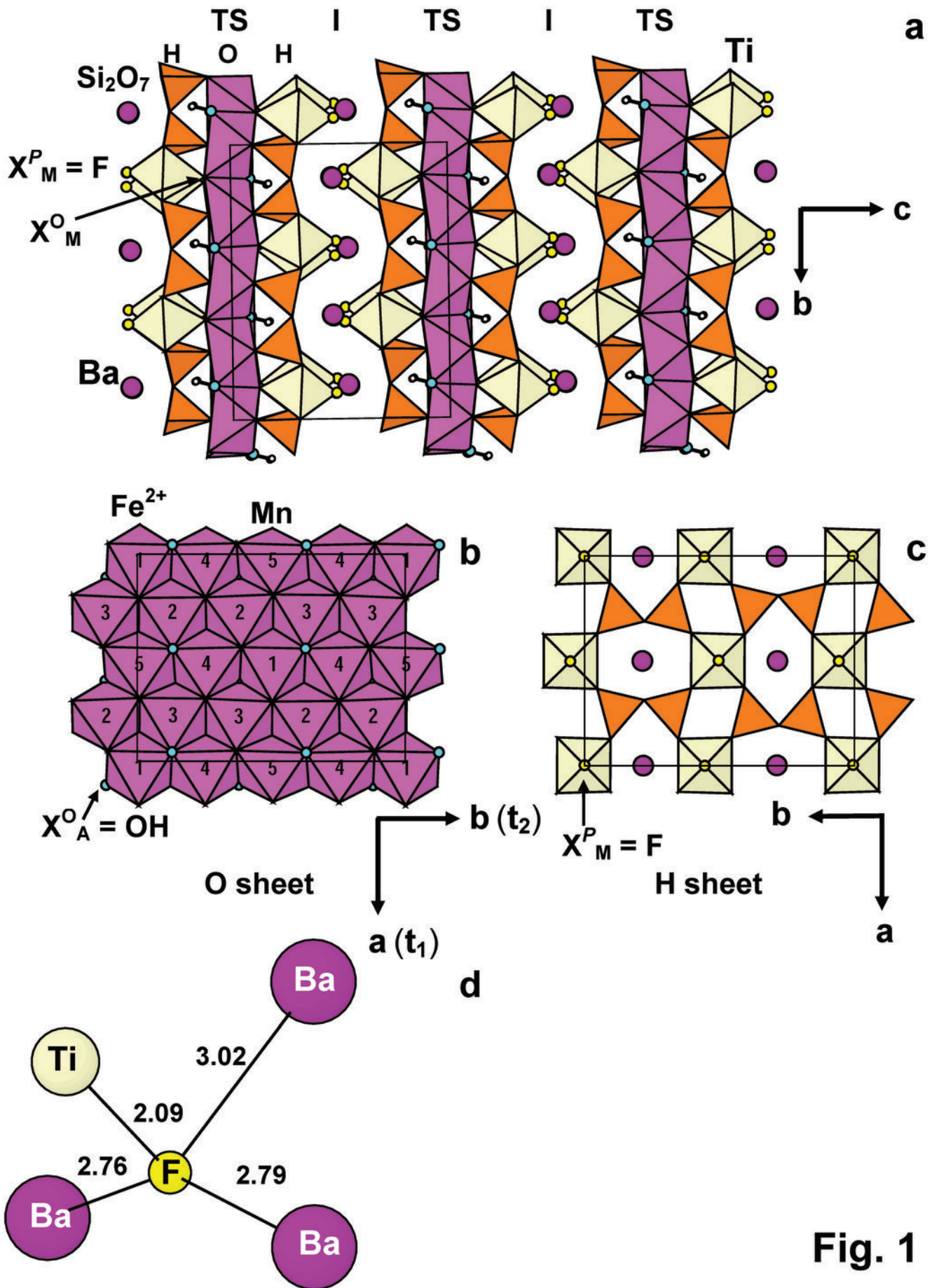


Fig. 1