FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION. XXII. TITANIUM SILICATES: REVISION OF THE CRYSTAL STRUCTURE OF JINSHAJIANGITE, NaBaFe²⁺₄Ti₂(Si₂O₇)₂O₂(OH)₂F, A GROUP-II TS-BLOCK MINERAL

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Abstract

The crystal structure of jinshajiangite from the Verkhnee Espe deposit, Kazakhstan, NaBaFe²⁺₄Ti₂(Si₂O₇)₂O₂(OH)₂F, was refined from a twinned crystal to $R_1 = 3.13\%$ on the basis of 6745 unique reflections [$F_o > 4\sigma F_o$], space group CT, Z = 8, *a* 10.7059(5), *b* 13.7992(7), *c* 20.760(1) Å, α 90.008(1), β 94.972(1), γ 89.984(1)°, *V* 3055.4(4) Å³. The crystal used for the structure refinement was analyzed by electron microprobe. The empirical formula was calculated on 19 (O + F), with (OH + F) = 3 *pfu*: (Na_{0.77}Ca_{0.23})₂₁(Ba_{0.60}K_{0.36})_{20.96}(Fe²⁺_{2.33}Fe³⁺_{0.26}Mn_{1.26}Zr_{0.04}Mg_{0.02}Zn_{0.01})_{23.92}(Ti_{1.79}Nb_{0.18}Mg_{0.02}Al_{0.01})₂₄ (Si₂O₇)₂O_{3.93}H_{1.93}F_{1.07}, *Z* = 8; Fe₂O₃ was calculated by analogy with jinshajiangite from Norra Karr, Sweden (Sokolova *et al.* 2009a) and H₂O from the crystal-structure analysis. In the crystal structure, TS (Titanium Silicate) and I (Intermediate) blocks alternate along **c**. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The topology of the TS block si as in Group II of the TS-block minerals where Ti (+Nb) = 2 *apfu*. In the O sheet, ten ^[6]*M*^O sites are occupied mainly by Fe²⁺, with $< M^O - \phi > = 2.181$ Å. In the H sheet, four ^[6]*M*^H sites are occupied mainly by Ti, with $< M^H - \phi > = 1.954$ Å, and eight ^[4]*Si* sites are occupied by Si, with <Si-O > = 1.622 Å. The M^H octahedra and Si₂O₇ groups constitute the H sheet. Fluorine atoms and OH groups are ordered at the X^P_M (H sheet) and X^O_A (O sheet) sites, respectively. The TS blocks link *via* common vertices of M^H octahedra, *i.e.*, M^H-X^P_M-M^H bridges. In the I block, Ba and K occur at the two A^P sites, with Ba > K, and the two B^P sites are occupied by Na and Ca, with Na > Ca. Jinshajiangite is isostructural with bobshannonite, Na₂KBa(Nb,Ti)₄Mn₈(Si₂O₇)₄O₄(OH)₄(O,F)₂, Z = 4.

Keywords: jinshajiangite, TS block, electron microprobe, crystal structure, Verkhnee Espe deposit, Kazakhstan.

INTRODUCTION

The TS (Titanium Silicate) block is the main structural unit in 40 minerals: 34 are listed in Sokolova & Cámara (2013); information on six additional minerals, kolskyite, emmerichite, saamite, bobshannonite, betalomonosovite, and fogoite-(Y), can be found in Cámara *et al.* (2013), Aksenov *et al.* (2014), Cámara *et al.* (2014a), Sokolova *et al.* (2015a), Sokolova *et al.* (2015b), and Cámara *et al.* (2015), respectively. The TS block consists of a central O (Octahedral) sheet and two adjacent H (Heteropolyhedral) sheets of [5–7]-coordinated polyhedra and Si₂O₇ groups. The TS block is characterized by a planar cell based on minimal lengths of translational vectors, $t_1 \sim 5.4$ and $t_2 \sim 7$ Å, and $\mathbf{t_1} \wedge \mathbf{t_2} \approx 90^\circ$. The general formula of the TS block is $A^P _2 B^P _2 M^H _2 M^O _4 (Si_2 O_7)_2 X_{4+n}$, where $M^H _2$ and $M^O _4$ = cations of the H and O sheets; $M^H =$ Ti, Nb, Zr, Y, Mn, Ca + REE, Ca; $M^O =$ Ti, Zr, Nb, Fe²⁺, Fe³⁺, 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 H₂O groups; $X_{4+n} = X^O _4 + X^P _n$, n = 0, 1, 1.5, 2, 4 (Sokolova 2006, Sokolova & Cámara, 2013). There are three topologically distinct TS blocks based on three types of

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linkage of H and O sheets. In the crystal structures of TS-block minerals, TS blocks either link directly or alternate with I (Intermediate) blocks. The I block consists of alkali and alkaline-earth cations, oxyanions PO₄, SO₄, and CO₃, and H₂O groups. The TS-block structures are divided into four Groups, based on the topology and stereochemistry of the TS block (Sokolova 2006). Each group of structures has a different linkage, content, and stereochemistry of Ti (+ $Nb + Zr + Fe^{3+} + Mg + Mn$). In Groups I, II, III, and IV, Ti = 1, 2, 3, and 4 *apfu* (atoms per formula unit) per $(Si_2O_7)_2$, respectively. In a TS-block structure, four types of self-linkage between adjacent TS blocks occur. Sokolova & Cámara (2013) introduced the concept of basic and derivative structures for TSblock 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 of 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.

The basic crystal structures of four Group-II TSblock minerals, jinshajiangite, perraultite, surkhobite, and bobshannonite, belong to the perraultite structuretype (Yamnova et al. 1998) and are characterized by doubled t_1 and t_2 unit-cell parameters (Table 1). Sokolova & Cámara (2016) considered Ba-containing structures of TS-block minerals and explained (1) the doubling of cell parameters relative to the planar cell based on minimal translations, t_1 and t_2 , in some Group-II and Group-III structures, and (2) the ordering of OH and F in Ba-containing structures. The work of Sokolova & Cámara (2016) gave us an impetus to revisit the crystal structure of jinshajiangite (Sokolova et al. 2009a). Here we report the revised crystal structure of jinshajiangite and consider the crystal chemistry of TS-block minerals with the perraultite structure-type.

Previous Work on the Perraultite Structure-Type Minerals

Jinshajiangite, $(Na,K)_5(Ba,Ca)_4(Fe^{2+},Mn)_{15}(Ti, Fe^{3+},Nb)_8(SiO_4)_{15}(F,O,OH)_{10}, Z = 2$, from the Jinsha-

jiang River, Sichuan Province, China, was described as a new mineral by Hong & Fu (1982). Chao (1991) described perraultite, ideally Na2KBa(Ti,Nb)4Mn8 $Si_8O_{32}(OH,F,H_2O)_7$, Z = 4, from Mont Saint-Hilaire, Québec, Canada, and suggested that jinshajiangite is isotypic with perraultite. Yamnova et al. (1998) solved the crystal structure of perraultite from the coastal region of the Azov sea (later described by Pekov et al. 1999) and gave the "generalized crystal-chemical" formula as follows: (Na,Ca)₂(Ba,K)₂(Mn,Fe)₈[(Ti, $Nb_4O_4(OH)_2Si_8O_{28}](OH,F)_4, Z = 4$ (Table 1). Sokolova (2006) wrote the ideal formula of perraultite as NaBaMn₄Ti₂(Si₂O₇)₂O₂(OH)₂F, Z = 8 and considered it as a Group-II TS-block mineral. Rastsvetaeva et al. (2008) reported the crystal structure and Mössbauer-spectroscopy data for surkhobite, (Ba,K)₂ CaNa(Mn,Fe²⁺,Fe³⁺)₈Ti₄(Si₂O₇)₄O₄(F,OH,O)₆, an ordered derivative of perraultite, with Ca ordered at one of the interstitial sites in the I block (Table 1). Sokolova et al. (2009a) solved the crystal structure of jinshajiangite from Norra Kärr, Tönköping province, Sweden, in space group C2/m, determined the Fe²⁺/ Fe³⁺ atomic ratio by Mössbauer spectroscopy, and wrote its ideal formula as: BaNaTi₂Fe²⁺ $_{4}$ (Si₂O₇)₂ $O_2(OH)_2F, Z = 8.$

OCCURRENCE

The crystal of jinshajiangite used in this work is a plate $(0.30 \times 0.25 \times 0.025 \text{ mm})$ of yellow color and is from the Verkhnee Espe deposit (48°03′-48°10′N, 81°26'-81°29'E) in Kazakhstan. Macroscopically, it does not show twinning. However, the diffraction data show the presence of twinning and refinement gives the ratio of twin components as 54.50 to 45.50%. The rare-metal (Zr, Nb, REEs, Th, etc.) Verkhnee Espe deposit was discovered in the 1950's. It is spatially and genetically related to an intrusion of alkali granite in the northern exocontact of the Akjailyautas granite massif (Stepanov & Bekenova 2009) that crops out as part of a belt of alkaline-granite dikes which extends 5 km NNE and more than 20 km SSW. At the Verkhnee Espe deposit, jinshajiangite often forms intergrowths with two other Group-II TS-block minerals: bafertisite and cámaraite (Sokolova et al. 2009b, Cámara et al. 2009) (Table 1). These hydrothermal minerals occur in fenites which are most enriched in alkalies and have been extensively recrystallized. The rocks underwent significant enrichment in F, Li, and rare elements, and loss of the typical hypidiomorphic texture and development of granoblastic texture. The source of Ba for these minerals may have been the adjacent tuffaceous aleurolites and dikes of basic and intermediate rocks. Jinshajiangite is also associated with ferrifluoro-leakeite (named fluoroleakeite by Cámara et al.

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Mineral	Str.**			Ide	al structura	l formula**			α (A) = ζ ⁽¹⁾	$b(\mathbf{A}) = 2l_2$ $\beta(^{\circ})$	(r) (1) (1)	.in .de	Ref.
		ВР	A^{P}	Mo₄	M ^H 。	(Si ₂ 0 ₇)2	X ⁰ 4	X ^P _M					
Jinshajiangite	B1(GII)	Na	Ва	Fe ²⁺ 4	Ti2	$(Si_2O_7)_2$	0 ₂ (OH) ₂	i LL	10.7059	13.7992	20.760	<u>5</u>	(1)
									90.008	94.972	89.984	8	
Perraultite***	B1(GII)	Na_2	Ba_2	Mn ₈	Ti ₄	(Si ₂ O ₇) ₄	O₄(OH,F)₄	(OH) ₂	10.731	13.841	20.845	8	(2)
									06	95.06	06	4	
Surkhobite****	B1(GII)	Na_2	Ba_3	Mn ₁₆	Ti _s	(Si ₂ 0 ₇) ₈	O ₈ F ₆	Ъ2	10.723	13.826	20.791	8	(3)
		Ca_2	¥				(OH) ₂	$(OH)_2$	06	95.00	06	0	
Bobshannonite***	B1(GII)	Na_2	K Ba	(Mn,Na) ₈	(Nb,Ti) ₄	(Si ₂ O ₇) ₄	O₄(OH)₄	$(0,F)_{2}$	10.839	13.912	20.98	<u>5</u>	(4)
									89.99	95.02	89.998	4	
			A^{P}_2	M ⁰ 4	M_2^{H}	(Si ₂ 0 ₇) ₂	X ⁰ ₄	$(X^P_M)_2$					
Bafertisite	B2(GII)		Ba_2	Fe^{2+}_4	Ti_2	$(Si_2O_7)_2$	0 ₂ (0H) ₂	Ъ	10.677	13.767	11.737	<u>5</u>	(2)
									90.12	112.28	90.02	4	
Hejtmanite	B2(GII)		Ba_2	Mn ₄	T_2	$(Si_2O_7)_2$	0 ₂ (0H) ₂	\mathbf{F}_{2}	10.716	13.795	11.778	<u>5</u>	(9)
									90.07	112.24	90.03	4	
		ВР	A_{3}^{P}	M08	M_{4}^{H}	(Si ₂ O ₇) ₄	×°8	$(X^{P}_{M})_{3}$					
Cámaraite***	D1(GII)	Na	Ba_3	Fe ²⁺ 8	Ti ₄	(Si ₂ O ₇) ₄	O₄(OH)₄	щ	10.696	13.7861	21.478	<u>5</u>	(7, 8)
									99.345	92.315	89.993	4	
Jinshajiangite component	B1(GII)	Na	Ba	Fe^{2+}_4	T_{1_2}	$(Si_2O_7)_2$	0 ₂ (OH) ₂	ш					
Bafertisite component	B2(GII)		Ba_2	Fe^{2+}_4	Ti ₂	(Si ₂ 0 ₇) ₂	0 ₂ (0H) ₂	F_2					
* $t_1\sim 5.4$ and $t_2\sim 7$ Å in (** Structure type, B (basic) *** por /Si O) · **** por /S	Group II; or D (deri	vative)	, and ge	neral formu	lae are fror	n Sokolova	& Cámara (2	013); form	iulae are per	(Si₂O ₇₎₂ , exce	ept for		

The invariant core of the TS block, **M⁰4M¹₂(Si₂O₇)₂X⁰4**, is shown in bold: M^H = cations of the H sheet, M^O = cations of the O sheet, The invariant core of the TS block, **M⁰4M¹₂(Si₂O₇)₂X⁰4**, is shown in bold: M^H = cations of the H sheet, M^O = cations of the O sheet not shared with Si; A^P and B^P = cations at the peripheral (*P*) sites (Sokolova 2006). The formula of cámaraite is the sum of the formulae of X⁰4 = anions of the O sheet not shared with Si; A^P and B^P = cations at the peripheral (*P*) sites (Sokolova 2006). The formula of cámaraite is the sum of the formulae of

References: (1) This work; (2) Yamnova et al. (1998); (3) Rastsvetaeva et al. (2008); (4) Sokolova et al. (2015a); (5) Cámara et al. (2016); (6) Sokolova et al. (2016); jinshajiangite and bafertisite components;

(7) Cámara et al. (2009); (8) revised formula: Sokolova & Cámara (2016).

2010; renamed to ferri-fluoro-leakeite by Hawthorne *et al.* 2012) as well as various rare-metal minerals: zircon, pyrochlore-group minerals, thorite, monazite, and xenotime. More details on the geological setting and paragenesis of these samples can be found in Sokolova *et al.* (2009b). This is the fourth occurrence of jinshajiangite after the three previously reported: Jinshajiang River, Sichuan Province, China (Hong & Fu 1982); Norra Kärr, Tönköping province, Sweden (Sokolova *et al.* 2009a); and Gremyakha-Vyrmes alkaline complex, Kola Peninsula, Russia (Lykova *et al.* 2010).

CHEMICAL COMPOSITION

The crystal used for the structure refinement was analyzed 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 µm. The following standards were used: diopside (Si, Ca); Mn(Ta_{1.7} Nb_{0.3})O₆ (Ta); Ba₂NaNb₅O₁₅ (Nb); baryte (Ba); titanite (Ti); andalusite (Al); fayalite (Fe); spessartine (Mn); forsterite (Mg); gahnite (Zn); zircon (Zr); albite (Na); orthoclase (K); and fluor-riebeckite (F). The elements Rb, Sr, and Cs were sought but not detected. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). The Fe₂O₃ was calculated by analogy with Mössbauer data for jinshajiangite from Norra Karr, Sweden (Sokolova et al. 2009a) and H₂O was calculated from the results of the crystal-structure refinement. Table 2 gives the chemical composition for jinshajiangite from the Verkhnee Espe deposit (mean of 10 determinations) compared with chemical compositions of jinshajiangite from the Jinshajiang River, Sichuan Province, China (Hong & Fu 1982) and Norra Karr, Sweden (Sokolova et al. 2009a). The empirical formula of jinshajiangite calculated for 19 (O + F), with (OH + F) = 3 pfu, is: $(Na_{0.77}Ca_{0.23})_{\Sigma 1}(Ba_{0.60}K_{0.36})_{\Sigma 0.96}$ $(Fe^{2+}_{2.33}Fe^{3+}_{0.26}Mn_{1.26}Zr_{0.04}Mg_{0.02}Zn_{0.01})_{\Sigma 3.92}(Ti_{1.79})$ Nb_{0.18}Mg_{0.02}Al_{0.01}) $_{\Sigma4}$ (Si₂O₇) $_{2}$ O_{3.93}H_{1.93}F_{1.07}, Z = 8; the ideal formula is NaBaFe²⁺₄Ti₂(Si₂O₇)₂O₂(OH)₂F, Z = 8.

In this paper, we use Z = 4 to discuss the crystal structure. However, we will write the ideal formula of jinshajiangite with Z = 8, which simplifies comparison of jinshajiangite with the other 39 TS-block minerals, which are characterized by the TS block of the form $A^P_2 B^P_2 M^H_2 M^O_4 (Si_2 O_7)_2 X_{4+n}$.

CRYSTAL STRUCTURE

Data collection and structure refinement

Single-crystal X-ray data for jinshajiangite were collected using a Bruker-AXS APEX three-circle

diffractometer with MoKa radiation, multilayer optics, and an APEX 1K CCD detector. The intensities of 23038 reflections with -15 < h < 15, -19 < k < 19, -29 < l < 29 were measured to $60^{\circ} 2\theta$ using 10 s per 0.2° frame. Unit-cell parameters and other miscellaneous information relating to data collection and structure refinement are given in Table 3. An absorption correction was done using the SADABS program (Sheldrick 2008). All calculations were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 2008). The crystal-structure refinement of jinshajiangite was done using data from a twinned crystal with two components related by the twin matrix $[100 \ 010 \ 001]$. As a starting model, we used the atom coordinates of bobshannonite including four H atoms (Sokolova et al. 2015a). The crystal structure was refined in space group $C\overline{1}$ to $R_1 = 3.13\%$, with a twin ratio of 0.5450(7):0.4550(7). The (Niggli) reduced unit-cell is: a 8.7314(3), b 8.7338(3), c 20.760(1) Å, α 93.051(1), β 93.039(1), γ 104.389(8)°, V 1527.7(1) Å³, space group $P\overline{1}$, Z = 2. The $P\overline{1}$ unit cell can be derived from the $C\overline{1}$ unit cell *via* the transformation matrix $\left[\frac{1}{2}-\frac{1}{2}0, \frac{1}{2}\frac{1}{2}0, 001\right]$. We chose the unconventional space group C1 for better comparison with the TS-block structures, which are characterized by two minimal translations, $t_1 \sim 5.4$ and $t_2 \sim 7$ Å in Group II, especially related structures with doubled t_1 and t_2 translations (Table 1). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson 1992). In the crystal structure of jinshajiangite, there are three groups of cation sites: M^{O} sites of the O sheet, $M^{\rm H}$ and Si sites of the H sheet, and peripheral $A^{\rm P}$ and B^P sites which occur in the I block; site labeling is in accord with Sokolova (2006). Site-scattering values were refined for the $M^{O}(1-10)$ sites with the scattering curve of Fe, $M^{\rm H}(1-4)$ sites (Ti), $A^{\rm P}(1,2)$ sites (Ba), and $B^{P}(1,2)$ sites (Na). The $A^{P}(2)$ site is split into three $A^{P}(21-23)$ subsites, partly occupied by Ba and K and separated by short distances: $A^{P}(21)-A^{P}(22) = 0.965$. $A^{P}(21)-A^{P}(23) = 0.41$, and $A^{P}(22)-A^{P}(23) = 0.70$ Å. The site-scattering values for the $A^{P}(21-23)$ subsites were refined and then fixed. The D (donor)-H distances were softly constrained to 0.98 Å. The four M^H(1A-4A) subsidiary peaks were found in the difference-Fourier map at distances 0.65 Å from the four Ti-dominant $M^{\rm H}(1-4)$ sites and were included in the refinement. Their site occupancies were refined with the scattering curve of Ti and are as follows (%): 9.1, 2.8, 11.4, and 5.7. Final atom coordinates and equivalent displacement parameters are listed in Table 4, selected 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

	Chemical of	composition (wt.%	»)		Unit forr	nula (<i>apfi</i>	u)***
	Hong & Fu (1982)	Sokolova <i>et al.</i> (2009a)	This work		Sokolov (200	va <i>et al.</i> 09a)	This work
	(1)	(2)	(3)		(2a)	(2b)	(3)
SiO ₂	27.10	27.56	27.41	Si	8.00	7.95	8.01
Al_2O_3	n.d.	n.d.	0.07				
TiO ₂	15.90	18.36	16.24	Ti	4.00	3.98	3.57
Nb_2O_5	1.03	0.12	2.74	Nb	0.02	0.02	0.36
Ta ₂ O ₅	0.07	n.d.	n.d.	Mg			0.05
ZrO_2	0.70*	0.51	0.22	AI			0.02
FeO	19.07	23.42	19.00	ΣM^H	4.02	4.00	4.00
Fe ₂ O ₃	1.64	2.89	2.34				
ZnO	n.a.	n.d.	0.10	Fe ²⁺	5.68	5.65	4.65
MnO	12.93	5.13	10.19	Fe ³⁺	0.64	0.63	0.52
MgO	0.28	0.44	0.19	Mn	1.26	1.25	2.52
CaO	2.94	2.52	1.45	Mg	0.20	0.19	0.03
BaO	9.80	10.24	10.46	Zr	0.08	0.07	0.07
SrO	0.08	n.d.	n.d.	Zn			0.02
K ₂ O	2.31	1.95	1.92	Na	0.14	0.05	
Na ₂ O	3.15	2.27	2.74	ΣM ^O	8.00	7.79	7.81
Cs_2O	n.a.	0.03	n.d.				
F	2.66	2.33	2.31	Ba	1.16	1.16	1.20
H ₂ O	0.36	2.00**	1.96**	K	0.72	0.72	0.72
O=F	-1.12	-0.98	-0.97	ΣA^P	1.88	1.88	1.92
Total	99.56	98.79	98.37				
				Na	1.14	1.22	1.55
				Ca	0.78	0.78	0.45
				ΣB^{P}	1.92	2.00	2.00
				OH	3.86	3.88	3.86
				F	2.14	2.13	2.14
				Σ	6.00	6.01	6.00

TABLE 2. CHEMICAL COMPOSITION AND UNIT FORMULA (Z=4) FOR JINSHAJIANGITE

(1) Bulk chemistry; (2, 3) electron-microprobe analysis; n.a. - not analyzed; n.d. - not detected.

* (Zr,Hf)O2:

** Calculated from crystal-structure refinement.

*** Formula calculated for (2a) on Si = 8 *apfu* (taken from Sokolova *et al.* 2009a) and (2b and 3) on 38 (O + F) *apfu*, with OH + F = 6 *pfu*.

Table 7, and details of hydrogen bonding in Table 8. Anisotropic displacement parameters, a table of structure-factors, and a Crystallography Information File (CIF) may be obtained from The Depository of Unpublished Data on the MAC website [document jinshajiangite CM54-5_10.3749/canmin.1600008].

Site-population assignment

Here we consider the cation sites of three groups: M^{O} sites of the O sheet, M^{H} sites of the H sheet, and peripheral A^{P} and B^{P} sites.

For the 10 M^{O} sites, the following cations are available (Table 2): 4.65 Fe²⁺ + 0.52 Fe³⁺ + 2.52 Mn +

0.07 Zr + 0.03 Mg + 0.02 Zn (total scattering 201.18 *epfu*); the aggregate refined scattering at these sites is 205.4 *epfu* (Table 6), in close accord with this composition. The refined site-scattering values at the 10 $M^{\rm O}$ sites vary from 24.4 to 26.7 electrons per site. The mean bond-lengths around these sites are very similar and values of aggregate cation radii derived from observed mean bond-lengths are ≥ 0.79 Å (^[6]r = 0.78 Å for Fe²⁺), indicating disorder of cations over the 10 $M^{\rm O}$ sites. Based on the bond lengths and corresponding site-scattering, we assign the following dominant cations: Mn to the three $M^{\rm O}(5,8,10)$ sites and Fe²⁺ to the other seven sites (Table 6).

TABLE 3. MISCELLANEOUS REFINEMENT DATA FOR JINSHAJIANGITE

a (Å)	10.7059(5)
b	13.7992(7)
С	20.760(1)
α (°)	90.008(1)
β	94.972(1)
γ	89.984(1)
<i>V</i> (Å ³)	3055.4(4)
Refl. ($I_{o} > 10\sigma I$)	5217
Space group	C1
Z, ideal formula	8, NaBaFe ²⁺ ₄ Ti ₂ (Si ₂ O ₇) ₂
	O ₂ (OH) ₂ F
Absorption coefficient (mm ⁻¹)	6.60
<i>F</i> (000)	3297.1
$D_{\text{calc.}}$ (g/cm ³)	3.764
Crystal size (mm)	0.30 imes 0.25 imes 0.025
Radiation/monochromator	MoKa/graphite
2θ _{max} (°)	59.99
<i>R</i> (int) (%)	3.47
Second component (%)	54.50(7)
Reflections collected	23038
Independent reflections	8810
$F_{\rm o} > 4\sigma F$	6745
Refinement method	Full-matrix least squares on F^2 , fixed weights
	proportional to $1/\sigma F_0^2$
Final $R_{(obs)}$ (%)	
$R_1 [F_0 > 4\sigma F]$	3.13
R_1 (all data)	3.96
wR ₂	8.72
Goodness of fit on F^2	1.061

* Second component of the crystal is related to the first component by the twin matrix $[\overline{1}00 \ 010 \ 00\overline{1}]$.

In TS-block minerals, Ti-dominant $M^{\rm H}$ sites are always fully occupied. Table 2 gives available cations, 3.57 Ti + 0.36 Nb + 0.05 Mg + 0.02 Al, total 4 *apfu* (Z = 4), and the aggregate refined scattering at these sites is 91.30 *epfu* (Table 6). Hence in accord with individual site-scattering values, we assign Ti + Nb + Mg + Al to the four $M^{\rm H}$ sites (Table 6).

There are two A^P sites in the crystal structure of jinshajiangite. The refined site-scattering value at the ${}^{[10]}A^P(1)$ site is 54.33 *epfu*, and mean bond-length $<A^P(1)-\phi> = 2.901$ Å (where ϕ is an unspecified anion) (Table 6) is consistent with the ionic radius of Ba (${}^{[10]}r = 1.52$ Å, Shannon 1976). Therefore we assign 0.97 Ba + 0.03 \Box to the $A^P(1)$ site. We are left with 0.23 Ba + 0.72 K *apfu* to assign to the $A^P(2)$ site, with total refined scattering of 29.46 *epfu*. The $A^P(2)$, and ${}^{[11]}A^P(23)$, which are 0.41–0.965 Å apart (Table 5). The refined site-scattering value at the $A^P(21)$ site is 16.45 *epfu* (Table 6), more than the 13.68 *epfu* that

can be provided by 0.72 K *apfu*. Hence we assign 0.23 Ba + 0.10 K *apfu* to the $A^{P}(21)$ site (calculated scattering of 14.78 *epfu*) and distribute 0.72 - 0.10 = 0.62 K *apfu* between the $A^{P}(22)$ and $A^{P}(23)$ sites. In accord with the refined site-scattering values for the $B^{P}(1,2)$ sites, we assign Na > Ca to these two sites (Table 6).

Description of the structure

Topology of the structure. Jinshajiangite is a Group II TS-block mineral. The overall topology of the basic crystal structure of jinshajiangite (space group $C\overline{1}$) is in accord with the perraultite structure-type (space group C2) (Yamnova et al. 1998); jinshajiangite is isostructural with bobshannonite (Table 1). In the structure of jinshajiangite, there are two independent TS blocks, *i.e.*, they are not related by any element of symmetry, and one I block (Fig. 1a). The TS₁ and TS₂ blocks are composed of H1-O1-H1 and H2-O2-H2 sheets, respectively. The $M^{O}(2,3,5,9,10)$ and $M^{O}(1,4,6,7,8)$ octahedra form close-packed O1 (Fig. 1b) and O2 sheets (Fig. 1c), respectively. In the H sheets, SiO₄ tetrahedra link via common vertices to form Si₂O₇ groups that are oriented along **b** $(b = 2t_2)$ (Fig. 1a, d, e). The Si₂O₇ groups and M^H octahedra share common vertices to form the two identical H sheets in each TS block. An O sheet and two adjacent H sheets link through common vertices of SiO₄ tetrahedra and M^H and M^O octahedra to form a TS block parallel to (001) (Fig. 1a). In the TS block, Si_2O_7 groups link to two M^O octahedra of the O sheet adjacent along b, as in Group II of Sokolova (2006) (Fig. 1a). In jinshajiangite, TS blocks are connected through common vertices of M^{H} octahedra, *i.e.*, $M^{H}-X^{P}M^{-}M^{H}$ bridges, as in astrophyllite- and kupletskite-group minerals (Sokolova et al. 2017), plus cations of the I block: Ba > K at the A^P sites and Na > Ca at the B^P sites (Fig. 1a, c).

Cation and anion sites. The cation sites are divided into three groups: M^{O} sites of the O sheet, M^{H} and *Si* sites of the H sheet, and peripheral A^{P} and B^{P} sites which occur in the I block. In accord with Sokolova (2006), we label the X anions: $2X^{O}_{M} = \text{common}$ vertices of $3M^{O}$ and M^{H} polyhedra; $2X^{O}_{A} = \text{common}$ vertices of $3M^{O}$ octahedra that occur approximately under the A^{P} sites (Fig. 1a, b); $2X^{P}_{M} = \text{apical anions of}$ M^{H} cations at the periphery of the TS block.

In the O sheets, there are seven Fe^{2+} -dominant $M^{O}(1-4,6,7,9)$ sites and three Mn-dominant $M^{O}(5,8,10)$ sites (Table 6). The $M^{O}(1,2,4,5,8,9)$ atoms are coordinated by four O atoms and two monovalent X^{O}_{A} anions, with $\langle M^{O}-\phi \rangle = 2.164-2.226$ Å. The $M^{O}(3,6,7,10)$ atoms are coordinated by five O atoms and a monovalent X^{O}_{A} anion, with $\langle M^{O}-\phi \rangle = 2.171-2.187$ Å. The ordering of Fe²⁺-dominant and

Atom	x/a	y/b	z/c	$U_{\rm eq}$ (Å ²)
M ^O (1)	0	1/2	1/2	0.0129(5)
M ^O (2)	0.25212(9)	0.49818(7)	0.99836(5)	0.0093(3)
M ^O (3)	0.00064(8)	0.62356(7)	0.99524(4)	0.0088(3)
M ^O (4)	0.00093(10)	0.74813(7)	0.49791(5)	0.0096(3)
M ^O (5)	1⁄4	3⁄4	0	0.0188(5)
M ^O (6)	0.25151(8)	0.62347(8)	0.50601(4)	0.0097(3)
M ^O (7)	0.24957(8)	0.12649(8)	0.50465(4)	0.0094(3)
M ^O (8)	0	0	1/2	0.0198(6)
M ^O (9)	1⁄4	1⁄4	0	0.0117(5)
M ^O (10)	-0.00172(8)	0.12656(8)	0.99419(4)	0.0087(3)
M ^H (1)	0.14136(12)	0.14472(10)	0.85156(7)	0.0049(3)
M ^H (2)	0.14099(9)	0.60488(10)	0.85105(5)	0.0063(3)
M ^H (3)	0.10786(16)	0.14494(10)	0.64873(9)	0.0046(3)
M ^H (4)	0.10804(9)	0.60478(10)	0.64812(5)	0.0062(3)
Si(1)	0.34398(17)	0.76630(13)	0.63032(9)	0.0082(3)
Si(2)	0.84396(15)	0.48456(13)	0.62976(8)	0.0061(3)
Si(3)	0.40630(15)	0.48407(13)	0.86929(8)	0.0057(3)
Si(4)	0.88459(17)	0.48471(13)	0.86934(8)	0.0063(3)
Si(5)	0.90616(16)	0.76514(13)	0.86946(9)	0.0075(3)
Si(6)	0.36667(16)	0.48335(13)	0.63111(8)	0.0062(3)
Si(7)	0.38322(16)	0.76691(13)	0.86924(9)	0.0072(3)
Si(8)	0.86544(17)	0.76533(12)	0.63028(9)	0.0082(3)
A ^P (1)	0.12480(6)	0.37425(5)	0.74982(3)	0.01181(6)
A ^P (21)	0.1239(2)	0.9010(2)	0.75035(12)	0.0400(8)
A ^P (22)	0.1245(3)	0.8311(2)	0.74966(12)	0.0246(5)
A ^P (23)	0.8539(12)	0.1216(18)	0.2530(7)	0.049(4)*
B ^P (1)	0.3754(3)	0.6250(2)	0.74941(13)	0.0149(4)
B ^P (2)	0.8744(3)	0.6248(2)	0.74992(13)	0.0166(4)
O(1)	0.0975(4)	0.7422(4)	0.0535(2)	0.0064(8)
O(2)	0.0947(4)	0.5016(4)	0.0521(2)	0.0062(8)
O(3)	0.1640(3)	0.7470(4)	0.4496(2)	0.0101(9)
O(4)	0.8327(5)	0.4954(4)	0.5516(2)	0.0114(9)
O(5)	0.8457(5)	0.7535(5)	0.5521(3)	0.0153(10)
O(6)	0.3483(5)	0.4924(4)	0.5518(2)	0.0090(9)
O(7)	-0.0846(4)	0.7539(4)	0.9473(2)	0.0071(8)
O(8)	0.4135(5)	0.4964(5)	0.9460(2)	0.0112(9)
O(9)	0.3327(3)	0.8762(2)	0.84933(17)	0.0140(7)
O(10)	0.2449(3)	0.6974(3)	0.66338(17)	0.0119(7)
0(11)	0.2729(3)	0.6978(3)	0.83625(18)	0.0120(7)
0(12)	0.0047(3)	0.0529(3)	0.83699(18)	0.0136(7)
O(13)	0.2457(3)	0.0533(3)	0.00498(17)	0.0120(7)
O(14) O(15)	0.0038(3)	0.0972(3)	0.63075(18)	0.0135(7)
O(15)	-0.024(4)	0.0522(3)	0.00300(10)	0.0140(8)
O(16)	-0.0248(3)	0.0955(3)	0.00203(10)	0.0107(7)
O(17)	0.2993(3)	0.0754(5)	0.04930(17)	0.0100(7)
O(10)	-0.0499(3)	0.0740(3)	0.65060(14)	0.0100(0)
O(20)	0.0140(3)	0.4006(3)	0.00109(10)	0.0120(7)
O(21)	0.2650(3)	0.2497(2)	0.83962(10)	0.0120(7)
O(22)	0.2368(3)	0.5005(3)	0.66200(17)	0.0134(7)
O(23)	0.0138(3)	0.5022(3)	0.83663(17)	0 0122(7)
O(24)	-0.0156(3)	0.2486(3)	0.66227(18)	0.0121(7)
O(25)	0.9160(3)	0.8747(2)	0.65036(14)	0.0112(6)

TABLE 4. ATOM COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS FOR JINSHAJIANGITE

Atom	x/a	y/b	z/c	$U_{\rm eq}$ (Å ²)
O(26)	0.2730(3)	0.0534(3)	0.83770(19)	0.0152(8)
O(27)	0.0139(3)	0.2501(3)	0.83750(17)	0.0136(7)
O(28)	0.7367(3)	0.7501(3)	0.66263(18)	0.0151(7)
Х ^о _м (1)	0.1532(3)	0.1348(4)	0.93890(18)	0.0093(8)
Х ^о _м (2)	0.1540(4)	0.6135(4)	0.93620(19)	0.0109(9)
Х ^о _м (3)	0.0954(4)	0.1361(4)	0.56145(19)	0.0117(9)
Х ^о _м (4)	0.0973(4)	0.6146(4)	0.5616(2)	0.0160(10)
X ^O _A (1)	0.1639(4)	0.3730(5)	0.95661(19)	0.0092(9)
$X^{O}_{A}(2)$	0.3375(4)	0.6233(5)	0.0438(2)	0.0102(9)
X ^O _A (3)	0.0871(4)	0.3759(5)	0.5446(2)	0.0134(10)
$X^{O}_{A}(4)$	0.0849(4)	0.8749(5)	0.5406(2)	0.0109(9)
X ^P _M (1)	0.1255(3)	0.6008(3)	0.74938(12)	0.0147(7)
X ^P _M (2)	0.1251(3)	0.1490(3)	0.75056(12)	0.0154(7)
H(1)	0.147(5)	0.392(4)	0.9118(10)	0.01109*
H(2)	0.292(5)	0.599(4)	0.080(2)	0.01226*
H(3)	0.047(5)	0.350(4)	0.581(2)	0.01613*
H(4)	0.100(6)	0.849(4)	0.5846(12)	0.01308*
Subsidiary	peaks			
М ^н (1А)	0.1422(16)	0.1145(13)	0.8552(8)	0.005*
М ^н (2А)	0.153(3)	0.654(3)	0.8434(16)	0.005*
M ^H (3A)	0.1101(16)	0.1198(11)	0.6499(8)	0.005*
M ^H (4A)	0.1131(19)	0.6627(17)	0.6445(10)	0.020(4)*

TABLE 4. CONTINUED.

Note: * U_{iso} (Å²)

Mn-dominant octahedra follows different patterns in the O₁ and O₂ sheets (Fig. 1b, c). However $Fe^{2+} > Mn$ in both sheets: O₁=2.19 Fe^{2+} +0.20 Fe^{3+} +1.45 Mn+ 0.07 Zr + 0.03 Mg + 0.06 \Box ; O₂ = 2.46 Fe^{2+} + 0.32 Fe^{3+} + 1.07 Mn + 0.07 Zr + 0.03 Mg + 0.06 \Box . Hence Fe^{2+} -dominant and Mn-dominant sites give ideally Fe^{2+}_4 (O₁) and Fe^{2+}_4 (O₂) *apfu* (Z = 4) and two O sheets sum to Fe^{2+}_8 *apfu* (Z = 4) or Fe^{2+}_4 *apfu* (Z = 8).

In the H sheets, four Ti-dominant $M^{\rm H}$ sites are coordinated by five O atoms and one F atom at the $X^{P}{}_{\rm M}$ site (Fig. 1a, d, e), with $< {\rm M}^{\rm H}-\phi> = 1.954$ Å (Tables 5 and 6). The eight tetrahedrally coordinated *Si* sites are occupied by Si, with $< {\rm Si-O}> = 1.622$ Å (Table 5). The cations of the two H sheets give ideally Ti₂ *apfu* (Z = 8). The H₁ and H₂ sheets are topologically identical (Fig. 1d, e) and differ in cation composition of the Ti-dominant $M^{\rm H}$ sites.

The peripheral sites, $2A^{P}$ and $2B^{P}$, are shifted from the H sheets of the TS block and occur in the I block. The $A^{P}(1)$ site is occupied by Ba at 97% and is coordinated by eight O atoms and two F atoms at the X^{P}_{M} sites, with $< A^{P}(1) - \phi > = 2.901$ Å (Tables 5 and 6). The $A^{P}(2)$ site is split into three ^[10] $A^{P}(21)$, ^[9] $A^{P}(22)$, and ^[11] $A^{P}(23)$ subsites which are 0.41– 0.965 Å apart (Table 5) and are partly occupied by Ba and K (Table 6). The total content of two A^{P} sites is ideally Ba *apfu* (Z = 8). The $B^{P}(1,2)$ sites are occupied by Na and Ca, where Na > Ca, and are coordinated by eight O atoms and two F atoms at the X_{M}^{P} sites, with a mean distance of 2.630 Å (Tables 5 and 6). The ideal composition of the two $B^{P}(1,2)$ sites is Na *apfu* (Z=8).

We write the cation part of the structural formula of jinshajiangite as the sum of the following cations: (1) B^{P} and A^{P} : NaBa; (2) M^{O}_{4} : Fe²⁺₄; and (3) M^{H}_{2} : Ti₂; ideally NaBaFe₄Ti₂ (Z = 8).

There are 28 anions, O(1-28) (Table 4), that coordinate the Si cations and hence they are O atoms. Four anions, $X^{O}_{M}(1-4)$, are ligands of three M^O cations and an M^H cation (Table 5) and they are O atoms, with bond-valence sums from 1.80 to 1.89 vu (valence units) (Table 7). The anions at the $X^{O}_{A}(1-4)$ sites are occupied by [3.86 (OH) + 0.14 F] pfu (Tables 2 and 6) and hence they are mainly O atoms of OH groups (Tables 4 and 6), with bond-valence sums of 1.11-1.16 vu (Table 7). Each OH group is bonded to three M^O cations of the O sheet (Fig. 1b, c). The H(1-4) atoms are involved in weak hydrogen bonding with O atoms that belong to the H sheets (Table 8). There are two $X^{P}_{M}(1,2)$ sites which are occupied solely by F atoms (Fig. 2a). Each F atom is a bridging anion for two Ti atoms ($M^{\rm H}$ sites) and two Na atoms (Na > Ca) $(B^{P} \text{ sites})$, plus each F atom is bonded to one Ba atom $[A^{P}(1) \text{ site}]$ and either another Ba atom $[A^{P}(21)]$ subsite, 33% occupancy] or a K atom $[A^{P}(22)$ subsite, 47% occupancy]. As the $A^{P}(21)$ and $A^{P}(22)$ subsites are partly occupied, the coordination number of F

$\begin{array}{l} M^{O}(1){-}X^{O}_{A}(3)a \\ M^{O}(1){-}O(4)b \\ M^{O}(1){-}X^{O}_{M}(4) \\ {<}M^{O}(1){-}\phi{>} \end{array}$	2.123(6) 2.166(5) 2.234(5) 2.174	×2 ×2 ×2	$\begin{array}{c} M^{O}(2) {-} O(2) c \\ M^{O}(2) {-} X^{O}{}_{A}(1) \\ M^{O}(2) {-} O(8) \\ M^{O}(2) {-} X^{O}{}_{A}(2) c \\ M^{O}(2) {-} X^{O}{}_{M}(2) \\ M^{O}(2) {-} X^{O}{}_{M}(1) d \\ {<} M^{O}(2) {-} \phi {>} \end{array}$	2.101(4) 2.118(6) 2.119(5) 2.134(6) 2.250(5) 2.421(5) 2.191		$\begin{array}{c} M^{O}(3){-}X^{O}{}_{A}(1)e \\ M^{O}(3){-}O7 \\ M^{O}(3){-}X^{O}{}_{M}(2) \\ M^{O}(3){-}O(2)c \\ M^{O}(3){-}O(1)a \\ M^{O}(3){-}O(2)a \\ {<}M^{O}(3){-}\phi{>} \end{array}$	2.099(4) 2.114(5) 2.137(4) 2.195(5) 2.236(5) 2.245(5) 2.171
$\begin{array}{l} M^{O}(4){=}O(3) \\ M^{O}(4){=}O(5)f \\ M^{O}(4){=}X^{O}{}_{A}(3)a \\ M^{O}(4){=}X^{O}{}_{A}(4) \\ M^{O}(4){=}X^{O}{}_{M}(3)a \\ M^{O}(4){=}X^{O}{}_{M}(4) \\ {<}M^{O}(4){=}\phi{>} \end{array}$	2.087(5) 2.087(5) 2.110(7) 2.125(6) 2.217(5) 2.443(5) 2.178		$\begin{array}{l} M^{O}(5){-}O(1)\\ M^{O}(5){-}X^{O}{}_{A}(2)\\ M^{O}(5){-}X^{O}{}_{M}(2)g\\ {<}M^{O}(5){-}\phi{>}\\ M^{O}(8){-}O(6)i \end{array}$	2.055(5) 2.148(6) 2.475(5) 2.226 2.027(5)	×2 ×2 ×2 ×2	$\begin{array}{l} M^{O}(6){-}X^{O}_{A}(4)h \\ M^{O}(6){-}X^{O}_{M}(4) \\ M^{O}(6){-}{-}O(3)h \\ M^{O}(6){-}O(4)b \\ M^{O}(6){-}O(3) \\ M^{O}(6){-}O(6) \\ {<}M^{O}(6){-}\phi{>} \end{array}$	2.073(4) 2.098(5) 2.172(6) 2.179(5) 2.228(6) 2.253(5) 2.167
$\begin{array}{l} M^{O}(7) - X^{O}{}_{A}(3)i \\ M^{O}(7) - X^{O}{}_{M}(3) \\ M^{O}(7) - O(5)j \\ M^{O}(7) - O(4)j \\ M^{O}(7) - O(6)i \\ M^{O}(7) - O(5)b \\ < M^{O}(7) - \phi > \end{array}$	2.100(5) 2.115(4) 2.219(6) 2.205(6) 2.224(5) 2.228(6) 2.182		$\begin{array}{l} M^{O}(9) - X^{O}_{A}(4) a \\ M^{O}(8) - X^{O}_{M}(3) \\ < M^{O}(8) - \phi > \\ \end{array} \\ \begin{array}{l} M^{O}(9) - X^{O}_{A}(1) g \\ M^{O}(9) - O(7) a \\ M^{O}(9) - X^{O}_{M}(1) g \\ < M^{O}(9) - \phi > \end{array}$	2.094(7) 2.443(5) 2.188 2.097(6) 2.162(5) 2.233(5) 2.164	×2 ×2 ×2 ×2 ×2 ×2	$\begin{array}{l} M^{O}(10) - X^{O}{}_{A}(2)k \\ M^{O}(10) - X^{O}{}_{M}(1) \\ M^{O}(10) - O(7)e \\ M^{O}(10) - O(8)j \\ M^{O}(10) - O(8)d \\ M^{O}(10) - O(1)a \\ < M^{O}(10) - \phi > \end{array}$	2.082(5) 2.100(4) 2.204(5) 2.211(6) 2.260(6) 2.266(5) 2.187
$\begin{array}{l} M^{H}(1){-}X^{O}_{M}(1) \\ M^{H}(1){-}O(26) \\ M^{H}(1){-}O(12) \\ M^{H}(1){-}O(21) \\ M^{H}(1){-}O(27) \\ M^{H}(1){-}X^{P}_{M}(2) \\ {<}M^{H}(1){-}\phi{>} \end{array}$	1.812(4) 1.930(4) 1.940(4) 1.992(4) 1.998(4) 2.003(2) 1.946		$\begin{array}{l} M^{H}(2){-}X^{O}_{M}(2)\\ M^{H}(2){-}O(14)\\ M^{H}(2){-}O(11)\\ M^{H}(2){-}O(23)\\ M^{H}(2){-}O(20)\\ M^{H}(2){-}X^{\mathcal{P}}_{M}(1)\\ {<}M^{H}(2){-}\phi{>} \end{array}$	1.765(4) 1.947(4) 1.952(4) 1.971(4) 2.004(4) 2.104(3) 1.957		$\begin{array}{l} M^{H}(3){-}X^{O}{}_{M}(3) \\ M^{H}(3){-}O(13) \\ M^{H}(3){-}O(15) \\ M^{H}(3){-}O(24) \\ M^{H}(3){-}O(28)j \\ M^{H}(3){-}X^{P}{}_{M}(2) \\ {<}M^{H}(3){-}\phi{>} \end{array}$	1.809(4) 1.950(4) 1.953(4) 1.983(4) 2.006(4) 2.107(3) 1.968
$\begin{array}{l} M^{H}(4) - X^{O}{}_{M}(4) \\ M^{H}(4) - O(16) \\ M^{H}(4) - O(10) \\ M^{H}(4) - O(19) \end{array}$	1.796(5) 1.937(4) 1.950(4) 1.992(4)		Si(1)–O(24)s Si(1)–O(10) Si(1)–O(17)	1.609(4) 1.620(4) 1.638(4) 1.665(5)		Si(2)–O(19)m Si(2)–O(4) Si(2)–O(13)s Si(2)–O(17)n	1.611(4) 1.624(5) 1.635(4) 1.643(4)
$egin{array}{l} M^{H}(4) - O(22) \ M^{H}(4) - X^{P}_{M}(1) \ < M^{H}(4) - \phi > \end{array}$	1.996(4) 2.002(2) 1.946		Si(1)–O(3)h <si(1)–o></si(1)–o>	1.632		<si(2)–o></si(2)–o>	1.628
Si(3)-O(8) Si(3)-O(12)s Si(3)-O(20) Si(3)-O(18)n <si(3)-o></si(3)-o>	1.598(5) 1.607(4) 1.615(4) 1.637(4) 1.614		Si(4)-O(23)m Si(4)-O(26)s Si(4)-O(2)b Si(4)-O(9)n <si(4)-o></si(4)-o>	1.611(4) 1.619(4) 1.637(5) 1.639(4) 1.627		Si(5)-O(21)s Si(5)-O(14)m Si(5)-O(7)m Si(5)-O(18)m <si(5)-o></si(5)-o>	1.598(4) 1.599(4) 1.617(5) 1.639(4) 1.613
Si(6)-O(22) Si(6)-O(15)s Si(6)-O(25)j Si(6)-O(6) <si(6)-o></si(6)-o>	1.598(4) 1.606(4) 1.628(4) 1.647(5) 1.620		Si(7)-O(1)h Si(7)-O(27)s Si(7)-O(11) Si(7)-O(9) <si(7)-o></si(7)-o>	1.605(5) 1.614(4) 1.623(4) 1.642(4) 1.621		Si(8)-O(28) Si(8)-O(16)m Si(8)-O(5) Si(8)-O(25) <si(8)-o></si(8)-o>	1.599(4) 1.619(4) 1.627(6) 1.645(4) 1.623
Si(1)-O(17)-Si(2)o Si(3)o-O(18)-Si(5)f Si(4)o-O(9)-Si(7) Si(6)s-O(25)-Si(8) <si-o-si></si-o-si>	133.3(2) 134.5(2) 132.7(2) 133.7(2) 133.6					Short distances $A^{P}(21)-A^{P}(22)$ $A^{P}(21)-A^{P}(23)b$ $A^{P}(22)-A^{P}(23)b$	0.965(3) 0.41(1) 0.70(2)

A ^P (1)–O(28)j	2.832(4)	A ^P (21)–O(25)f	2.925(4)	A ^P (22)–O(11)	2.940(5)
A ^P (1)–O(27)	2.834(4)	A ^P (21)–O(18)	2.928(4)	A ^P (22)–O(10)	2.945(5)
A ^P (1)–O(20)	2.839(4)	A ^P (21)–O(9)	2.930(4)	A ^P (22)–O(14)	2.960(5)
A ^P (1)–O(24)	2.846(4)	A ^P (21)–O(17)	2.962(4)	A ^P (22)–O(25)f	2.966(4)
A ^P (1)–O(19)	2.850(4)	A ^P (21)–O(15)p	3.099(5)	A ^P (22)–O(16)	2.971(4)
A ^P (1)–O(23)	2.854(4)	A ^P (21)–O(12)p	3.103(5)	A ^P (22)–O(9)	2.973(4)
A ^P (1)–O(22)	2.860(4)	A ^P (21)–O(13)p	3.113(5)	A ^P (22)–O(17)	2.981(5)
A ^P (1)–O(21)	2.863(4)	A ^P (21)–O(26)p	3.128(5)	A ^P (22)–O(18)	2.989(4)
$A^{P}(1) - X^{P}_{M}(2)$	3.108(4)	A ^P (21)–X ^P _M (2)p	3.423(5)	$A^{P}(22) - X^{P}_{M}(1)$	3.178(5)
$A^{P}(1) - X^{P}_{M}(1)$	3.126(4)	A ^P (21)–O(11)	3.622(5)	$< A^{P}(22)-\phi>$	2.989
< A ^P (1)-φ>	2.901	< A ^P (21)–O>	3.123		
A ^P (23)–O(17)b	2.72(1)	B ^P (1)–O(15)s	2.381(5)	B ^P (2)–O(13)s	2.359(5)
A ^P (23)–O(9)b	2.79(1)	$B^{P}(1) - O(10)$	2.389(4)	B ^P (2)–O(14)m	2.394(5)
A ^P (23)–O(25)q	3.04(1)	B ^P (1)–O(12)s	2.403(5)	B ^P (2)–O(16)m	2.397(5)
A ^P (23)–O(18)b	3.14(1)	$B^{P}(1) - O(11)$	2.409(4)	B ^P (2)–O(26)s	2.412(5)
A ^P (23)–O(13)r	3.19(2)	$B^{P}(1) - X^{P}_{M}(2)s$	2.692(4)	$B^{P}(2) - X^{P}_{M}(2)s$	2.691(4)
A ^P (23)–O(10)b	3.27(2)	$B^{P}(1) - X^{P}_{M}(1)$	2.696(4)	$B^{P}(2) - X^{P}_{M}(1)m$	2.709(4)
A ^P (23)–O(26)r	3.28(2)	B ^P (1)–O(24)s	2.812(5)	B ^P (2)–O(23)m	2.804(5)
A ^P (23)–O(11)b	3.33(2)	B ^P (1)–O(22)	2.825(5)	B ^P (2)–O(28)	2.825(5)
A ^P (23)–O(15)r	3.40(2)	B ^P (1)–O(27)s	2.838(5)	B ^P (2)–O(19)m	2.849(5)
A ^P (23)–O(12)r	3.47(2)	B ^P (1)–O(20)	2.846(5)	B ^P (2)–O(21)s	2.862(5)
A ^P (23)–O(16)b	3.50(2)	$< B^{P}(1)-\phi>$	2.629	< B ^P (2)-φ>	2.630
< A ^P (23)–O>	3.194			., .	

TABLE 5. CONTINUED.

 $\varphi = \mathsf{O}, \mathsf{F}, \mathsf{OH};$

Symmetry operators: a: -x, -y+1, -z+1; b: -x+1, -y+1, -z+1; c: x, y, z+1; d: $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+2$; e: -x, -y+1, -z+2; f: x-1, y, z; g: x, y, z-1; h: $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; i: $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; j: $x-\frac{1}{2}, y-\frac{1}{2}, z$; k: $x-\frac{1}{2}, y-\frac{1}{2}, z$; k: $x-\frac{1}{2}, y-\frac{1}{2}, z$; h: $x-\frac$

varies from 5 to 6. Occurrence of F at the $X_{M}^{P}(1,2)$ sites is in accord with the bond-valence sums of 0.96 vu at each X_{M}^{P} anion (Table 7). Note that the two ^{[5–} $^{6]}X_{M}^{P}(1,2)$ sites cannot be occupied by OH groups as there is no space to accommodate those OH groups including the hydrogen bonds. Hence in the TS block of jinshajiangite, we observe ordering of F atoms at the $X_{M}^{P}(1,2)$ sites in the H sheets and OH groups at the $X_{A}^{O}(1-4)$ sites in the O sheet.

We write the anion part of the formula as the sum of (1) O_{28} belonging to four Si_2O_7 groups; (2) four X^O_M and four X^O_A anions, giving O_4 and (OH)₄; and (3) the two X^P_M anions giving F_2 , ideally $(Si_2O_7)_4O_4(OH)_4F_2$, Z=4 or $(Si_2O_7)_2O_2(OH)_2F$, Z=8.

In accord with the perraultite-type general formula, $B^{P}A^{P}M_{4}^{O}M_{4}^{H}(Si_{2}O_{7})_{2}X_{4}^{O}X_{M}^{P}$ (Sokolova 2006), we write the structural formula of jinshajiangite as NaBaFe²⁺₄Ti₂(Si₂O₇)₂O₂(OH)₂F, Z = 8, in accord with Sokolova *et al.* (2009a).

Crystal Chemistry of Jinshajiangite and Related Group-II Minerals

In the crystal structure of jinshajiangite, there are two symmetrically independent TS_1 and TS_2 blocks.

They each have (1) O sheets of the same topology, with different patterns of Fe2+-dominant and Mndominant octahedra, and (2) two H₁ and H₂ sheets of the same topology, with slightly different aggregate compositions of Ti-dominant $M^{\rm H}$ sites. The ideal composition of each TS block is $Fe^{2+}_{4}Ti_{2}(Si_{2}O_{7})_{2}$ $O_2(OH)_2F$, Z = 8. Hence we can say that ideally there is only one type of TS block in the structure of jinshajiangite. We showed earlier that there is only one type of I block [ideally NaBa, Z = 8] and there is only one type of self-linkage of TS blocks, via $M^{H}-X^{P}_{M}$ M^H bridges. We conclude that jinshajiangite, a Group-II TS-block mineral, has a *basic* structure [structure type B2(GII)]. Ideal structural formulae for Group-II minerals jinshajiangite, perraultite, surkhobite, and bobshannonite (the perraultite structure-type); bafertisite and hejtmanite (bafertisite structure-type); and cámaraite (related to the perraultite and bafertisite structure-types) are presented in Table 1. Six minerals (excluding cámaraite) have basic structures in accord with Sokolova & Cámara (2013). Cámaraite has a derivative structure, with one type of TS block, two types of I block, and two types of self-linkage of TS blocks. The structure of cámaraite can be built of

Site*	Refined site-scattering (epfu)	Assigned site-population (appu)	Calculated site- scattering (epfu)	$<$ cation- ϕ $>_{obs}$.**	ld comp (<i>a</i> j	eal osition ofu)
	()	Z = 4	((7		Z = 8
		Cations				
М ^О (1)	12.5(1)	0.45 Fe ²⁺ + 0.02 Zn + 0.03 □	12.30	2.174		
М ^О (2)	26.7(1)	0.82 Fe ²⁺ + 0.09 Mn + 0.07 Zr	26.37	2.191		
		$+ 0.02 \square$				
M ^O (3)	25.5(1)	$0.60 \text{ Fe}^{2+} + 0.38 \text{ Mn} + 0.02 \square$	25.10	2.171		
<i>M</i> ^O (4)	26.3(1)	$0.83 \text{ Fe}^{2+} + 0.17 \text{ Mn}$	25.83	2.178		
M ^O (5)	12.9(1)	$0.40 \text{ Mn} + 0.10 \text{ Fe}^{2+}$	12.60	2.226		
$M^{\circ}(6)$	25.5(1)	$0.64 \text{ Fe}^{2+} + 0.32 \text{ Fe}^{3+} + 0.04 \square$	24.96	2.167		
$M^{\circ}(7)$	25.4(1)	$0.49 \text{ Fe}^{-1} + 0.47 \text{ Mn} + 0.04 \square$	24.49	2.182		
$M^{\circ}(8)$	12.3(1)	$0.43 \text{ Mn} + 0.05 \text{ Fe}^{-1} + 0.02 \square$	12.05	2.188		
$M^{2}(9)$	12.4(1)	$0.25 \text{ Fe}^{-1} + 0.20 \text{ Fe}^{-1} + 0.03 \text{ Mg} + 0.02 \square$	12.06	2.164		
$N^{-}(10)$	25.9(1)	$0.58 \text{ Mm} + 0.42 \text{ Fe}^{-1}$	25.42	2.187	⊏ ₀ ²⁺	⊏ ∘ ²⁺
2 <i>IVI</i> [*] (1–10)	205.4	4.65 Fe ⁻¹ + 0.52 Fe ⁻¹ + 2.52 Min + 0.07 Zr + 0.03 Mg + 0.02 Zn + 0.19 □	201.18		Fe 8	Fe 4
<i>M</i> ^H (1)	23.0(1)	0.91 Ti + 0.09 Nb	23.71	1.946		
$M^{H}(2)$	23.3(1)	0.89 Ti + 0.11 Nb	24.02	1.957		
$M^{H}(3)$	22.2(1)	0.88 Ti + 0.05 Mg + 0.09 Nb	22.90	1.968		
$M^{H}(4)$	22.8(1)	0.89 Ti + 0.09 Nb + 0.02 Al	23.51	1.946		
$\Sigma M^{H}(1-4)$	91.3	3.57 Ti + 0.36 Nb + 0.05 Mg + 0.02 Al	94.16		Ti ₄	Ti ₂
^[10] <i>A^P</i> (1)	54.33(9)	0.97 Ba + 0.03 □	54.32	2.901		
^[10] <i>A^P</i> (21)	16.45 [†]	0.23 Ba + 0.10 K + 0.67 □	14.78	3.123		
^[9] A ^P (22)	9.87 [†]	0.47 K + 0.53 □	8.93	2.989		
^[11] A ^P (23)	3.14 [†]	0.15 K + 0.85 □	2.85	3.194		
$\Sigma A^{P}(2)$	29.46	0.72 K + 0.23 Ba + 0.05 □	26.56			
Σ <i>Α^Ρ</i> (1,2)	83.79	1.20 Ba + 0.72 K + 0.08 □	80.88		Ba ₂	Ba
^[10] <i>B</i> ^P (1)	12.62(7)	0.78 Na + 0.22 Ca	12.98	2.629		
$^{[10]}B^{P}(2)$	12.64(7)	0.77 Na + 0.23 Ca	13.07	2.630		
$\Sigma B^{P}(1,2)$	25.26	1.55 Na + 0.45 Ca	26.05		Na ₂	Na
		Anions				
$^{[4]}X^{O}_{M}(1-4)$		4.00 O			O ₄	O ₂
$^{[3]}X^{O}_{A}(1-4)$		3.86 (OH) + 0.14 F			$(OH)_4$	(OH) ₂
X ^P _M (1,2)		2.00 F			F ₂	F

TABLE 6. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR JINSHAJIANGITE

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

** $\phi = 0$, OH, F.

[†] Site scattering was refined and then fixed.

structural fragments of minerals of the same group, jinshajiangite and bafertisite (Table 1).

Doubled minimal translations t_1 and t_2

Sokolova & Cámara (2016) considered Ba-containing structures of TS-block minerals and explained doubling of minimal translations t_1 and t_2 using the crystal structure of bafertisite as an example. Below we review their findings.

The t₁ and t₂ translations double in the Group-II structures where (a) the I block is composed of just one close-packed layer of Ba (or Ba + K + Na); (b) the [6]-coordinated Ti (+ Nb) atoms occur

						Anion**				
Cation	X ⁰ _M (1)	Х ⁰ _M (2)	X ^O _M (3)	Х ^о _м (4)	^[3] X ^O _A (1)	^[3] X ^O _A (2)	^[3] X ^O _A (3)	^[3] X ^O _A (4)	^[6] X ^P _M (1)	^[6] X ^P _M (2)
M ^O (1)				0.27			0.36			
M ^O (2)		0.26			0.37	0.35				
M ^O (3)		0.35			0.38					
$M^{O}(4)$			0.28	0.17			0.37	0.36		
M ^O (5)		0.17				0.37				
M ^O (6)				0.39				0.41		
$M^{O}(7)$			0.37				0.38			
M ^O (8)	0.18		0.17					0.39		
M ^O (9)	0.27				0.39					
M ^O (10)	0.38					0.40				
M ^H (1)	0.97									0.33
M ^H (2)		1.11							0.32	
М ^н (З)			0.98							0.32
M ^H (4)				1.02					0.32	
A ^P (1)									0.11	0.11
A ^P (21)										0.02
A ^P (22)									0.03	
B ^P (1)									0.09	0.09
B ^P (2)									0.09	0.09
Σ	1.80	1.89	1.80	1.85	1.14	1.12	1.11	1.16	0.96	0.96

TABLE 7. BOND-VALENCE VALUES* FOR SELECTED ANIONS IN JINSHAJIANGITE

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

** $X^{O}_{M}(1-4) = \dot{O}$ atoms; $X^{O}_{A}(1-4) = OH$, with minor F; $X^{P}_{M}(1,2) = F$; coordination numbers are given for non-[4]-coordinated anions.

in the H sheets; and (c) the apical X_{M}^{P} anions of the Ti occur in the layer of cations in the I block.

- (2) To satisfy bond-valence requirements of X_{M}^{P} anions, Ti (+ Nb) octahedra tilt to allow F (+ O) atoms to shift toward Ba (+ K + Na); and to compensate for that shift, SiO₄ tetrahedra of Si₂O₇ groups rotate to maintain six-membered $A^{P}(1)$ and $A^{P}(2)$ rings in the H sheet. As a result of these distortions of polyhedra, the $A^{P}(1)$ ring shortens along t_{2} , the $A^{P}(2)$ ring elongates along t_{2} , and the B^P rings elongate along $[t_{1} \pm t_{2}]$.
- (3) Doubled minimal translations in seven Group-II structures (Table 1), $2t_1$ and $2t_2$, are due to distortion of rings of polyhedra in the H sheets.

Here we examine the doubling of the t_1 and t_2 minimal translations in jinshajiangite. Sokolova & Cámara (2016) described two rings of polyhedra in the H sheet: (1) the six-membered A^P ring of polyhedra consisting of SiO₄ tetrahedra of two Si₂O₇ groups and two M^H polyhedra, and (2) the four-membered B^P ring of polyhedra consisting of two SiO₄ tetrahedra and two M^H polyhedra (Fig. 2b). In jinshajiangite, the sixmembered A^P(1) ring is shortened along t₂ and the sixmembered A^P(2) ring is elongated along t₂ (Fig. 2b). Figure 2b also shows Ba, K, Na, and F atoms in the I block. Fluorine atoms at the $X^P_M(1)$ and $X^P_M(2)$ sites are each bonded to five or six cations: two Ti at the M^H sites, two Na at the B^P sites, one Ba at the $A^P(1)$ site, and either a Ba atom $[X^P_M(2) - A^P(21)$ subsite, 33%

D–H (Å)	H…A (Å)	D…A (Å)	∠ DHA (°)
0.97(1)	2.83(6)	3.228(6)	105(4)
0.97(1)	2.53(4)	3.357(7)	144(5)
0.98(1)	2.10(3)	2.990(6)	150(5)
0.98(1)	2.33(2)	3.277(7)	164(5)
0.98(1)	2.45(5)	3.076(6)	121(4)
0.98(1)	2.52(6)	3.029(5)	112(4)
	D-H (Å) 0.97(1) 0.97(1) 0.98(1) 0.98(1) 0.98(1) 0.98(1)	D-H (Å) H…A (Å) 0.97(1) 2.83(6) 0.97(1) 2.53(4) 0.98(1) 2.10(3) 0.98(1) 2.33(2) 0.98(1) 2.45(5) 0.98(1) 2.52(6)	D-H (Å) H···A (Å) D···A (Å) 0.97(1) 2.83(6) 3.228(6) 0.97(1) 2.53(4) 3.357(7) 0.98(1) 2.10(3) 2.990(6) 0.98(1) 2.33(2) 3.277(7) 0.98(1) 2.45(5) 3.076(6) 0.98(1) 2.52(6) 3.029(5)

TABLE 8. HYDROGEN BONDING IN JINSHAJIANGITE

a: $-x + \frac{1}{2}$, $-y + \frac{3}{2}$, -z + 1; b: x - 1, y, z.



FIG. 1. A general view of the crystal structure of jinshajiangite which consists of TS and I blocks (a) and the details of the TS₁ and TS₂ blocks: the close-packed O₁ (b) and O₂ (c) sheets of Fe²⁺- and Mn-dominant M^O octahedra, the H₁ (d) and H₂ (e) sheets of Ti-dominant M^H octahedra and Si₂O₇ groups, and the I block of Ba, K, and Na atoms superimposed on the H sheets (d, e). SiO₄ tetrahedra are orange and Ti-, Fe²⁺-, and Mn-dominant octahedra are pale yellow, green, and magenta, respectively; labels 1–10 correspond to M^O(1–10) octahedra (b, c); labels 1–4 on pale yellow correspond to M^H(1–4) octahedra (d, e); and labels 1–8 on orange correspond to Si(1–8) tetrahedra (d, e); Ba and K atoms at the A^P sites and Na atoms at the B^P sites in the I block are shown as raspberry and green and navy blue spheres; O and H atoms of OH groups at the X^O_A sites are shown as red and small grey spheres and O–H bonds are shown as black lines; F atoms at the X^P_M sites are shown as yellow spheres. Unit cell is shown by thin black lines.



FIG. 2. Jinshajiangite: the F atom at the $X_{M}^{P}(1)$ site coordinated by the six cations (a) and the I block superimposed on the H₁ sheet (b). Legend as in Figure 1, bonds Ba(K)–F < 3.2 Å and 3.2 < Ba(K)–F < 3.5 Å are shown as thin black solid and dashed lines, respectively; all linear dimensions are in Å.

t₂

occupancy] or a K atom $[X_{M}^{P}(1) - A^{P}(22)]$ subsite, 47% occupancy] (Fig. 2a). Such [5–6] coordination satisfies the bond-valence requirements of F. In the jinshajiangite structure, A^{P} sites occur at 6.85–6.96 Å along t₂ (Fig. 2b) and the occurrence of F atoms halfway between Ba atoms would result in Ba–F bonds of 3.43–3.48 Å, too long to satisfy the bond-valence requirements of F.

Hence to satisfy the bond-valence requirements, F atoms move closer to the Ba atom at the $A^{P}(1)$ site (see arrows in Fig. 2b), with a corresponding F-F distance of 6.23 Å. Shift of the F atoms causes tilting of the Ti octahedra, and the Ti-Ti distance decreases to 6.35 Å. To maintain the $A^{P}(1)$ ring in the H sheet, SiO₄ tetrahedra of Si₂O₇ groups in that ring rotate toward each other in the plane of the ring, with an O-O-O angle of ~82.2° (Fig. 2b). To compensate for shortening of the $A^{P}(1)$ ring along t_{2} , the $A^{P}(2)$ ring elongates along t_2 , with the F–F distance increasing to 7.57 Å, the Ti-Ti distance increasing to 7.45 Å, and SiO₄ tetrahedra of Si₂O₇ groups in that ring rotating away from each other in the plane of the ring, with a resulting O–O–O angle of \sim 149.4° (Fig. 2b). Tilting of Ti octahedra and rotation of SiO₄ tetrahedra results in elongation of the four-membered B^P rings along the $[t_1]$ \pm t₂] directions.

On the ordering of F and OH in Group-II TS-block minerals

In the TS blocks in the crystal structure of jinshajiangite, there is order of F atoms at the $X_{M}^{P}(1,2)$ sites in the H sheets and OH groups at the $X_{A}^{O}(1-4)$ sites in the O sheet. This order occurs as the [5-6] $X_{M}^{P}(1,2)$ sites cannot be occupied by OH groups as there is no space to accommodate those OH groups including the hydrogen bonds. The X_{M}^{P} anions occur in the H sheets of the TS blocks where TS blocks connect *via* bridges $M^{H}-X_{M}^{P}-M^{H}$ (Fig. 1a), as in astrophyllite- and kupletskite-group minerals (Sokolova *et al.* 2017). The composition of the X_{M}^{P} anion depends on the composition of the M^{H} cations. In bobshannonite, a Nb- and K-analogue of perraultite (Table 1), each X_{M}^{P} main is bonded to six cations: two M^{H} [(Nb,Ti)], two B^P (Na), and two A^P (Ba and K), and its composition is (O,F).

Cámara *et al.* (2016) and Sokolova *et al.* (2016) showed that in the crystal structures of bafertisite and hejtmanite, F atoms and OH groups are ordered at the [4]-coordinated X^P_{M} sites in the H sheets and the X^O_A sites in the O sheet, respectively. In accord with these new findings for bafertisite and hejtmanite, Sokolova & Cámara (2016) reported corrected ideal structural formulae for bafertisite, hejtmanite, and cámaraite (Table 1). Analogous revision of the crystal structure

and chemical composition and the ideal structural formula was recently done for nafertisite, Na₃ $Fe^{2+}_{10}Ti_2(Si_6O_{17})_2O_2(OH)_6F(H_2O)_2$ (Cámara *et al.* 2014b).

On perraultite and surkhobite

Yamnova *et al.* (1998) determined the crystal structure of perraultite and Rastsvetaeva *et al.* (2008) used the perraultite model to refine the crystal structure of surkhobite. However, structure work on the perraultite-type minerals is almost always complicated by the presence of twinning by pseudomerohedry. We solved the crystal structure of bobshannonite and refined the crystal structure of jinshajiangite in space group $C\overline{1}$ using data from twinned crystals where two components are related by the twin matrix $[\overline{100 \ 010 \ 001}]$ which corresponds to the twin axis 2_y . The crystal structures of bobshannonite and jinshajiangite belong to the perraultite structure-type (Yamnova *et al.* 1998) and they are basic structures (Sokolova & Cámara 2013).

Below, we outline some problems with the crystal structures of perraultite and surkhobite.

Figure 3 shows the two H sheets in the structures of perraultite and surkhobite in accord with structural data and the site-population assignments of Yamnova *et al.* (1998) and Rastsvetaeva *et al.* (2008) (Table 1).

- (1) Inspection of the H_1 and H_2 sheets in both minerals shows that they are not identical (Fig. 3) as they should be in a basic structure (see above). The geometry of the H_1 sheets (Fig. 3a, c) is identical to the geometry of the H_1 and H_2 sheets in jinshajiangite (cf. Figs. 1d, e, and 2): one six-membered ring of polyhedra is shortened along **b** and another six-membered ring of polyhedra is elongated along b. The geometry of the H₂ sheets (Fig. 3a, c) seems quite distorted. As we noted above, crystals of perraultite-type minerals are usually twins by pseudomerohedry. We suggest that the occurrence of two different H sheets in both structures is due to the incorrect monoclinic symmetry, space group C2, used for structure refinement: the monoclinic 2_v axis is in fact a twin 2_v axis (see above).
- (2) The X_{M}^{P} sites in both H sheets in perraultite (Fig. 3a, b) and in the H₁ sheet in surkhobite (Fig. 3a) are occupied by OH groups (see also Table 1). Above, we showed that in the TS block in the crystal structure of jinshajiangite, F atoms are ordered at the $X_{M}^{P}(1,2)$ sites in the H sheets and OH groups are ordered at the $X_{A}^{O}(1-4)$ sites in the O sheet. The F atoms must occur at the $[5-6]X_{M}^{P}(1,2)$ sites, because these sites cannot be occupied by OH groups, as there is no space to accommodate those



FIG. 3. The H sheets of Ti-dominant M^H octahedra and Si₂O₇ groups and the I blocks of Ba, K, Na, and Ca atoms superimposed on the H sheets in the structures of perraultite (a, b) and surkhobite (c, d). Legend as in Figure 1, Ca atoms are shown as medium pink spheres.

OH groups including the hydrogen bonds. Hence the previous assignment of OH groups to the X_{M}^{P} sites is incorrect.

(3) In surkhobite, the order of Ca and Na at the B^P sites in the H₁ and H₂ sheets, respectively, is very unlikely [see (1) about identical H sheets in basic structures].

We originally refined the crystal structure of jinshajiangite in space group C2/m and encountered problems (1) and (2) (listed above). Current refinement of the structure in space group $C\overline{1}$ solved those

problems. The crystal structures of perraultite and surkhobite need to be examined, particularly the space-group symmetry and the almost certain presence of twinning by pseudomerohedry.

SUMMARY

 Jinshajiangite, NaBaFe²⁺₄Ti₂(Si₂O₇)₂O₂(OH)₂F, Z
= 8, is triclinic, space group C1, a 10.7059(5), b 13.7992(7), c 20.760(1) Å, α 90.008(1), β
94.972(1), γ 89.984(1)°, V 3055.4(4) Å³.

- (2) Previous refinements of jinshajiangite in the space groups C2/m and C2 did not recognize the presence of pervasive twinning by pseudomerohedry that simulated monoclinic symmetry from a triclinic structure, producing structural arrangements with unlikely geometrical configurations of the H sheet.
- (3) Refinement of the structure in space group CI [see (1)] produced identical H sheets with sensible geometry, as expected for a Group-II TS-block structure.
- (4) Jinshajiangite is a TS-block mineral of Group-II. The crystal structure of jinshajiangite is an alternation of TS and I blocks. The *basic* crystal structure of jinshajiangite [structure type B2(GII)] has the following four characteristics: (a) there are two symmetrically independent TS_1 and TS_2 blocks which correspond topologically to a single type of TS block; (b) the two H sheets of the TS block are identical; (c) there is only one type of TS blocks.
- (5) In the structure of jinshajiangite, F atoms and OH groups are ordered at the X^P_M sites in the H sheets and $X^O_A(1-4)$ sites in the O sheet, respectively. The $X^P_M(1,2)$ anion sites are [5–6]-coordinated and hence *must* be occupied by F as there is no space to accommodate OH groups including the hydrogen bonds within this coordination.
- (6) Jinshajiangite belongs to the perraultite structuretype and is isostructural with bobshannonite, Na₂KBa(Nb,Ti)₄Mn₈(Si₂O₇)₄O₄(OH)₄(O,F)₂, Z = 4.

ACKNOWLEDGMENTS

We are grateful for reviews by Associate Editor Jim Evans, Daniel Atencio, and an anonymous reviewer. FC acknowledges support by the University of Torino "Progetti di ricerca finanziati dall'Università degli Studi di Torino (ex 60 %)"– year 2014. This work was also supported by a Canada Research Chair in Crystallography and Mineralogy and by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada to FCH, and by Innovation Grants from the Canada Foundation for Innovation to FCH.

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- Received January 17, 2016. Revised manuscript accepted April 11, 2016.