

From structure topology to chemical composition. VII. Titanium silicates: the crystal structure and crystal chemistry of jinshajiangite

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Abstract: The crystal structure of jinshajiangite, ideally $\text{BaNaTi}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}$, a 10.6785(8), b 13.786(1), c 20.700(2) Å, β 94.937(1)°, V 3035.93(6) Å³, sp. gr. $C2/m$, $Z = 8$, $D_{\text{calc.}}$ 3.767 g/cm³, from Norra Kärr, Tönköping province, Sweden, has been refined to R_1 5.69 % on the basis of 3193 unique reflections ($F_0 > 4\sigma F$). Electron microprobe analysis gave (wt%): SiO₂ 27.56, Nb₂O₅ 0.12, TiO₂ 18.36, ZrO₂ 0.51, FeO 23.42, Fe₂O₃ 2.89 [the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.10(9) was determined by Mössbauer spectroscopy], MnO 5.13, MgO 0.44, CaO 2.52, BaO 10.24, K₂O 1.95, Na₂O 2.27, F 2.33, H₂O 2.00 (calc. from structure refinement: OH + F = 3 *apfu*), O = F – 0.98, total 98.76. The empirical formula is $(\text{Ba}_{0.58}\text{K}_{0.36})_{\Sigma 0.94}(\text{Na}_{0.57}\text{Ca}_{0.39})_{\Sigma 0.96}(\text{Fe}_{2.84}^{2+}\text{Mn}_{0.63}\text{Fe}_{0.32}^{3+}\text{Mg}_{0.10}\text{Zr}_{0.04}\text{Na}_{0.07})_{\Sigma 4.00}(\text{Ti}_{2.00}\text{Nb}_{0.01})_{\Sigma 2.01}(\text{Si}_2\text{O}_7)_2\text{O}_{2.12}(\text{OH})_{1.93}\text{F}_{1.07}$, calculated on the basis of 4 Si *apfu*. The crystal structure of jinshajiangite can be described as a combination of a TS block and an I block. The TS (titanium silicate) block consists of HOH sheets (H-heteropolyhedral, O-octahedral), and is a component of 27 Ti-disilicate minerals. In the O sheet, there are five [6]-coordinated M^{O} sites occupied mainly by Fe^{2+} and Mn^{2+} , with minor Fe^{3+} , Mg, Zr and Na with $\langle M^{\text{O}}\text{--O} \rangle = 2.175$ Å. Five M^{O} sites give ideally Fe^{2+}_4 *pfu*. In the H sheet, there are three [6]-coordinated M^{H} sites occupied solely by Ti ($\text{Ti} = 2$ *apfu*), with $\langle M^{\text{H}}\text{--O} \rangle = 1.953$ Å, and four [4]-coordinated Si sites occupied solely by Si, with $\langle \text{Si--O} \rangle = 1.619$ Å. The M^{H} octahedra and (Si_2O_7) groups constitute the H sheet. Linkage of H and O sheets *via* common vertices of M^{H} octahedra and (Si_2O_7) groups with M^{O} (1–5) octahedra results in a TS block. The topology of the TS block is as in Group II of the Ti disilicates ($\text{Ti} = 2$ *apfu*). There are six interstitial sites, three [9–10]-coordinated Ba-dominant A^{P} sites with $\langle A^{\text{P}}\text{--O} \rangle = 2.98$ Å and three [10]-coordinated Na-dominant B^{P} sites with $\langle B^{\text{P}}\text{--O} \rangle = 2.600$ Å. The total content of three A^{P} sites sums to ~ 1 *apfu* = $\text{Ba}_{0.58}\text{K}_{0.36}$ or ideally 1 Ba *pfu*. The total content of the three B^{P} sites is $\text{Na}_{0.57}\text{Ca}_{0.39}$ or ideally 1 Na *pfu*. Along *c*, the TS blocks link *via* common vertices of M^{H} octahedra (as in astrophyllite-group minerals) and A^{P} and B^{P} sites which constitute the I block. Jinshajiangite is an Fe^{2+} analogue of perraultite, ideally $\text{BaNaTi}_2\text{Mn}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}$, and its crystal structure is topologically identical to that of perraultite.

Key-words: jinshajiangite, structure refinement, Mössbauer spectroscopy, EMP analysis, titanium silicate, structure topology, chemical formula.

1. Introduction

Jinshajiangite from the Jinshajiang River, Sichuan Province, China, was described as a new mineral by Hong & Fu (1982) who reported monoclinic symmetry, a 10.732, b 13.847, c 20.817 Å, β 95.05°, possible space groups $C2/m$, Cm or $C2$; the chemical analysis (bulk chemistry) is given in Table 1. The empirical formula $(\text{Na}_{3.36}\text{K}_{1.62})_{\Sigma 4.98}(\text{Ba}_{2.11}\text{Ca}_{1.73}\text{TR}_{0.09}\text{Sr}_{0.02})_{\Sigma 3.95}(\text{Fe}_{8.77}^{2+}\text{Mn}_{6.02}^{2+}\text{Mg}_{0.05})_{\Sigma 14.84}(\text{Ti}_{6.57}\text{Fe}_{0.68}^{3+}\text{Nb}_{0.26}\text{Mg}_{0.18}\text{Zr}_{0.18}\text{Al}_{0.12}\text{Ta}_{0.01})_{\Sigma 8.00}(\text{Si}_{14.90}\text{Al}_{0.11})_{\Sigma 15.01}\text{O}_{64.17}(\text{F}_{4.62}\text{OH}_{1.21})_{\Sigma 5.83}$ was calculated on the anion basis $\text{F} + \text{O} + \text{OH} = 70$ *apfu* (atoms per formula unit), and the “ideal” formula was given as $(\text{Na,K})_5(\text{Ba,Ca})_4(\text{Fe}^{2+},\text{Mn})_{15}(\text{Ti,Fe}^{3+},\text{Nb})_8(\text{SiO}_4)_{15}(\text{F,O,OH})_{10}$, with $Z = 2$, $D_{\text{meas}} = 3.61$ g cm^{–3} (Hong & Fu, 1982).

The crystal structure of jinshajiangite had not been solved at the time that the description was published. Perraultite from Mont Saint-Hilaire, Quebec, Canada, was described as a new mineral by Chao (1991) who reported a chemical analysis, gave the empirical formula as $\text{Na}_{2.02}\text{K}_{1.00}\text{Ba}_{1.02}(\text{Mn}_{7.73}\text{Fe}_{0.27}^{2+}\text{Mg}_{0.03})_{\Sigma 8.03}(\text{Ti}_{2.08}\text{Nb}_{1.77}\text{Zr}_{0.02})_{\Sigma 3.87}(\text{Si}_{8.01}\text{Al}_{0.01})_{\Sigma 8.02}\text{O}_{32.00}[(\text{OH})_{5.62}\text{F}_{0.78}(\text{H}_2\text{O})_{0.60}]_{\Sigma 7.00}$ calculated on the anion basis $\text{F} + \text{O} + \text{OH} + \text{H}_2\text{O} = 38$ *apfu*, and the “ideal” formula as $\text{Na}_2\text{KBaMn}_8(\text{Ti,Nb})_4\text{Si}_8\text{O}_{32}(\text{OH,F,H}_2\text{O})_7$, with $Z = 4$. Based on similarities in chemical composition, monoclinic symmetry and almost identical unit-cell dimensions, Chao (1991) suggested that jinshajiangite is isotypic with

Table 1. Chemical composition (wt%) and unit formula (*apfu*) for jinshajiangite.

Hong & Fu (1982) bulk chemistry		This work electron-microprobe analysis ^a		
SiO ₂	27.10	27.56	Si	4.00
TiO ₂	15.90	18.36		
Nb ₂ O ₅	1.03	0.12	Ti	2.00
Ta ₂ O ₅	0.07	n.d.	Nb	0.01
ZrO ₂	0.70 ^b	0.51	ΣM^H	2.01
FeO	19.07	23.42		
Fe ₂ O ₃	1.64	2.89	Fe ²⁺	2.84
MnO	12.93	5.13	Fe ³⁺	0.32
MgO	0.28	0.44	Mn ²⁺	0.63
CaO	2.94	2.52	Mg	0.10
BaO	9.80	10.24	Zr	0.04
SrO	0.08	n.d.	Na	0.07
K ₂ O	2.31	1.95	ΣM^O	4.00
Na ₂ O	3.15	2.27		
F	2.66	2.33	Ba	0.58
H ₂ O	0.36	2.00 ^c	K	0.36
O = F	-1.12	-0.98	ΣA^P	0.94
Total	99.56	98.76		
			Na	0.57
			Ca	0.39
			ΣB^P	0.96
			OH	1.93
			F	1.07

^aAl, Cs, Ta, Sr not detected (nd).^bZrO₂ = ZrO₂ + HfO₂.^cCalculated from crystal-structure analysis.

perraultite. A second occurrence of perraultite, from the coastal region of the Azov Sea, Russia, was described by Pekov *et al.* (1999), and Yamnova *et al.* (1998) solved the crystal structure of perraultite from this locality: *a* 10.731, *b* 13.841, *c* 20.845 Å, β 95.06°, sp. gr. *C*2, and gave the “generalized” formula (Na,Ca)(Ba,K)(Mn,Fe)₄[(Ti,Nb)₂O₂(OH)Si₄O₁₄](OH,F)₂, *Z* = 8. The major features of the perraultite structure were given as follows: (1) the HOH block (notation introduced by Ferraris *et al.*, 1996) is the major structural unit of the structure, where O = sheet of (Mn,Fe²⁺) octahedra, H = heteropolyhedral sheet of (Si₂O₇) groups and (Ti,Nb) octahedra; (2) HOH blocks link through common vertices of (Ti,Nb) octahedra; (3) Ba, K, Na and Ca atoms occur in the interstitial space between two HOH blocks and constitute the intermediate (I) layer. Unaware of the structure work of Yamnova *et al.* (1998), Christiansen *et al.* (1999) proposed a structure model for perraultite and stated that “jinshajiangite appears to be a Ti-rich Fe analogue of perraultite structure model”, in accord with the suggestion by Chao (1991). Sokolova (2006) considered structural hierarchy and stereochemistry for 24 titanium disilicate minerals. The structures of these minerals contain the TS (titanium silicate) block, a central trioctahedral (O) sheet and two adjacent (H) sheets of different polyhedra including (Si₂O₇) groups. She established the relation between structure topology and chemical composition for those minerals and divided

them into four groups, characterized by different topology and stereochemistry of the TS block. Each group of structures has a different linkage of H and O sheets in the TS block, and a different arrangement of Ti (= Ti + Nb) polyhedra. In a structure, the TS block can alternate with another block, an intermediate (I) block, so called as it is intercalated between two TS blocks. In Groups I, II, III and IV, Ti equals 1, 2, 3 and 4 *apfu*, respectively. Sokolova (2006) gave the ideal formula of perraultite as (Na Ba)Mn₄Ti₂(Si₂O₇)₂O₂(OH)₂F and considered it as a Group-II mineral, Ti = 2 *apfu*, based on the Ti content and the topology of the linkage between the H and O sheets. Sokolova (2006) did not consider jinshajiangite as its structure was unknown at that time. Surkhobite was originally described as a Ca-Fe²⁺ analogue of perraultite (Es'kova *et al.*, 2003; Rozenberg *et al.*, 2003), with the simplified formula (Na,Ca)(Ba,K)(Fe²⁺,Mn)₄Ti₂(Si₂O₇)₂O₂(F,OH,O)₃, where Fe²⁺ > Mn and *Z* = 8. However, surkhobite was redefined (Rastsvetaeva *et al.*, 2008a) as (Ba,K)₂CaNa(Mn,Fe²⁺,Fe³⁺)₈Ti₄(Si₂O₇)₄O₄(F,OH,O)₆, where Mn > Fe²⁺ and *Z* = 4, an ordered derivative of perraultite.

This paper presents the structure of the jinshajiangite as a continuation of our work on Ti disilicate minerals with the TS block [delindeite (Sokolova & Cámara, 2007), barytolamprophyllite (Sokolova & Cámara, 2008), borne-manite (Cámara & Sokolova, 2007), nabalamprophyllite (Sokolova & Hawthorne, 2008a), nacareniobsite-(Ce) (Sokolova & Hawthorne, 2008b)]. The site nomenclature is that proposed by Sokolova (2006).

2. Experimental details

We extracted a golden red prismatic single crystal of jinshajiangite (0.14 × 0.10 × 0.08 mm) that was associated with aegirine and albite in a sample from Norra Kärr, Tönköping province, Sweden [described by Holtstam (1998) and purchased from A. Petrov].

2.1. Mössbauer spectroscopy

Transmission Mössbauer spectroscopy measurements were done at room temperature (RT) on the jinshajiangite single crystal using a ⁵⁷Co(Rh) point source. The spectra were analyzed using a Voigt-based quadrupole-splitting distribution (QSD) method (Rancourt & Ping, 1991). The centre shift (CS) is given relative to α -Fe at RT.

Figure 1 shows the RT Mössbauer spectrum of the jinshajiangite single crystal. It is fit by a Voigt-based QSD analysis to a model having two generalized sites, one for Fe²⁺ (solid-line spectrum) and one for Fe³⁺ (dashed-line spectrum). In the structure of jinshajiangite, there are five octahedrally coordinated sites occupied by Fe (Tables 3 and 5), and yet there is only one discernable peak due to Fe²⁺ in the Mössbauer spectrum (Fig. 1). This complete overlap of several Fe²⁺ peaks in Mössbauer spectra is not unusual for structure with close-packed

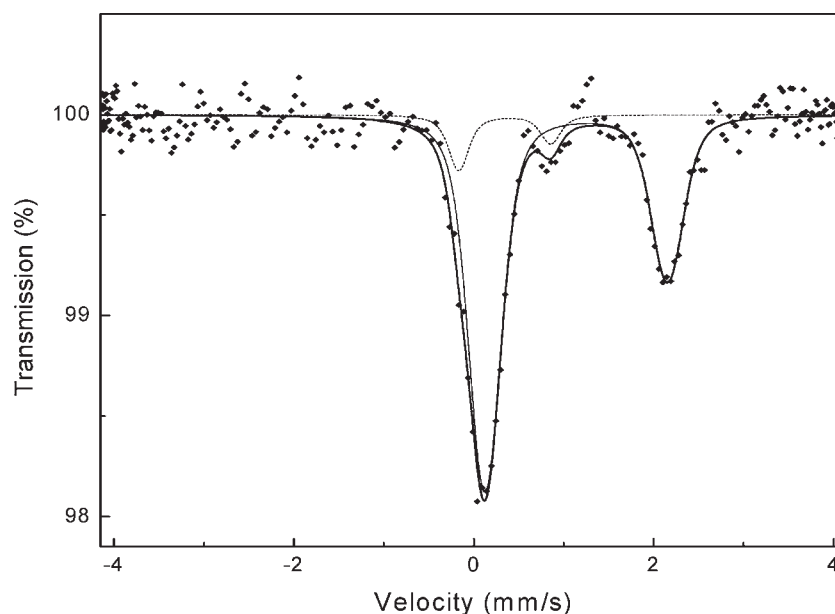


Fig. 1. Room-temperature Mössbauer spectrum of the jinshajiangite single crystal. Solid-line subspectrum: Fe^{2+} site; dashed-line subspectrum: Fe^{3+} site.

octahedra, *e.g.* cummingtonite-grunerite (Hawthorne, 1983). The linewidth of the asymmetric elemental doublets of the QSD was allowed to vary during the fitting procedure. The refined hyperfine parameters are: CS = 1.14 mm/s, QS = 2.03 mm/s and a relative area of 90 % for Fe^{2+} ; CS = 0.34 mm/s, QS = 1.02 mm/s and 10 % relative area for Fe^{3+} . Assuming equal recoil-free fractions for Fe^{2+} and Fe^{3+} , the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio determined by Mössbauer spectroscopy is 0.10(9).

2.2. Electron-microprobe analysis

The crystal of jinshajiangite used for Mössbauer spectroscopy was mounted in a Perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 keV, a specimen current of 20 nA, a beam size of 10 μm , and count times on peak and background of 20 and 30 s for major and minor elements (< 1 wt%), respectively. The following standards were used for *K* and *L* X-ray lines: F: topaz; Na: jadeite; Nb, Ba: $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$; Si, Ca: diopside; Fe: fayalite; Mn: spessartine; K: orthoclase; Cs: pollucite; Ti: titanite; Zn: baddeleyite; Mg: forsterite; Sr: tausonite; Al: andalusite; Zr: ZrO_2 ; Ta: manganotantalite. Data were reduced using the PAP procedure of Pouchou & Pichoir (1985). The amount of H_2O was calculated from structure refinement: $(\text{OH}) + \text{F} = 3$ apfu. Table 1 gives the chemical composition, which is the mean of 10 determinations, and the empirical formula is $(\text{Ba}_{0.58}\text{K}_{0.36})_{\Sigma 0.94}(\text{Na}_{0.57}\text{Ca}_{0.39})_{\Sigma 0.96}(\text{Fe}^{2+}_{2.84}\text{Mn}_{0.63}\text{Fe}^{3+}_{0.32}\text{Mg}_{0.16}\text{Zr}_{0.04}\text{Nb}_{0.07})_{\Sigma 4.00}(\text{Ti}_{2.00}\text{Nb}_{0.01})_{\Sigma 2.01}(\text{Si}_2\text{O}_7)_2\text{O}_{2.12}(\text{OH})_{1.93}\text{F}_{1.07}$, $Z = 8$, calculated on the basis of 4 Si apfu. From the chemical data of Hong & Fu (1982) (Table 1), we calculate the empirical formula for

their jinshajiangite sample on the basis of 4 Si apfu: $(\text{Ba}_{0.57}\text{K}_{0.44})_{\Sigma 1.01}(\text{Na}_{0.90}\text{Ca}_{0.47}\text{Sr}_{0.01})_{\Sigma 1.38}(\text{Fe}^{2+}_{2.35}\text{Mn}_{1.62}\text{Al}_{0.06}\text{Mg}_{0.06}\text{Zr}_{0.02})_{\Sigma 4.11}(\text{Ti}_{1.84}\text{Fe}^{3+}_{0.18}\text{Nb}_{0.07})_{\Sigma 2.09}(\text{Si}_2\text{O}_7)_2\text{O}_{1.66}(\text{OH})_{1.76}\text{F}_{1.24}$, $Z = 8$, $D_{\text{calc}} = 3.767\text{ g cm}^{-3}$. Comparison of these two formulae shows that they are similar, but the formula (EMPA) proposed here has better stoichiometry in terms of sums of specific groups of cations than that based on the bulk-chemistry data of Hong & Fu (1982), *e.g.* ΣB^P , ideally 1.0, = 0.96 vs. 1.38 and ΣM^O , ideally 4.0, = 4.00 vs. 4.11. With $Z = 8$, the simplified formula is $(\text{Ba},\text{K})(\text{Na},\text{Ca})(\text{Fe}^{2+},\text{Mn})_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH},\text{F})_3$.

2.3. Data collection and crystal-structure refinement

A single crystal of jinshajiangite was mounted on a Bruker AXS SMART APEX diffractometer fitted with a CCD detector and $\text{MoK}\alpha$ -radiation. The intensities of 23129 reflections were collected to 55.00° 2θ using 30 s per 0.2° frame, and an empirical absorption correction (SADABS, Sheldrick, 1998) was applied. The refined unit-cell parameters (Table 2) were obtained from 8188 reflections with $I > 10\sigma$. The crystal structure of jinshajiangite was solved by direct methods with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick, 1997) and refined in sp. gr. $C2/m$ to $R_1 = 5.69$ % and a GoF of 1.271. We observed weak reflections ($\leq 3\sigma F$) that indicated a supercell with a doubled *c* cell-parameter (*i.e.*, $a_s = a$, $b_s = b$, $c_s = 2c$) and tried to refine the structure with that larger cell but this was not successful. We think that the superstructure reflections are due to order of K along the *c*-axis (see discussion in the section *Cation sites*). We also refined the crystal structure of jinshajiangite in space groups $C2$ and Cm , resulting in R_1 values of 5.40 and

Table 2. Miscellaneous refinement data for jinshajiangite.

a (Å)	10.6785(8)
b	13.786(1)
c	20.700(2)
β (°)	94.937(1)
V (Å ³)	3035.93(6)
Space group	$C2/m$
Z	8
Absorption coefficient (mm ⁻¹)	6.64
$F(000)$	3288.0
$D_{\text{calc.}}$ (g/cm ³)	3.767
Crystal size (mm)	0.14 × 0.10 × 0.08
Radiation/filter	MoK α /graphite
2 θ -range for data collection (°)	55.00
$R(\text{int})$ (%)	5.57
Reflections collected	23129
Unique reflections	4589
Independent reflections	3634
$F_o > 4\sigma F$	3193
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$
Goodness of fit on F^2	1.271
Final R (obs) (%) [$F_o > 4\sigma F$]	$R_1 = 5.69$ $R_1 = 6.38$
R indices (all data) (%)	$wR_2 = 15.30$ GooF = 1.270

6.08 %, respectively. For the structure models obtained in the acentric space groups $C2$ and Cm , we observed high values in the correlation matrix between pairs of atoms that are equivalent in the centrosymmetric space group $C2/m$, and negative principal mean-square atomic-displacements for ~30 % of the cations and more than 50 % of the anions. Hence we reject these non-centrosymmetric space-group models. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). R indices are given in Table 2, and are expressed as percentages. Site scattering values at the M^H , M^O , A^P and B^P sites were refined with the scattering curves of Ti, Fe, Ba and Ca, respectively. As site occupancies for M^H sites refined to unity (within assigned standard deviations), they were fixed as such in accord with the chemical analysis (Table 1). At the last stages of the refinement, two peaks with magnitudes of 6.0 and 2.8 e/Å³ were found in the difference-Fourier map and they were labelled $A^P(2A)$ and $A^P(3A)$, respectively. The $A^P(2A)$ and $A^P(3A)$ peaks occur at short distances from the $A^P(2)$ atom, 0.75 Å, and $A^P(3)$ atom, 1.054 Å. The displacement parameters for $A^P(2A)$ and $A^P(3A)$ were constrained to be equal to those of the $A^P(2)$ and $A^P(3)$ atoms. The refined occupancies at these subsidiary sites are 0.06 and 0.01 Ba for $A^P(2A)$ and $A^P(3A)$, respectively. Due to negative atomic displacement parameters of O(4) and O(5), these two O atoms were refined as isotropic. The Si–O(11), Si–O(13), Si–O(14) and Si–O(15) distances were too short (~1.54 Å), a relatively common feature in the refinement of TS-block structures, and the relevant distances were softly constrained to be equal to 1.58 Å in order to give us better stereochemical

results. This constraint results in higher displacement parameters compared to other O atoms. Seven of the atoms [$M^H(1)$, $M^H(2)$, O(1), O(11), O(13), O(14), O(15)] exhibit very anisotropic-displacement parameters. The TS-block structures are commonly polytypic (lamprophyllite: Johnsen, 1996; Krivovichev *et al.*, 2003; nabalamprophyllite: Rastsvetaeva & Chukanov, 1999; Sokolova and Hawthorne, 2008a; nechelyustovaita: Nèmeth *et al.*, 2008) and polytypic intergrowths are common (Johnsen, 1996; Nèmeth *et al.*, 2005, 2008). The occurrence of the TS block in these minerals also gives rise to epitactic relations on a very fine scale. This behaviour finds expression in the occurrence of residual maxima in the electron density in these structures (Krivovichev *et al.*, 2003; Sokolova and Hawthorne, 2004, 2008a), and in the unreasonable anisotropic behaviour of some of the atoms in the structure. We are rarely, if ever, dealing with a single crystal in these minerals, and the unreasonable anisotropic behaviour of some of the atoms and the occurrence of residual maxima in the electron density [the $A^P(2A)$ and $A^P(3A)$ sites in Table 3] show that this is the case here. Details of the data collection and structure refinement are given in Table 2, final atom parameters are given in Table 3, selected interatomic distances and angles in Table 4, refined site-scattering values and assigned populations for selected sites in Table 5, and bond-valence values in Table 6. A list of observed and calculated structure factors has been deposited at the EJM and is freely available on the GSW website.

2.4. Site-population assignment

Table 1 shows that the M^O sites are occupied by 2.84 Fe²⁺, 0.32 Fe³⁺, 0.63 Mn²⁺, 0.10 Mg, 0.04 Zr and 0.07 Na, and the aggregate refined scattering at these sites (99.6 *epfu*, Table 5) is in close accord with this composition. The refined site-scattering values at the five M^O sites are equal within their assigned standard deviations when adjusted for differences in site multiplicity (Table 5). However, the mean bond-lengths around these sites show a considerable range of values, 2.164–2.190 Å, indicating significant order of cations over these sites. The $M^O(1)$, $M^O(2)$ and $M^O(3)$ sites have similar mean bond-lengths, ~2.168 Å, whereas the $M^O(4)$ and $M^O(5)$ sites have significantly longer mean bond-lengths, ~2.185 Å, indicating that the larger cations, particularly Mn²⁺, must be assigned to the $M^O(4)$ and $M^O(5)$ sites, and the smaller cations, Mg and Fe³⁺, must be assigned to the $M^O(1)$, $M^O(2)$ and $M^O(3)$ sites. Thus the minor Na and Zr were assigned to $M^O(5)$, and Fe²⁺ and all Mn²⁺ were assigned to the remainder of $M^O(5)$ and $M^O(4)$ in amounts that reflect the differences in the observed $\langle M^O(4)–O \rangle$ and $\langle M^O(5)–O \rangle$ distances. The remaining Fe²⁺, together with all Mg and Fe³⁺, were assigned equally to the $M^O(1)$, $M^O(2)$ and $M^O(3)$ sites.

In jinshajiangite, the numbers of $A^P(1)$, $A^P(2)$ and $A^P(3)$ sites in the formula unit are 0.25, 0.50 and 0.50, respectively (Table 3). However, there is a short distance $A^P(3)–A^P(3)'$ ($g: -x, -y, -z$) of 1.054 Å (Table 4), and

Table 3. Final atom coordinates and displacement parameters ($\text{\AA}^2$) for jinshajiangite.

Atom	Equipoint fraction	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
M ^O (1)	0.5	0.12348(12)	0	0.74395(7)	0.0046(7)	0.0090(8)	0.0094(7)	0	0.0012(5)	0	0.0076(5)
M ^O (2)	0.5	0.37436(12)	0	0.25460(7)	0.0054(7)	0.0083(8)	0.0101(8)	0	0.0006(5)	0	0.0079(5)
M ^O (3)	1.0	0.37433(9)	0.12400(7)	0.75126(5)	0.0057(6)	0.0082(6)	0.0135(6)	−0.0001(4)	0.0016(4)	0.0011(3)	0.0091(4)
M ^O (4)	1.0	0.37424(9)	0.24820(7)	0.24466(5)	0.0049(6)	0.0083(6)	0.01291(6)	0.0001(4)	0.0012(4)	0.0000(3)	0.0087(4)
M ^O (5)	0.5	0.12389(9)	0.12619(7)	0.25122(5)	0.0064(6)	0.0120(6)	0.0169(6)	−0.0040(4)	0.0049(4)	−0.0031(4)	0.0115(4)
M ^H (1)	0.5	0.26682(19)	0	0.60285(11)	0.0011(9)	0.130(3)	0.0105(10)	0	−0.0009(7)	0	0.0474(9)
M ^H (2)	1.0	0.23339(19)	0	0.39818(10)	0.0009(9)	0.122(3)	0.0111(10)	0	−0.0014(7)	0	0.0449(9)
M ^H (3)	1.0	0.48335(10)	0.23021(7)	0.89798(5)	0.0017(5)	0.0017(5)	0.0033(5)	0.0004(4)	0.0005(4)	−0.0003(4)	0.0022(3)
Si(1)	1.0	0.01953(19)	0.14135(14)	0.61950(9)	0.0236(10)	0.0087(9)	0.0085(8)	0.0004(7)	0.0014(7)	−0.0008(7)	0.0136(4)
Si(2)	1.0	0.25761(15)	0.10891(12)	0.11917(8)	0.0017(7)	0.0049(8)	0.0081(8)	0.0000(6)	−0.0003(6)	0.0006(6)	0.0050(4)
Si(3)	1.0	0.21756(15)	0.10937(12)	0.88055(8)	0.0016(7)	0.0043(8)	0.0084(8)	0.0000(6)	0.0004(6)	−0.0002(6)	0.0048(4)
Si(4)	1.0	0.47947(19)	0.13996(14)	0.37992(9)	0.0226(10)	0.0086(9)	0.0085(8)	−0.0006(7)	0.0009(7)	−0.0007(7)	0.0133(4)
A ^P (1)	0.25	½	0	0	0.0048(4)	0.0066(4)	0.0052(4)	0	0.0003(3)	0	0.0055(3)
A ^P (2)	0.5	¼	¼	½	0.0123(6)	0.0331(17)	0.0154(6)	−0.0004(4)	0.0000(4)	−0.0006(4)	0.0203(5)
A ^P (3)	0.5	0	0.0382(2)	0	0.0217(14)	0.0389(16)	0.0252(19)	0	0.0035(11)	0	0.0285(10)
B ^P (1)	0.25	½	0	½	0.031(3)	0.032(3)	0.018(2)	0	0.0013(17)	0	0.0271(15)
B ^P (2)	0.25	0	0	½	0.029(3)	0.028(3)	0.017(2)	0	0.0014(17)	0	0.0245(15)
B ^P (3)	0.5	¼	¼	0	0.0234(17)	0.0217(17)	0.0123(15)	0.0001(10)	−0.0004(11)	−0.0103(11)	0.0192(10)
O(1)	0.5	0.2081(6)	0	0.0991(3)	0.008(3)	0.004(3)	0.013(3)	0	0.001(2)	0	0.0083(12)
O(2)	1.0	0.3590(4)	0.1254(3)	0.9123(2)	0.004(2)	0.0050(19)	0.011(2)	0.0024(16)	−0.0036(16)	−0.0023(16)	0.0070(9)
O(3)	1.0	0.1489(4)	0.1787(3)	0.0869(2)	0.007(2)	0.005(2)	0.012(2)	0.0012(17)	−0.0002(16)	0.0008(16)	0.0080(9)
O(4)	0.5	0.1738(6)	0	0.8990(3)	0.0060(12)						
O(5)	1.0	0.3879(4)	0.1252(3)	0.0872(2)	0.0081(9)						
O(6)	1.0	0.1201(4)	0.1783(3)	0.9138(2)	0.0049(19)	0.0024(19)	0.013(2)	−0.0012(17)	−0.0006(16)	0.0005(16)	0.0069(9)
O(7)	1.0	0.2749(4)	0.1193(4)	0.1973(2)	0.002(2)	0.018(2)	0.014(2)	−0.0001(18)	−0.0007(17)	−0.0038(17)	0.0111(10)
O(8)	1.0	0.2128(5)	0.1207(4)	0.8025(2)	0.009(2)	0.021(3)	0.014(2)	−0.001(2)	0.0020(18)	0.0012(19)	0.0147(10)
O(9)	1.0	0.0355(4)	0.1304(3)	0.6984(2)	0.014(2)	0.006(2)	0.005(2)	0.0003(16)	−0.0009(17)	−0.0003(17)	0.0085(9)
O(10)	1.0	0.4615(4)	0.1279(3)	0.3012(2)	0.013(2)	0.004(2)	0.0047(19)	−0.0009(16)	−0.0006(16)	0.0001(16)	0.0075(9)
O(11)	1.0	0.1056(5)	0.0961(8)	0.4141(3)	0.006(3)	0.212(12)	0.016(3)	−0.001(5)	0.003(2)	0.028(5)	0.078(4)
O(12A) ^a	1.0	0.4254(10)	0.2497(7)	0.4004(5)	0.011(3)	0.005(3)	0.012(3)	0.000(2)	−0.007(3)	−0.000(2)	0.0099(15)
O(12B) ^a	1.0	0.4552(9)	0.2488(6)	0.6002(5)	0.011(3)	0.005(3)	0.012(3)	0.000(2)	−0.007(3)	−0.000(2)	0.0099(15)
O(13)	1.0	0.1353(5)	0.0979(8)	0.5866(3)	0.009(3)	0.230(13)	0.013(3)	0.002(5)	0.007(2)	0.031(5)	0.084(4)
O(14)	1.0	0.3652(5)	0.0973(8)	0.4144(3)	0.010(3)	0.215(12)	0.015(3)	−0.006(5)	0.007(2)	−0.030(5)	0.080(4)
O(15)	1.0	0.3942(5)	0.0953(9)	0.5876(3)	0.008(3)	0.238(13)	0.017(3)	0.002(5)	0.002(2)	−0.034(5)	0.087(4)
O(16)	1.0	0.4744(4)	0.2382(3)	0.8126(2)	0.005(2)	0.012(2)	0.010(2)	0.0047(17)	0.0009(17)	0.0057(17)	0.0090(9)
O(17)	0.5	0.2174(7)	0	0.3112(3)	0.008(3)	0.038(5)	0.010(3)	0	0.001(3)	0	0.0188(16)
O(18)	0.5	0.2811(7)	0	0.6903(3)	0.008(3)	0.040(5)	0.008(3)	0	0.002(3)	0	0.0186(16)
X _A ^O (1)	1.0	0.2910(4)	0.2484(3)	0.7067(2)	0.007(2)	0.013(2)	0.0023(19)	−0.0001(16)	−0.0024(16)	0.0013(16)	0.0075(9)
X _A ^O (2)	0.5	0.4648(7)	0	0.7943(4)	0.008(3)	0.019(4)	0.030(4)	0	0.003(3)	0	0.0189(16)
X _A ^O (3)	0.5	0.0350(6)	0	0.2082(4)	0.006(3)	0.013(3)	0.027(4)	0	0.003(3)	0	0.0154(14)
X _M ^P	0.5	0.2496(7)	0	0.5004(4)	0.001(4)	0.151(13)	0.004(4)	0	0.001(3)	0	0.052(4)
F	0.5	½	0.2257(4)	0	0.010(3)	0.010(3)	0.003(2)	0	−0.0003(19)	0	0.0079(10)
Subsidiary peaks											
A ^P (2A)	1.0	0.2509(7)	0.1955(14)	0.5004(4)	0.012(3)	0.0331(6)	0.0154(17)	−0.0004(6)	0.0000(4)	−0.0006(4)	0.0203(14)
A ^P (3A)	0.5	0.003(3)	0	0.969(2)	0.022(2)	0.03898(14)	0.0252(16)	0	0.0035(19)	0	0.0285(12)

^aO(12A) and O(12B) are 50 % occupied by O atoms.

Table 4. Selected interatomic distances (Å) and angles (°) for jinshajiangite.

M ^O (1)–X _A ^O (3)a	2.034(7)		M ^O (2)–X _A ^O (2)b	2.068(7)			
M ^O (1)–O(18)	2.095(7)		M ^O (2)–O(17)	2.126(7)			
M ^O (1)–O(9)	2.203(5)	×2	M ^O (2)–O(10)	2.180(4)	×2		
M ^O (1)–O(8)	2.225(5)	×2	M ^O (2)–O(7)	2.242(5)	×2		
<M ^O (1)–φ>	2.164		<M ^O (2)–φ>	2.173			
M ^O (3)–O(8)	2.102(5)		M ^O (4)–O(16)c	2.089(5)		M ^O (5)–O(7)	2.041(5)
M ^O (3)–X _A ^O (1)	2.109(5)		M ^O (4)–X _A ^O (1)d	2.106(5)		M ^O (5)–O(9)f	2.072(5)
M ^O (3)–X _A ^O (2)	2.122(5)		M ^O (4)–O(10)	2.191(5)		M ^O (5)–X _A ^O (1)d	2.107(5)
M ^O (3)–O(10)c	2.140(5)		M ^O (4)–O(8)d	2.219(5)		M ^O (5)–X _A ^O (3)	2.139(4)
M ^O (3)–O(16)	2.235(5)		M ^O (4)–O(9)d	2.220(5)		M ^O (5)–O(17)	2.313(5)
M ^O (3)–O(18)	2.299(5)		M ^O (4)–O(7)	2.251(5)		M ^O (5)–O(16)	2.470(5)
<M ^O (3)–φ>	2.168		<M ^O (4)–φ>	2.179		<M ^O (5)–φ>	2.190
Si(1)–O(11)f	1.580(1) ^a		Si(2)–O(3)	1.608(5)	Si(1)d–O(12A)–Si(4)		127.4(7)
Si(1)–O(13)	1.580(1) ^a		Si(2)–O(5)	1.607(5)	Si(1)i–O(12B)–Si(4)c		125.8(6)
Si(1)–O(9)	1.634(5)		Si(2)–O(7)	1.617(5)	Si(1)i–O(12)–Si(4)c		141.3
Si(1)–O(12A)d ^b	1.678(10)		Si(2)–O(1)	1.633(3)	Si(2)–O(1)–Si(2)j		133.6(4)
Si(1)–O(12B)e ^b	1.696(9)		<Si(2)–O>	1.616	Si(3)–O(4)–Si(3)j		134.8(4)
<Si(1)–O>	1.620						
			Si(4)–O(15)c	1.580(1) ^a			
Si(3)–O(6)	1.607(5)		Si(4)–O(14)	1.580(1) ^a			
Si(3)–O(2)	1.610(5)		Si(4)–O(10)	1.633(5)			
Si(3)–O(8)	1.620(5)		Si(4)–O(12A)	1.686(10)			
Si(3)–O(4)	1.633(3)		Si(4)–O(12B)c	1.691(9)			
<Si(3)–O>	1.618		<Si(4)–O>	1.620			
M ^H (1)–O(18)	1.804(7)		M ^H (2)–O(17)	1.795(7)		M ^H (3)–O(16)	1.766(5)
M ^H (1)–O(15)	1.936(7)	×2	M ^H (2)–O(11)	1.951(6)	×2	M ^H (3)–O(3)d	1.935(5)
M ^H (1)–O(13)	1.956(7)	×2	M ^H (2)–O(14)	1.952(7)	×2	M ^H (3)–O(6)i	1.936(5)
M ^H (1)–X _M ^P	2.109(8)		M ^H (2)–X _M ^P	2.112(8)		M ^H (3)–O(5)c	2.002(4)
<M ^H (1)–φ>	1.950		<M ^H (2)–φ>	1.952		M ^H (3)–O(2)	2.002(4)
						M ^H (3)–F	2.105(1)
A ^P (1)–O(5)	2.836(4)	×4	A ^P (2)–O(12B) ^b	2.885(9)	×2	<M ^H (3)–φ>	1.958
A ^P (1)–O(2)c	2.842(4)	×4	A ^P (2)–O(12A) ^b	2.90(1)	×2		
A ^P (1)–F	3.112(5)	×2	A ^P (2)–O(14)	3.07(1)	×2	A ^P (3)–O(1)	2.940(6)
<A ^P (1)–φ> ^c	2.894		A ^P (2)–O(13)	3.08(1)	×2	A ^P (3)–O(4)a	2.960(6)
			A ^P (2)–O(11)	3.09(1)	×2	A ^P (3)–O(6)f	2.992(5)
A ^P (2)–A ^P (2A)	0.75(2)		A ^P (2)–O(15)	3.12(1)	×2	A ^P (3)–O(3)	3.004(5)
A ^P (2A)–A ^P (2A)d	1.50(4)		<A ^P (2)–O>	3.05		A ^P (3)–F	3.254(6)
A ^P (3)–A ^P (3)g	1.054(7)					<A ^P (3)–φ>	3.005
A ^P (3)–A ^P (3A)a	0.83(3)						
A ^P (3A)–A ^P (3A)k	1.30(8)					B ^P (3)–O(6)h	2.379(4)
						B ^P (3)–O(3)	2.388(4)
B ^P (1)–O(14)	2.564(9)	×4	B ^P (2)–O(11)	2.556(8)	×4	B ^P (3)–F	2.6905(7)
B ^P (1)–O(15)	2.577(9)	×4	B ^P (2)–O(13)	2.584(9)	×4	B ^P (3)–O(5)	2.816(5)
B ^P (1)–X _M ^P	2.675(7)	×2	B ^P (2)–X _M ^P	2.664(7)	×2	B ^P (3)–O(2)d	2.822(5)
<B ^P (1)–φ>	2.591		<B ^P (2)–φ>	2.589		<B ^P (3)–φ>	2.619

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

^aThe Si–O distances are softly constrained to the value 1.580 Å and hence the standard deviations are very low.

^bO(12A) and O(12B) sites are 50 % occupied by O atoms and have to be taken into account alternatively.

^cφ = O, OH, F.

hence the number of A^P cations is $0.25 + 0.50 + 0.50/2 = 1.0$ apfu. The cations to be assigned to the A^P and B^P are Ba, K, Ca and Na (Table 5). The <A^P–O> and <B^P–O> distances are in the ranges 2.89–3.05 and 2.59–2.62 Å, respectively. On the basis of their relative radii (Shannon, 1976), Ba and K were assigned to the A^P sites, and Ca and Na were assigned to the B^P sites, and the resulting aggregate site-populations are in accord with the aggregate refined site-scattering values (Table 5). At the A^P sites, the maximum refined site-scattering value is at the

A^P(1) site: 13.33 epfu (Table 5) for a site multiplicity of 0.25 (Table 3); thus we assign this site as filled completely with Ba. This leaves three species, Ba, K and □, to be assigned to the A^P(2) and A^P(3) sites. There is no rigorous way of assigning these three species to the two A^P(2) and A^P(3) sites, but the refined site-scattering values indicate that Ba is dominant at A^P(2), □ and K are dominant at A^P(3), and the assigned values (Table 5) are in accord with this argument. The refined site-scattering values at the B^P sites indicate identical

Table 5. Refined site-scattering (*epfu*) and assigned site-populations (*apfu*) for jinshajiangite.

Site	Refined site-scattering	Site population	Calculated site-scattering	$\langle X-\phi \rangle_{\text{calc.}}^a$ (Å)	$\langle X-\phi \rangle_{\text{obs.}}$ (Å)
$M^O(1)^b$	12.4(1)	0.40 Fe ²⁺ + 0.10 Fe ³⁺	13.0	2.128	2.164
$M^O(2)$	12.3(1)	0.38 Fe ²⁺ + 0.07 Fe ³⁺ + 0.05 Mg	12.3	2.130	2.173
$M^O(3)$	24.8(2)	0.80 Fe ²⁺ + 0.15 Fe ³⁺ + 0.05 Mg	25.3	2.127	2.168
$M^O(4)$	25.0(2)	0.77 Fe ²⁺ + 0.23 Mn ²⁺	25.8	2.167	2.179
$M^O(5)$	25.1(2)	0.49 Fe ²⁺ + 0.40 Mn ²⁺ + 0.04 Zr + 0.07 Na	25.1	2.184	2.190
ΣM^O	99.6	2.84 Fe ²⁺ + 0.32 Fe ³⁺ + 0.63 Mn ²⁺ + 0.10 Mg + 0.04 Zr + 0.07 Na = 4 <i>apfu</i>	101.5		
$M^H(1)^c$	11	0.5 Ti		1.978	1.950
$M^H(2)$	11	0.5 Ti		1.978	1.952
$M^H(3)$	22	1.00 Ti		1.969	1.958
ΣM^H	44	2.00 Ti = 2 <i>apfu</i>			
$^{[10]}A^P(1)$	13.33(7)	0.25 Ba	14.0	2.886	2.894
$^{[10]}A^P(2)$	17.5(2)	0.26 Ba + 0.18K + 0.06 □	18.0		3.05
$^{[9]}A^P(3)$	7.5(1)	0.18 K + 0.07 Ba + 0.25 □	7.3		3.005
ΣA^P ^d	38.3	0.58 Ba + 0.36 K + 0.06 □ = 1 <i>apfu</i>	39.3		
$^{[10]}B^P(1)$	3.83(8)	0.15 Na + 0.10 Ca	3.7	2.630	2.591
$^{[10]}B^P(2)$	3.83(8)	0.15 Na + 0.10 Ca	3.7	2.630	2.589
$^{[10]}B^P(3)$	7.6(1)	0.30 Na + 0.20 Ca	7.3	2.630	2.619
ΣB^P	15.3	0.60 Na + 0.40 Ca = 1.00 <i>apfu</i>	14.7		

^aCalculated by summing constituent ionic radii; values from Shannon (1976), ϕ = O, (OH), F.

^bCoordination numbers are given for non octahedral sites.

^cin accord with chemical analysis, site, occupancies for three M^H sites were fixed.

^dAs the $A^P(3)$ site can be only 50 % occupied (see discussion in the text), the sum of three A^P sites, equals 1 *apfu* = 0.25 $A^P(1)$ + 0.5 $A^P(2)$ + 0.25 $A^P(3)$.

occupancies, and Na and Ca were assigned on this basis (Table 5).

3. Description of the structure

3.1. Cation sites

The crystal structure of jinshajiangite (sp. gr. *C2/m*) is topologically identical to the crystal structure of perraultite (sp. gr. *C2*) (Yamnova *et al.*, 1998). We divide the cation sites (Table 3) into 3 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 constitute the I block. Also in accord with Sokolova (2006), we label anions X^O , X^H and X^P (anions of O and H sheets and peripheral anions); X_M^O = common vertices of M^O and M^H polyhedra; X_A^O = common vertices of M^O and A^P polyhedra; X_M^P = apical anions of M^H polyhedra at the periphery of the TS block. We will describe the composition of each structural fragment within a planar cell common to Ti disilicate minerals with the TS block: it is based on translation vectors, $\mathbf{t}_1$ and $\mathbf{t}_2$, with $t_1 \sim 5.5$ and $t_2 \sim 7$ Å and $\mathbf{t}_1 \wedge \mathbf{t}_2$ close to 90° (Sokolova, 2006). We will consider jinshajiangite and compare it to perraultite.

3.1.1. O sheet

There are five [6]-coordinated M^O sites in the O sheet (Tables 3 and 4). The $M^O(1-4)$ sites are occupied mainly

by Fe²⁺, with minor Fe³⁺, Mn²⁺ and Mg (Table 5). The $M^O(5)$ site is occupied by approximately equal amounts of Fe²⁺ and Mn²⁺ with minor Zr and Na (Table 5). The $M^O(1,2,4)$ atoms are coordinated by five O atoms and a monovalent anion, X_A^O (see discussion below) with $\langle M^O(1,2,4)-\phi \rangle = 2.164, 2.173$ and 2.179 Å (where ϕ = unspecified anion), respectively. The $M^O(3)$ and $M^O(5)$ atoms are coordinated by four O atoms and two monovalent X_A^O anions, with $\langle M^O(3,5)-\phi \rangle = 2.168$ and 2.190 Å. The $\langle M^O(5)-\phi \rangle$ length is the longest in the O sheet; this is due to the presence of significant Mn²⁺ ($r = 0.83$ Å, Shannon, 1976). The five [6]-coordinated M^O sites contain 2.84 Fe²⁺ + 0.32 Fe³⁺ + 0.63 Mn²⁺ + 0.10 Mg + 0.04 Zr + 0.07 Na = 4 *apfu*, ideally Fe₄²⁺ *pfu*. In perraultite, eight [6]-coordinated M^O sites give Mn_{2.5}²⁺ Fe_{1.5}²⁺, ideally Mn₄²⁺ *pfu*.

3.1.2. H sheet

There are three [6]-coordinated M^H sites in the H sheet, and these are occupied solely by Ti (Tables 3 and 5). All three M^H sites are coordinated by five O atoms and one monovalent anion, F or OH, with $\langle M^H-\phi \rangle = 1.953$ Å. Note the short distances from each M^H cation to each X_M^O anion: $M^H(1)-O(18) = 1.804$ Å, $M^H(2)-O(17) = 1.795$ Å and $M^H(3)-O(16) = 1.766$ Å (Table 4). There are four tetrahedrally coordinated Si sites occupied solely by Si, with $\langle Si-O \rangle = 1.619$ Å (Table 4). The cations of the two H sheets give Ti₂ Si₄ *pfu*, as in perraultite.

Table 6. Bond-valence^a (vu) table for jinshajiangite.

	M ^O (1)	M ^O (2)	M ^O (3)	M ^O (4)	M ^O (5)	M ^H (1)	M ^H (2)	M ^H (3)	Si(1)	Si(2)	Si(3)	Si(4)	A ^P (1)	A ^P (2)	A ^P (3)	B ^P (1)	B ^P (2)	B ^P (3)	Σ
O(1)										0.99 ^{×2} →	1.06		0.23 ^{×4} ↓		0.06 ^{×2} ↓→			0.11 ^{×2} ↓	2.10
O(2)								0.59										0.25 ^{×2} ↓	1.99
O(3)								0.70		1.06					0.05 ^{×2} ↓				2.06
O(4)											0.99 ^{×2} →				0.06 ^{×2} ↓→				2.10
O(5)								0.59		1.06			0.23 ^{×4} ↓		0.05 ^{×2} ↓			0.11 ^{×2} ↓	1.99
O(6)								0.70		1.03								0.25 ^{×2} ↓	2.06
O(7)		0.27 ^{×2} ↓		0.27	0.48						1.03								2.05
O(8)	0.28 ^{×2} ↓		0.38	0.29															1.98
O(9)	0.30 ^{×2} ↓			0.29	0.44						1.03								2.02
O(10)		0.31 ^{×2} ↓	0.34	0.31					0.99			0.99							1.95
O(11)							0.67 ^{×2} ↓		1.14					0.09 ^{×2} ↓			0.18 ^{×4} ↓		2.08
O(12A) ^b									0.44			0.43		0.07 ^{×2} ↓					0.94
O(12B) ^b									0.42			0.43		0.08 ^{×2} ↓					0.93
O(13)						0.66 ^{×2} ↓			1.14					0.09 ^{×2} ↓			0.17 ^{×4} ↓		2.06
O(14)						0.69 ^{×2} ↓						1.14		0.09 ^{×2} ↓	0.17 ^{×4} ↓				2.07
O(15)												1.14		0.08 ^{×2} ↓	0.17 ^{×4} ↓				2.08
O(16)			0.27	0.40	0.17			1.12											1.96
O(17)		0.36			0.24 ^{×2} →	1.03													1.87
O(18)	0.39		0.23 ^{×2} →			1.00													1.85
X ^O _A (1) ^c																			1.16
X ^O _A (2) ^c			0.37	0.39	0.40														1.13
X ^O _A (3) ^c		0.41	0.36 ^{×2} →																1.20
X ^P _M					0.37 ^{×2} →	0.39	0.38									0.12 ^{×2} ↓	0.13 ^{×2} ↓	0.10 ^{×2} ↓→	1.02
F																			0.99
Total	2.01	1.93	1.95	1.95	2.10	4.09	4.09	4.02	4.13	4.14	4.14	4.13	0.12 ^{×2} ↓	1.00	0.03	1.60	1.66	1.64	
Aggr.	2.20	2.14	2.15	2.00	2.01	4.00	4.00	4.00	4.00	4.00	4.00	4.00	2.00	1.40	0.64	1.40	1.40	1.40	
charge																			

^aBond-valence parameters are from Brown (1981).^bO(12A) and O(12B) are 50 % occupied by O atoms.^cX^O_A(1), X^O_A(2) and X^O_A(3) are occupied by monovalent anions, OH and minor F.^dX^P_M is occupied by OH and F in a ratio 1:1.

3.1.3. Interstitial sites

In the perraultite-type structure, there are six interstitial sites, 3 A^P and 3 B^P . The $A^P(2)$ site is occupied by (Ba + K) at 88 %, with Ba > K, and is coordinated by ten O atoms, with $\langle A^P(2)-O \rangle = 3.05$ Å. Note that the O(12A) and O(12B) sites are 50 % occupied by O atoms and must be taken into account as ligands of the $A^P(2)$ cation at 50 % (Tables 3 and 4). The $A^P(3)$ site is occupied by (K + Ba) at 50 %, with K > Ba, and is coordinated by eight O atoms and one F atom, with $\langle A^P(3)-O \rangle = 3.005$ Å (Tables 4 and 5). We suggest that the positional disorder of cations at the $A^P(3)$ site is due to the long-range order of K atoms in the supercell of jinshajiangite ($c_s = 2c$). The total content of three A^P sites sums to ~ 1 apfu: Ba_{0.58} K_{0.36}, ideally 1 Ba pfu with $Z = 8$. In perraultite (sp. gr. C2), two A^P sites (out of three) have partial occupancy; the total content of the $^{[10]}A^P(1)$, $^{[9]}A^P(2)$ and $^{[9]}A^P(3)$ sites is Ba_{0.63} K_{0.30}□_{0.07}, ideally 1 Ba pfu.

The three B^P sites are occupied by Na and Ca in the ratio 3 : 2, in accord with the observed site-scattering values (Tables 3 and 5). The three B^P sites are coordinated by eight O atoms and one monovalent anion, X_M^P in the terminology of Sokolova (2006). For the $B^P(1)$ and $B^P(2)$ sites, $X_M^P = (OH)_{0.5}F_{0.5}$; for the $B^P(3)$ site, $X_M^P = F$ and the mean distances are 2.591, 2.589 and 2.619 Å for the $B^P(1)$, $B^P(2)$ and $B^P(3)$ sites, respectively (Table 4). We did not observe Ca-dominance at any of these sites. The total content of the three B^P sites is Na_{0.60}Ca_{0.40}, ideally 1 Na pfu. In perraultite, the three [10]-coordinated B^P sites are occupied by Na_{0.25},Na_{0.125}Ca_{0.125} and Na_{0.375}Ca_{0.125} (Yamnova *et al.*, 1998) giving in total Na_{0.75}Ca_{0.25} apfu, ideally 1 Na pfu.

3.2. Anion considerations

There are fifteen anion sites, O(1)–O(15), that coordinate the Si sites and they are occupied by O atoms (Table 6). The O(12A) and O(12B) atoms are separated by 1.28 Å and must each be half occupied by O atoms (Table 6). Three anions, O(16)–O(18) [X_M^O in the terminology of Sokolova (2006)], are ligands of three $[M^O]^{2+}$ cations and an $[M^H]^{4+}$ cation, and they are occupied by O atoms. Attached to the M^H octahedra are the F and X_M^P atoms. During refinement of the structure, values of displacement parameters lower than the average for the O atoms indicated that the F site is occupied solely by F, corresponding to 0.5 F pfu (Tables 3 and 6). As chemical analysis gave F = 1.07 apfu (Table 1), we are left with 0.57 apfu F that we assigned to the X_M^P site [= F_{0.32}(OH)_{0.18}] in accord with the bond-valence sum of 1.02 vu at X_M^P . There are three anion sites, here designated as X_A^P , that receive bond valence from three $[M^O]^{2+}$ cations: the $X_A^P(1)$, $X_A^P(2)$ and $X_A^P(3)$ sites with equipoint fractions of 1.0, 0.5 and 0.5 apfu, respectively, corresponding to 2 apfu in total, and we assign (OH)_{1.75}F_{0.25}, ideally (OH)₂, to these three sites. We can write the anion part of the formula as the sum of (1) the H sheet: O₁₄ (belonging to two Si₂O₇ groups) + (2) the O sheet: three X_M^O and three X_A^O sites, giving O₂ and (OH)_{1.75}F_{0.25} + (3) the apical anions of the M^H polyhedra at the periphery of the TS

block: two X_M^P sites, giving F_{0.82}(OH)_{0.18}, ideally O₁₄O₂(OH)₂F.

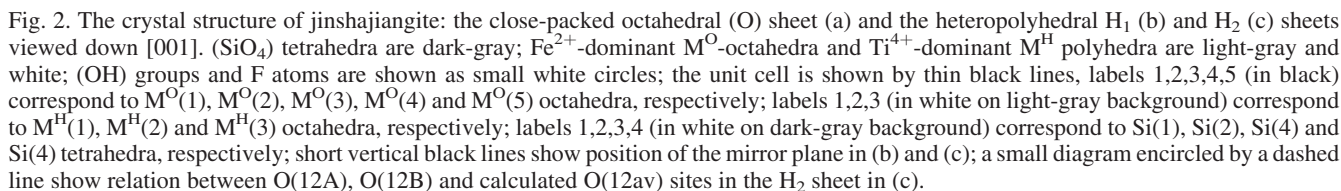
In accord with the perraultite-type general formula, $A^P B^P [M^H] M_4^O (Si_2O_7)_2 X_4^O X_M^P$ (Sokolova, 2006), we write the structural formula of jinshajiangite as (Ba,K) (Na,Ca) Ti₂(Fe²⁺,Mn)₄(Si₂O₇)₂O₂(OH)₂F where Ba > K, Na > Ca, and the end-member formula as BaNaTi₂Fe₄²⁺(Si₂O₇)₂O₂(OH)₂F, $Z = 8$. Both these formulae are in agreement with the empirical formula given above.

3.3. Topology of the structure

The overall topology of the crystal structure of jinshajiangite is in accord with the perraultite structure-type (Yamnova *et al.*, 1998), and jinshajiangite is the 27th Ti disilicate with the TS block. In the structure of jinshajiangite, the $M^O(1)$, $M^O(2)$, $M^O(3)$, $M^O(4)$ and $M^O(5)$ octahedra form a close-packed octahedral (O) sheet (Fig. 2a). In the H sheet, (SiO₄) tetrahedra link *via* common vertices to form (Si₂O₇) groups that are oriented along **b** (Fig. 2b, c). The (Si₂O₇) groups and M^H octahedra share common vertices to form the H sheet. The H₁ sheet consists of $M^H(3)$ octahedra and two independent (Si₂O₇) groups, with Si(2) and Si(3) central atoms, respectively (Fig. 2b). Two tetrahedra of each (Si₂O₇) group are related by a mirror plane, m_y . The H₂ sheet consists of $M^H(1)$ and $M^H(2)$ octahedra and an (Si₂O₇) group formed by Si(1) and Si(4) central atoms (Fig. 2c). In the H₂ sheet, the $M^H(1)$ and $M^H(2)$ sites have point symmetry m (the mirror plane m_y). Details of the split of the bridging O(12) site (see discussion above) are shown in Fig. 2c. The two H sheets are topologically (but not crystallographically) identical. An O sheet and two adjacent H sheets link through common vertices of (SiO₄) tetrahedra and M^H and M^O octahedra to form an HOH block parallel to (001) (Fig. 3). Figure 3 shows that in the TS block, (Si₂O₇) groups link to two M^O octahedra of the O sheet adjacent along **b**, as in Group II of Sokolova (2006). In jinshajiangite, different TS blocks are connected through common vertices of M^H octahedra (which are F atoms and OH groups), plus interstitial cations at the A^P and B^P sites (Fig. 3). Note that there is no correlation between anion disorder at the O(12) site (in the H₂ sheet) and cation disorder at the $A^P(3)$ site (adjacent to two H₁ sheets).

4. The relation between jinshajiangite and perraultite

While this paper was in review, Rastsvetaeva *et al.* (2008b) reported on the crystal structure of jinshajiangite from the Norra Kärr complex, Sweden, the same locality as that of the jinshajiangite that is described here. As the results of Rastsvetaeva *et al.* (2008b) are so different from those reported here, we must address these differences in detail; we also compare them to the structure and composition of perraultite (Yamnova *et al.*, 1998). The cell



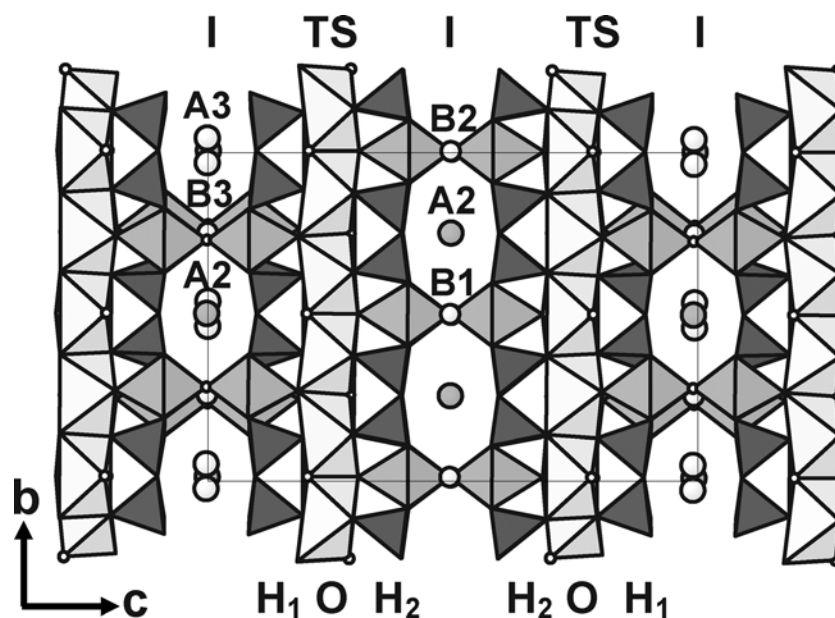


Fig. 3. General view of the crystal structure of jinshajiangite projected onto (100). Legend as in Fig. 2, the interstitial Ba-dominant and K-dominant A^P sites are shown as large light-gray and white circles, respectively; Na-dominant B^P sites are shown as smaller white circles. Titanium silicate and intermediate blocks are labeled TS and I in the upper part of the diagram, and the sequence of sheets within one TS block is shown in the lower part of the diagram, i.e., H_1 –O– H_2 .

Table 7. Unit-cell dimensions and space groups reported for jinshajiangite and perraultite.

	Jinshajiangite			Perraultite
	Powder diffraction	Single crystal	Single crystal	Single crystal
a (Å)	10.696	5.350	10.6785	10.731
b (Å)	13.800	6.909	13.786	13.841
c (Å)	20.705	20.96	20.700	20.845
β (°)	94.96	99.83	94.937	95.06
V (Å ³)	3044.7	763	3035.93	3084.0
Space group	–	$P2/m$	$C2/m$	$C2$
Reference	(1)	(1)	(2)	(3)

References: (1) Rastsvetaeva *et al.* (2008b); (2) This work; (3) Yamnova *et al.* (1998).

dimensions and space groups from these studies are given in Table 7.

4.1. Crystal structure

The cell dimensions for jinshajiangite given in the present work are similar to those of perraultite, and the bond topologies of the structures are identical. The space groups are not the same, $C2/m$ vs. $C2$, but Yamnova *et al.* (1998) state that the lower space group arises from order of Mn^{2+} and Fe^{2+} . In the present work, we examined this issue of lower symmetry ($C2$ or Cm vs. $C2/m$) and rejected both $C2$ and Cm symmetry. Rastsvetaeva *et al.* (2008b) reported single-crystal cell dimensions and space group for

jinshajiangite that are very different from the other values in Table 7, and these contradict their cell dimensions refined from powder-diffraction data that are compatible with the cell dimensions for jinshajiangite and perraultite (Table 7). Thus there is a complete disconnect between the two sets of values for the unit cell of jinshajiangite reported by Rastsvetaeva *et al.* (2008b).

Examining the structure reported for jinshajiangite by Rastsvetaeva *et al.* (2008b), we note the following points:

- (1) There are two additional anion sites in the I block of the structure of jinshajiangite reported by Rastsvetaeva *et al.* (2008b) compared to the structures reported here for jinshajiangite and the structure of perraultite reported by Yamnova *et al.* (1998). The presence of these two additional sites make the topology of the structure reported by Rastsvetaeva *et al.* (2008b) different from that of perraultite and the jinshajiangite structure reported here. Rastsvetaeva *et al.* (2008b) assign these two additional sites, O(3) and O(15), as OH. There are two important points with regard to these sites; (i) The sums of the bond valence incident at O(3) and O(15) are 0.64 and 0.56 *vu*; these sums indicate that O(3) and O(15) cannot be OH. (ii) These two O-atoms occur at impossibly short distances from other O atoms: O(3)–O(11) = 2.097 and O(15)–O(10) = 2.156 Å, respectively. The positions and the assignments of the O(3) and O(15) sites cannot be correct.
- (2) There are major disparities between the incident bond-valence sums and the aggregate charges at several sites in the structure reported by Rastsvetaeva *et al.* (2008b), e.g. Ti(1) receives 5.43 *vu* whereas its charge

is 4^+ ; Si(1) receives 4.52 *vu* whereas its charge is 4^+ ; Na receives 1.82 *vu* whereas its charge is 1^+ ; F receives 1.84 *vu* whereas its charge is 1^- . In particular, the incident bond-valence at Ti(1) is 5.43 *vu* whereas Ti is assigned to this site (aggregate charge 4^+), and there are no cations of sufficiently high charge present in the structure to produce an aggregate charge of 5.43^+ at this site. Either cations have been wrongly assigned to the various sites, or there are major errors in the positional coordinates of the structure reported by Rastsvetaeva *et al.* (2008b). The sum of the assigned site populations are in accord with the rather imprecise chemical formula given, indicating that there must be major errors in the positional coordinates of the structure.

- (3) For the SiO_4 tetrahedra, some bond lengths are too short: $\text{Si}(1)\text{--O}(7) = 1.49$, $\text{Si}(2)\text{--O}(5) = 1.52$ Å.

4.2. Chemical formulae

- (1) Rastsvetaeva *et al.* (2008b) give the ideal chemical formula of jinshaijiangite from Norra Kärr as $\text{BaKNaCaTi}_4\text{Fe}_6^{2+}\text{Mn}_2(\text{Si}_2\text{O}_7)_4\text{O}_2(\text{OH})_8\text{F}_2$. Above, we show that O(3) and O(15) cannot be assigned as OH and the anion at the F site cannot be F according to the incident bond-valence.
- (2) There are 40 anions in the formula of jinshaijiangite given by Rastsvetaeva *et al.* (2008b), whereas there are 38 anions in the formula of perraultite and the structure of jinshaijiangite reported in this study. The formula that they give for jinshaijiangite is not a perraultite-type formula and the structure is not isostructural with perraultite (unlike all of the data for jinshaijiangite presented here).

Rastsvetaeva *et al.* (2008b) named the mineral that they examined (i) jinshaijiangite, (ii) iron-rich variety . . . of jinshaijiangite, and (iii) a polymorph of jinshaijiangite. These expressions are all self-excluding, and none is correct, particularly as the structure reported here for jinshaijiangite from Norra Kärr is topologically and chemically compatible with the structure of perraultite reported by Yamnova *et al.* (1998). Possibly their structure is an intergrowth of two or more phases, as this type of behaviour is common in TS-block minerals (*e.g.*, Krivovichev *et al.*, 2003; Sokolova & Hawthorne, 2004, 2008a and b).

5. Possible Group-II structures with two types of I block

In bafertisite (Guan *et al.*, 1963), ideally $\text{Ba}_2\text{Ti}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_4$, and perraultite (Yamnova *et al.*, 1998), ideally $\text{BaNaTi}_2\text{Mn}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}$, the topology of the TS block is identical (Sokolova, 2006). In bafertisite, the TS blocks do not link directly but alternate with I blocks composed of Ba atoms. Yamnova *et al.*

(1998) pointed out the difference in the I block compositions of perraultite and bafertisite, (BaNa) and Ba_2 , respectively. Pekov *et al.* (1999) suggested combination of four minerals, bafertisite, hejtmanite, ideally $\text{Ba}_2\text{Ti}_2\text{Mn}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_4$ (Rastsvetaeva *et al.*, 1991), perraultite and jinshaijiangite, into a “bafertisite-family”, and proposed two possible solid-solution series between Fe^{2+} and Mn^{2+} end-members of the same topology: bafertisite-hejtmanite and jinshaijiangite-perraultite. Obviously, both series display homovalent isomorphism at the cation sites of the O sheet: $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$.

Jinshaijiangite, $\text{BaNaTi}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_4\text{F}$, and bafertisite, $\text{BaTi}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_4$, have (1) a TS block ideally of the same topology and chemical composition, $\text{Ti}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, and (2) different I blocks, BaNa and Ba_2 . The identical nature of the TS blocks and the similarity of the I blocks in jinshaijiangite and bafertisite suggest the possibility of forming atomic and/or nanoscale intergrowths of these two structures. The common presence of intergrowths in these minerals emphasizes the reality of this suggestion and leads us to predict the existence of structures with a TS block of the form $[\text{Ti}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2]$ and two I blocks of the types found in jinshaijiangite and bafertisite.

6. Summary

The average structure of jinshaijiangite, ideally $\text{BaNaTi}_2\text{Fe}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}$, is monoclinic, sp. gr. $C2/m$. Jinshaijiangite is a Fe^{2+} analogue of perraultite, ideally $\text{BaNaTi}_2\text{Mn}_4^{2+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\text{F}$, and its crystal structure is topologically identical to that of perraultite (Yamnova *et al.*, 1998).

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