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FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION. XXIX. REVISION OF THE CRYSTAL STRUCTURE OF PERRAULTITE, $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, A SEIDOZERITE-SUPERGROUP TS-BLOCK MINERAL FROM THE OKTYABR'SKII MASSIF, UKRAINE, AND DISCREDITATION OF SURKHOBITE

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Abstract

The crystal structure of perraultite from the Oktyabr'skii massif, Donetsk region, Ukraine (bafertisite group, seidozerite supergroup), ideally $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, $Z = 4$, was refined in space group $C\bar{1}$ to $R_1 = 2.08\%$ on the basis of 4839 unique reflections [$F_o > 4\sigma F_o$]; $a = 10.741(6)$, $b = 13.841(8)$, $c = 11.079(6)$ Å, $\alpha = 108.174(6)$, $\beta = 99.186(6)$, $\gamma = 89.99(1)°$, $V = 1542.7(2.7)$ Å^3. Refinement was done using data from a crystal with three twin domains which was part of a grain used for electron probe microanalysis. In the perraultite structure [structure type B1(BG), B – basic, BG – bafertisite group], there is one type of TS (Titanium-Silicate) block and one type of **I** (Intermediate) block; they alternate along **c**. The TS block consists of HOH sheets (H – heteropolyhedral, O – octahedral). In the O sheet, the ideal composition of the five $^{[6]}M^O$ sites is Mn_4 *apfu*. There is no order of Mn and Fe^{2+} in the O sheet. The M^H octahedra and Si_2O_7 groups constitute the H sheet. The ideal composition of the two $^{[6]}M^H$ sites is Ti_2 *apfu*. The TS blocks link *via* common vertices of M^H octahedra. The **I** block contains $A^P(1,2)$ and $B^P(1,2)$ cation sites. The $A^P(1)$ site is occupied by Ba and the $A^P(2)$ site by K > Ba; the ideal composition of the $A^P(1,2)$ sites is Ba *apfu*. The $B^P(1)$ and $B^P(2)$ sites are each occupied by Na > Ca; the ideal composition of the $B^P(1,2)$ sites is Na *apfu*. We compare perraultite and surkhobite based on the work of Sokolova *et al*. (2020) on the holotype sample of surkhobite: space group $C\bar{1}$, $R_1 = 2.85$ %, $a = 10.728(6)$, $b = 13.845(8)$, $c = 11.072(6)$ Å, $\alpha = 108.185(6)$, $\beta = 99.219(5)$, $\gamma = 90.001(8)°$, $V = 1540.0(2.5)$ Å^3; new EPMA data. We show that (1) perraultite and surkhobite have identical chemical composition and ideal formula $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$; (2) perraultite and surkhobite are isostructural, with no order of Na and Ca at the $B^P(1,2)$ sites. Perraultite was described in 1991 and has precedence over surkhobite, which was redefined as "a Ca-ordered analogue of perraultite" in 2008. Surkhobite is not a valid mineral species and its discreditation was approved by CNMNC IMA (IMA 20-A).

Keywords: perraultite, bafertisite group, seidozerite supergroup, TS block, crystal-structure refinement, electron probe microanalysis, discreditation of surkhobite.

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INTRODUCTION

Jinshajiangite, ideally $NaBaFe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F$; perraultite, ideally $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$; bobshannonite, ideally $Na_2KBa(Mn_7Na)Nb_4(Si_2O_7)_4O_4(OH)_4O_2$; and surkhobite, $KBa_3Ca_2Na_2Mn_{16}Ti_8(Si_2O_7)_8O_8(OH)_4(F,O,OH)_8$ (current IMA formula) are isostructural bafertisite-group minerals of the seidozerite supergroup of TS-block minerals (Memorandum 56-SM/16; Sokolova & Cámara 2017). The ideal formulae of perraultite and jinshajiangite are in accord with the current nomenclature of the seidozerite supergroup (Sokolova & Cámara 2017); the ideal formula of bobshannonite (revised) is in accord with Sokolova *et al*. (2020). Jinshajiangite, surkhobite, and bobshannonite belong to the structure type of perraultite (Yamnova *et al*. 1998) and we call them perraultite-type minerals. The main structural unit of the perraultite-type minerals is a TS-block which consists of HOH sheets (H = heteropolyhedral, O = octahedral) and is characterized by a planar cell based on translation vectors, $\mathbf{t_1}$ and $\mathbf{t_2}$, with $t_1 \sim 5.5$ and $t_2 \sim 7$ Å and $t_1 \wedge t_2$ close to 90°. The seidozerite-supergroup minerals are divided into four groups based on the Ti content (+ Nb + Zr + Fe^{3+} + Mg + Mn), topology, chemical composition, and stereochemistry of the TS block (Sokolova 2006, 2010, Sokolova & Cámara 2013, Sokolova & Cámara 2017). In the bafertisite group, Ti (+ Nb) = 2 *apfu* (atoms per formula unit). A TS-block structure is composed either solely of TS blocks or it is an alteration of TS blocks and **I** (Intermediate) blocks which consist of alkali and alkaline-earth cations, H_2O groups, and oxyanions $(PO_4)^{3-}$, $(SO_4)^{2-}$, and $(CO_3)^{2-}$. Sokolova & Cámara (2013) introduced the concept of *basic* and *derivative structures* for TS-block minerals. A *basic structure* has the following four characteristics: (1) there is only one type of TS block; (2) the two H sheets of the TS block are identical; (3) there is only one type of **I** block or it is absent; (4) there is only one type of self-linkage of TS blocks. *Basic structures* obey the general structural principles 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*.

Basic structures of the perraultite-type minerals are characterized by doubled t_1 and t_2 unit-cell parameters: structure type B1(BG) (B – basic, BG – bafertisite group) in accord with Sokolova & Cámara (2013).

Jinshajiangite from the Jinshajiang River, Sichuan Province, China, was described by Hong & Fu (1982). Perraultite from Mont Saint-Hilaire, Québec, Canada, was described by Chao (1991). Yamnova *et al*. (1998) solved the crystal structure of perraultite from the Oktyabr'skii (formerly Mariupol'skii) massif, Donetsk region, Ukraine (Table 1). A description of perraultite from the Oktyabr'skii massif was given by Pekov *et al*. (1999). Bobshannonite from Mont Saint-Hilaire, Québec, Canada, was described by Sokolova *et al*. (2015). The detailed history of the investigation of these minerals is given in Sokolova *et al*. (2020).

Surkhobite was described from the Darai-Pioz Massif, Tajikistan, by Eskova *et al*. (2003) (IMA 2002-037) as a Ca-analogue of jinshajiangite ($Fe^{2+} >$ Mn in the O sheet, Na > Ca in the **I** block) and its structure was refined by Rozenberg *et al*. (2003), who used the atom coordinates of perraultite from Yamnova *et al*. (1998). Surkhobite was discredited (IMA 06-E) as EPMA analysis of the holotype sample showed Na > Ca in the **I** block. Surkhobite was subsequently revalidated (IMA 07-A) and redefined as a Ca-ordered analogue of perraultite (Mn > Fe^{2+} in the O sheet, Na > Ca) with a new formula $(Ba,K)_2CaNa(Mn,Fe^{2+},Fe^{3+})_8Ti_4(Si_2O_7)_4O_4(F,OH,O)_6$, $Z = 4$ and a simplified formula $KBa_3Ca_2Na_2Mn_{16}Ti_8(Si_2O_7)_8O_8(OH)_4(F,O,OH)_8$, $Z = 2$ (Table 1) (for details, see Rastsvetaeva *et al*. 2008). However, the structure refinement on which the Ca ordering was based ignored the pervasive twinning that Jin *et al*. (2018) and Sokolova *et al*. (2020) showed is always present in these minerals.

Jin *et al*. (2018) studied jinshajiangite from the type locality, Jinshajiang River, Sichuan Province, China, by TEM (Transmission Electron Microscopy) and refined its crystal structure in space group $P\bar{1}$, with $c \sim 11$ Å compared to $c \sim 21$ Å in previous refinements of jinshajiangite. Based on the TEM data and precession photographs, Jin *et al*. (2018) reported four types of twinning for the crystal structure of jinshajiangite and suggested that (1) all minerals with the perraultite-type structure, jinshajiangite itself plus perraultite, surkhobite, and bobshannonite, should have the same $P\bar{1}$ structure as jinshajiangite with ~10 Å d_{001} spacing, *i.e*., with the $c \sim 11$ Å instead of the previously reported $c \sim 21$ Å, and (2) all previously proposed monoclinic space groups were pseudosymmetry generated by nanoscale polysynthetic twinning on the (001) composition plane.

Jin *et al*. (2018) refined the crystal structure of jinshajiangite using the (Niggli) reduced unit cell (space group $P\bar{1}$) based on the two diagonals of the planar cell that has translation vectors $\mathbf{t_1}$ and $\mathbf{t_2}$: $\mathbf{a}_{\text{jin}} = -\mathbf{t_1} - \mathbf{t_2}$ and $\mathbf{b}_{\text{jin}} = -\mathbf{t_1} + \mathbf{t_2}$, whereas the 50 TS-block minerals of the seidozerite supergroup have planar unit

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TABLE 1. STRUCTURAL DATA FOR PERRAULTITE AND SURKHOBITE (STRUCTURE TYPE B1BG)*

	Ideal structural formula**								*a* (Å) α(°)	*b* (Å) β(°)	*c* (Å) γ(°)	*V* (Å^3)	Sp. gr.	*Z*	R_1 (%)	Ref.
Mineral	A^P	B^P	$M^O{}_4$	$M^H{}_2$	$(Si_2O_7)_2$	$(X^O{}_M)_2$	$(X^O{}_A)_2$	$X^P{}_M$								
									Monoclinic							
Perraultite	Ba	Na	Mn_4	Ti_2	$(Si_2O_7)_2$	O_2	$(OH)_2$	F	10.731	13.841	20.845	3084.0	$C2$	8	6.2	(1)
									90	95.06	90					
Surkhobite	K Ba_3	Ca_2 Na_2	Mn_{16}	Ti_8	$(Si_2O_7)_8$	O_8	$F_6(OH)_2$	$F_2(OH)_2$	10.723	13.826	20.791	3071.0	$C2$	2	4.3	(2)
									90	95.00	90					
									Triclinic***							
Perraultite	Ba	Na	Mn_4	Ti_2	$(Si_2O_7)_2$	O_2	$(OH)_2$	F	10.741	13.841	11.079	1542.7	$C\bar{1}$	4	2.08	(3)
									108.174	99.186	89.99					
									8.760	8.760	11.079	771.4	$P\bar{1}$	2	1.98	
									81.467	110.130	104.366					
Surkhobite	Ba	Na	Mn_4	Ti_2	$(Si_2O_7)_2$	O_2	$(OH)_2$	F	10.728	13.845	11.072	1540.0	$C\bar{1}$	4	2.85	(4)
									108.185	99.219	90.001					
									8.756	8.756	11.070	769.7	$P\bar{1}$	2	2.87	
									81.458	110.171	104.46					
Jinshajiangite	Ba	Na	$Fe^{2+}{}_4$	Ti_2	$(Si_2O_7)_2$	O_2	$(OH)_2$	F	10.720	13.823	11.044	1532.0	$C\bar{1}$	4	2.73	(4)
									108.222	99.28	89.989					
									8.744	8.743	11.039	765.0	$P\bar{1}$	2	2.69	
									81.46	110.26	104.44					
Bobshannonite	Ba K	Na_2	(Mn_7Na)	Nb_4	$(Si_2O_7)_4$	O_4	$(OH)_4$	O_2	10.831	13.903	11.149	1572.6	$C\bar{1}$	2	2.02	(4)
									108.145	99.215	90.007					
									8.812	8.813	11.149	786.3	$P\bar{1}$	1	2.03	
									81.532	110.127	104.158					

* Structure type (B1BG: B – basic, BG – bafertisite group); ideal structural formula for perraultite is in accord with Sokolova & Cámara (2017);
Surkhobite (2) has a "crystallochemicall formula"; formulae are per $(Si_2O_7)_2$, except for surkhobite (2): per $(Si_2O_7)_8$ and bobshannonite: per $(Si_2O_7)_8$.

** Atoms' labelling: M^H = cations of the H sheet, M^O = cations of the O sheet, A^P and B^P = cations at the peripheral (*P*) sites;
$X^O{}_M$ = common anions for three M^O octahedra of the O sheet and one M^H octahedron of the H sheet; $X^O{}_A$ = common anions for three M^O octahedra of the O sheet; $X^P{}_M$ = bridging anion between two M^H octahedra (Sokolova 2006).

*** The second line reports a reduced cell.

References (the most recent structure work): (1) Yamnova *et al.* (1998); (2) Rastsvetaeva *et al.* (2008); (3) this work; (4) Sokolova *et al.* (2020).

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cells based on translation vectors $\mathbf{t_1}$ and $\mathbf{t_2}$. Following the work of Jin *et al.* (2018), Sokolova *et al.* (2020) refined the crystal structures of jinshajiangite, surkhobite (holotype), and bobshannonite (holotype) using two unit cells: (a) the (Niggli) reduced unit cell, space group $P\bar{1}$, $c \sim 11$ Å, and (b) an unconventional unit cell, space group $C\bar{1}$, $c \sim 11$ Å, to make comparison to the TS-block structures more straightforward. The triclinic $C\bar{1}$ unit cell with $c \sim 21$ Å, previously used for jinshajiangite (Cámara *et al.* 2016) and bobshannonite (Sokolova *et al.* 2015), and the triclinic $C\bar{1}$ unit cell with $c \sim 11$ Å are related by the transformation matrix (–100 0–10 ¼ ¼ ½).

Recently, we obtained a sample of perraultite from the Oktyabr'skii massif, from which Yamnova *et al.* (1998) solved the crystal structure of perraultite (Table 1) and to which Rastsvetaeva *et al.* (2008) related the crystal structure of surkhobite as a Ca-ordered analogue of perraultite. Here we report chemical composition and crystal-structure refinement of perraultite from the Oktyabr'skii massif. Details of the chemical composition and structure-refinement results for perraultite from the Oktyabr'skii massif are given in comparison with analogous data for holotype surkhobite (Fersman Mineralogical Museum, Moscow, Russia, registration # 2882/1) which are taken from Sokolova *et al.* (2020).

Chemical Composition of Perraultite

Electron probe microanalysis

Electron probe microanalysis was done on a crystal of perraultite from the Oktyabr'skii massif; part of this crystal was then used for the X-ray single-crystal data collection and crystal-structure refinement. The crystal of perraultite was analyzed with a Cameca SX-100 electron-microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μm, and count times on peak and background of 20 and 10 s, except for F, for which count times of 30 and 15 s on peak and background were used. The following standards and crystals were used for *K* or *L* X-ray lines: F: fluoro-riebeckite; Na: albite; Ba: benitoite; Si, Ca: diopside; Fe: fayalite; Mg: forsterite; Mn: spessartine; K: orthoclase; Ti: titanite; Zr: zircon; Ta: $Mn(Ta_{1.70}Nb_{0.30})O_6$; Zn: gahnite; Nb: $Ba_2NaNb_5O_{15}$; Sr: $SrTiO_3$; Al: andalusite; Cs: pollucite. Data were reduced using the φ(ρZ) procedure of Pouchou & Pichoir (1985). Strontium, Cs, and Pb were sought but not detected. The chemical composition of perraultite is given in Table 2 [analysis (3)] and is the mean of nine determinations. Table 2 also reports analyses of perraultite from Mont St. Hilaire, Canada [(1), Chao 1991] and from Oktyabr'skii massif, Ukraine [(2), Pekov *et al.* 1999]. Analyses (2) and (3) are accompanied by structure work from Yamnova *et al.* (1998) and this work, respectively. Analyses (2) and (3) are very close in oxide values, as they are from specimens of perraultite from the same locality, Oktyabr'skii massif; hence in this paper, we used the wet-chemistry results of Pekov *et al.* (1999) for the assignment of the Fe^{2+}/Fe^{3+} ratio in our analysis (3). The amount of H_2O was calculated from structure-topology requirements, (OH) + F = 3 *apfu*. Table 2 [analysis (3)] gives the empirical formula of perraultite based on 19 (O + F) anions: $(Na_{0.71}Ca_{0.28}\square_{0.01})_{\Sigma1}(Ba_{0.58}K_{0.41}Rb_{0.03})_{\Sigma1.02}(Mn_{2.52}Fe^{2+}{}_{1.20}Fe^{3+}{}_{0.08}Zn_{0.08}Mg_{0.04}Al_{0.02}Zr_{0.02}\square_{0.04})_{\Sigma4}(Ti_{1.84}Nb_{0.16}Ta_{0.01})_{\Sigma2.01}(Si_{3.97}O_{14})O_2[(OH)_{1.69}F_{0.31}]_{\Sigma2}F$, $Z = 4$. Further in the paper, we will refer to Fe^{2+} and Fe^{3+} and we will use Mn instead of Mn^{2+}, as only divalent Mn has been reported so far for TS-block minerals of the seidozerite supergroup.

Analyses (4) and (5) for holotype surkhobite are taken from the literature (they are accompanied by structure-refinement results, see below). For holotype surkhobite, analyses (4) of Rastsvetaeva *et al.* (2008) and (5) of Sokolova *et al.* (2020) are in close agreement, which is not surprising as they are from parts of the same crystal. The empirical formulae for holotype surkhobite [analyses (4) and (5)] were calculated on 19 (O + F) anions: (4) $(Na_{0.65}Ca_{0.40})_{\Sigma1.05}(Ba_{0.65}K_{0.35}Sr_{0.02})_{\Sigma1.02}(Mn_{2.04}Fe^{2+}{}_{1.72}Fe^{3+}{}_{0.24})_{\Sigma4}(Ti_{1.79}Nb_{0.14}Mg_{0.03}Zr_{0.02}\square_{0.02})_{\Sigma2}(Si_{4.01}O_{14})O_2[(OH)_{1.15}O_{0.48}F_{0.37}]_{\Sigma2}F$ and (5) $(Na_{0.59}Ca_{0.39}\square_{0.02})_{\Sigma1}(Ba_{0.59}K_{0.38}Cs_{0.02}Sr_{0.01})_{\Sigma1}(Mn_{1.83}Fe^{2+}{}_{1.77}Fe^{3+}{}_{0.24}Mg_{0.03}Al_{0.03}\square_{0.10})_{\Sigma4}(Ti_{1.82}Nb_{0.10}Zr_{0.08})_{\Sigma2}(Si_{3.97}O_{14})O_2[(OH)_{1.79}F_{0.21}]_{\Sigma2}F$, Z = 4.

Crystal Structure of Perraultite

Experimental details

Data collection. Single-crystal X-ray data for perraultite were collected using a Bruker APEX II ULTRA three circle diffractometer equipped with a rotating anode generator (Mo*K*α), multilayer optics, and an APEX II 4K CCD detector. The intensities of reflections were collected with a frame width of 0.2° and a frame time of 1 s. Unit-cell parameters of perraultite were determined using 9831 reflections ($I > 10\sigma I$). In this work, we integrated single-crystal X-ray data on two triclinic unit cells: (a) the (Niggli) reduced unit cell, space group $P\bar{1}$, $c \sim 11$ Å, and (b) an unconventional unit cell, space group $C\bar{1}$, $c \sim 11$ Å (Table 3). An empirical absorption correction for twinned crystals (TWINABS, Sheldrick 2015) was applied. CELL_NOW – Version 2008_2 (Sheldrick 2015) was used to obtain HKLF 5 files.

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TABLE 2. CHEMICAL ANALYSES* (wt.%) AND FORMULA UNITS (*apfu*) FOR PERRAULTITE AND SURKHOBITE

	Perraultite			Surkhobite	
	(1)	(2)	(3)	(4)	(5)
Locality	Mont Saint-Hilaire, Canada Holotype	Oktyabr'skii massif, Ukraine		Darai-Pioz Massif, Tajikistan Holotype	Holotype
Oxide					
Ta_2O_5	n.a.	0.11	0.17	n.d.	n.d.
Nb_2O_5	13.35	1.24	2.47	2.14	1.45
ZrO_2	0.12	1.09	0.33	0.34	1.19
TiO_2	9.44	17.83	16.96	16.14	16.73
SiO_2	27.32	27.72	27.44	27.17	27.40
Al_2O_3	0.03	0.03	0.10	0.02	0.16
Fe_2O_3**	n.a.	0.75	0.71	2.11	2.20
FeO	1.12	12.06	9.94	13.92	14.63
BaO	8.88	10.64	10.30	11.16	10.41
SrO	n.a.	0.05	n.d.	0.26	0.21
ZnO	n.a.	1.02	0.72	n.d.	n.d.
MnO	31.14	19.28	20.56	16.32	14.96
CaO	n.d.	1.48.	1.78	2.53	2.48
MgO	0.06	0.04	0.20	0.13	0.13
Cs_2O	n.a.	n.d	n.d.	n.d	0.28
Rb_2O	n.a.	n.a.	0.30	n.a.	n.d.
K_2O	2.68	1.67	2.23	1.87	2.03
Na_2O	3.52	2.76	2.53	2.27	2.10
F	0.84	2.18	2.86	2.94	2.65
H_2O***	3.49	1.79	1.76	1.17	1.85
O=F	–0.35	–0.92	–1.20	–1.24	–1.12
Total	101.64	99.80	100.15	99.25	99.74
Formula unit calculated on the basis of 19 (O + F)					
Ta			0.01		
Nb	0.86	0.08	0.16	0.14	0.10
Zr	0.01	0.08	0.02	0.02	0.08
Ti	1.01	1.94	1.84	1.79	1.82
Si	3.90	4.02	3.97	4.01	3.97
Fe^{3+}		0.08	0.08	0.24	0.24
Al	0.01	0.01	0.02		0.03
Ba	0.50	0.60	0.58	0.65	0.59
Sr				0.02	0.02
Zn			0.08		
Fe^{2+}	0.13	1.46	1.20	1.72	1.77
Mn	3.77	2.37	2.52	2.04	1.83
Ca		0.23	0.28	0.40	0.39
Mg	0.01	0.01	0.04	0.03	0.03
Cs					0.02
Rb			0.03		
K	0.49	0.31	0.41	0.35	0.38
Na	0.97	0.78	0.71	0.65	0.59
F	0.38	1.00	1.31	1.37	1.21
OH	0.68	1.73	1.69	1.15	1.79
H_2O	1.32				
ΣCat	11.66	11.97	11.95	12.06	11.84

* Electron probe microanalysis; ** Fe^{2+}/Fe^{3+}: (2) wet chemistry; (3) assigned in accord with (2); (4) Mössbauer spectroscopy; (5) assigned in accord with (4); *** H_2O: (1) TGA; (2, 4) Penfield method; (3, 5) calculated in accord with required number of monovalent anions: OH + F = 3 *pfu*; Abbreviations: n.a. = not analyzed; n.d. = not detected. References: (1) Chao (1991); (2) Pekov *et al.* (1999); (3) this work; (4) Rastsvetaeva *et al.* (2008); (5) Sokolova *et al.* (2020).

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TABLE 3. MISCELLANEOUS STRUCTURE-REFINEMENT DATA* FOR PERRAULTITE AND SURKHOBITE

	Perraultite This work		Surkhobite Sokolova *et al.* (2020)		Perraultite Yamnova *et al.* (1998)	Surkhobite Rastsvetaeva *et al.* (2008)
Crystal system	Triclinic		Triclinic		Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C\bar{1}$	$P\bar{1}$	$C\bar{1}$	$C2$	$C2$
a (Å)	8.760(6)	10.741(6)	8.756(5)	10.728(6)	10.731(2)	10.723(1)
b (Å)	8.760(5)	13.841(8)	8.756(5)	13.845(8)	13.841(4)	13.826(2)
c (Å)	11.079(7)	11.079(6)	11.070(6)	11.072(6)	20.845(6)	20.791(4)
α (°)	81.467(5)	108.174(6)	81.458(5)	108.185(6)	90	90
β (°)	110.130(5)	99.186(6)	110.171(5)	99.219(5)	95.06(2)	95.00(1)
γ (°)	104.366(6)	89.99(1)	104.46(1)	90.001(8)	90	90
V (Å^3)	771.4(1.4)	1542.7(2.7)	769.7(1.3)	1540.0(2.5)	3084(1)	3071
Z	2	4	2	4	8	8
Absorption coefficient (mm^{-1})	6.60	6.60	6.60	6.60		
F(000)	826.7	1671.2	826.5	1653.1		
$D_{calc.}$ (g/cm^3)	3.747	3.747	3.750	3.749	3.670	3.980
Crystal description	Reddish-orange prismatic		Brownish-red prismatic		Yellowish-orange to brownish-red	Brownish-red
Crystal size (mm)	0.120 × 0.100 × 0.020		0.140 × 0.100 × 0.025		0.40 × 0.25 × 0.10	0.40 × 0.20 × 0.20
Instrument	Bruker APEX II ULTRA		Bruker APEX II ULTRA		$P\bar{1}$ Syntex	Enraf Nonius
$2\theta_{max}$ (°)	62.18	62.30	50.00**	50.00**	109.60	78.11
No. of measured***,	9088		7343			
independent and	4957	4993	2718	2719	3452	3686
observed [F_o $> 4\sigma F$] reflections	4818	4839	2651	2657		
R_σ (%)	1.32	1.41	1.75	1.99		
Indices range						
h_{min}, h_{max}	–12, 11	–15, 15	–10, 9	–12, 12		–17, 17
k_{min}, k_{max}	–12, 12	–20, 19	–10, 10	–16, 15		–22, 22
l_{min}, l_{max}	0, 16	0, 16	0, 13	0, 13		0, 33
Frame width (°), time (s)	0.2, 1		0.3, 2			
No. and fraction (%)	3	3	2	2		
of twin domains	76.7(3)	76.2(3)	65.4(2)	65.7(2)		
	22.1(3)	22.2(3)	34.6(2)	34.3(1)		
	1.2(2)	1.6(1)				
Absorption correction****	TWINABS		TWINABS		DIFABS	DIFABS
Final R_{obs} (%)						
$R_1[F_o > 4\sigma F]$, R_1(all)	1.98, 2.07	2.08, 2.20	2.87, 2.90	2.85, 2.88	6.2	4.3
wR_2	6.56	6.94	8.14	8.01		
Goodness of fit on F^2	1.171	1.190	1.132	1.024		
No. refined parameters	311	311	311	311		
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e^- Å^{-3})	1.57, –1.42	1.30, –1.52	1.32, –1.04	1.34, –1.09		

* Radiation/monochromator: Mo$K\alpha$/ graphite; ** structure refinement; *** HKLF 5; **** TWINABS – Version 2008/2 (Sheldrick 2015).

Structure refinement. The crystal structure of perraultite was refined with the Bruker SHELXTL-2014/3 (version 3) system of programs (Sheldrick 2015) in space group $P\bar{1}$ using the atom coordinates of Jin *et al*. (2018) and in space group $C\bar{1}$ [for both $P\bar{1}$ and $C\bar{1}$ structure-refinements, coordinates of the H(1) and H(2) atoms were taken from the difference-Fourier map and included in the refinement] (Table 4). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992). To go from the $P\bar{1}$ unit-cell to the $C\bar{1}$ unit cell, we used the following transformation matrix: (–1–10 –110 00–1). The crystal-structure refinement was done using a crystal with three twin domains. The twin

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TABLE 4. ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR PERRAULTITE, SPACE GROUP $C\bar{1}$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
$M^O(1)$	0	0	½	0.0062(3)	0.0075(3)	0.0112(3)	0.00343(19)	0.00093(17)	0.00007(18)	0.00825(17)
$M^O(2)$	½	0	½	0.0074(3)	0.0256(4)	0.0231(3)	0.0184(3)	–0.0048(2)	–0.0055(2)	0.0171(2)
$M^O(3)$	0.24838(3)	0.87343(3)	0.48770(3)	0.00648(16)	0.00740(18)	0.00921(16)	0.00235(15)	0.00131(10)	0.00076(14)	0.00776(11)
$M^O(4)$	0.74689(3)	0.87093(3)	0.49025(3)	0.00686(16)	0.00750(18)	0.00922(16)	0.00262(15)	0.00146(10)	0.00032(15)	0.00785(11)
$M^O(5)$	0.49753(3)	0.74723(3)	0.49547(3)	0.0065(2)	0.0085(2)	0.0138(2)	0.00171(16)	–0.00019(14)	0.00114(15)	0.01020(14)
$M^H(1)$	0.53378(3)	0.31997(3)	0.20268(3)	0.00493(16)	0.00531(19)	0.00683(17)	0.00221(12)	0.00149(11)	0.00067(11)	0.00556(11)
$M^H(2)$	0.53351(3)	0.78119(3)	0.20066(3)	0.00489(16)	0.00507(19)	0.00723(17)	0.00196(12)	0.00157(11)	0.00067(11)	0.00566(11)
Si(1)	0.77783(6)	0.95008(5)	0.23880(6)	0.0057(3)	0.0052(3)	0.0067(3)	0.0014(2)	0.0015(2)	0.0005(2)	0.00590(12)
Si(2)	0.30102(6)	0.95095(5)	0.23684(6)	0.0057(3)	0.0053(3)	0.0069(3)	0.0016(2)	0.0014(2)	0.0008(2)	0.00599(13)
Si(3)	0.77813(6)	0.16840(5)	0.23814(6)	0.0058(3)	0.0052(3)	0.0064(3)	0.0018(2)	0.0016(2)	0.0010(2)	0.00574(12)
Si(4)	0.30023(6)	0.16904(5)	0.23767(6)	0.0056(3)	0.0055(3)	0.0066(3)	0.0020(2)	0.0013(2)	0.0004(2)	0.00586(12)
$A^P(1)$	0	0	0	0.01113(9)	0.01074(10)	0.00989(9)	0.00272(8)	0.00199(6)	0.00082(8)	0.01068(6)
$A^P(2)$	0.49963(11)	0.03578(10)	0.00007(12)	0.0147(4)	0.0561(7)	0.0187(4)	0.0072(6)	0.0038(3)	0.0008(5)	0.0308(3)
$B^P(1)$	¼	¼	0	0.0195(6)	0.0151(6)	0.0032(5)	0.0011(5)	0.0018(4)	0.0118(5)	0.0130(3)
$B^P(2)$	¾	¼	0	0.0184(6)	0.0130(6)	0.0033(4)	0.0008(5)	0.0007(3)	–0.0089(5)	0.0121(3)
O(1)	0.90437(16)	0.91856(14)	0.17663(17)	0.0091(7)	0.0119(8)	0.0138(8)	0.0061(6)	0.0058(6)	0.0049(6)	0.0107(3)
O(2)	0.15495(16)	0.91749(14)	0.17383(17)	0.0074(7)	0.0120(8)	0.0140(8)	0.0066(6)	0.0001(6)	–0.0016(6)	0.0107(3)
O(3)	0.66365(16)	0.22114(13)	0.17299(16)	0.0091(7)	0.0108(8)	0.0118(7)	0.0058(6)	0.0027(6)	0.0044(6)	0.0100(3)
O(4)	0.39438(16)	0.22217(14)	0.17394(16)	0.0094(7)	0.0114(8)	0.0114(7)	0.0057(6)	0.0026(6)	–0.0012(6)	0.0102(3)
O(5)	0.66352(16)	0.86496(13)	0.17115(16)	0.0094(7)	0.0076(7)	0.0110(7)	0.0014(6)	0.0022(6)	–0.0025(6)	0.0097(3)
O(6)	0.39450(16)	0.86586(13)	0.17199(16)	0.0089(7)	0.0078(7)	0.0115(7)	0.0014(6)	0.0021(6)	0.0038(6)	0.0097(3)
O(7)	0.40305(16)	0.66962(13)	0.17398(17)	0.0096(7)	0.0085(7)	0.0137(8)	0.0015(6)	0.0059(6)	–0.0007(6)	0.0106(3)
O(8)	0.65453(16)	0.66956(13)	0.17208(17)	0.0073(7)	0.0090(7)	0.0144(8)	0.0023(6)	–0.0003(6)	0.0019(6)	0.0108(3)
O(9)	0.72537(14)	0.05000(14)	0.20068(15)	0.0090(6)	0.0062(7)	0.0130(7)	0.0040(6)	0.0005(5)	–0.0002(6)	0.0094(3)
O(10)	0.33998(14)	0.05024(14)	0.19769(15)	0.0110(6)	0.0065(7)	0.0129(6)	0.0041(6)	0.0053(5)	0.0025(6)	0.0095(3)
O(11)	0.80699(17)	0.97656(15)	0.39455(17)	0.0091(7)	0.0090(8)	0.0073(7)	0.0016(6)	0.0008(6)	0.0006(6)	0.0088(3)
O(12)	0.32079(17)	0.97945(15)	0.39313(17)	0.0099(7)	0.0099(8)	0.0075(7)	0.0020(6)	0.0010(6)	0.0003(6)	0.0093(3)
O(13)	0.30960(17)	0.71842(15)	0.39388(17)	0.0089(7)	0.0092(8)	0.0072(7)	0.0006(6)	0.0013(6)	0.0004(6)	0.0089(3)
O(14)	0.31839(17)	0.21915(15)	0.39332(17)	0.0095(7)	0.0089(8)	0.0075(7)	0.0018(6)	0.0013(6)	0.0001(6)	0.0088(3)
$X^O_M(1)$	0.56498(15)	0.35495(15)	0.37534(15)	0.0092(6)	0.0111(8)	0.0080(6)	0.0014(6)	0.0004(5)	0.0006(6)	0.0099(3)
$X^O_M(2)$	0.56385(15)	0.83178(15)	0.37291(15)	0.0093(6)	0.0134(9)	0.0082(6)	0.0031(6)	0.0005(5)	–0.0009(6)	0.0105(3)
$X^O_A(1)$	0.56402(15)	0.60170(18)	0.41054(15)	0.0118(7)	0.0123(8)	0.0095(6)	0.0028(7)	0.0014(5)	0.0006(7)	0.0114(3)
$X^O_A(2)$	0.56399(14)	0.10444(17)	0.41416(15)	0.0101(6)	0.0107(7)	0.0098(6)	0.0022(7)	0.0017(5)	0.0007(7)	0.0105(3)
X^P_M	0.50062(15)	0.27386(10)	0.00091(14)	0.0151(6)	0.0138(6)	0.0078(6)	0.0020(5)	0.0011(5)	0.0005(5)	0.0126(3)
H(1)	0.547(3)	0.585(3)	0.317(1)	0.01366(0)*						
H(2)	0.548(3)	0.083(3)	0.3205(10)	0.01254(0)*						

* U_{iso}

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matrices for three domains used in SHELX are as follows: 1 → 2 (–100/010/0 –0.5 –1), 1 → 3 (–100/0–10/0.33 0.5 1), 1 → 3 (100/0–10/–0.33 0 –1). The ratio of twin domains and other miscellaneous information on structure refinement are given in Table 3.

Site-scattering values were refined for the M^{O}(1–5) sites of the O sheet with the scattering curves of Fe, M^{H}(1,2) sites of the H sheet with the scattering curve of Ti, and peripheral sites which occur in the **I** block: A^{P}(1) site (Ba), A^{P}(2) site (K), and B^{P}(1,2) sites (Na); site labelling is in accord with Sokolova (2006). The A^{P}(2) site is disordered off the inversion center at ½00, and the two points of the A^{P}(2) site are 0.99 Å apart. Two H atoms were found in the Difference-Fourier map, and the D(donor)–H distances were softly constrained to 0.98 Å. No subsidiary peaks were found in the Difference-Fourier map. Tables 3 to 8 contain information pertinent to the structure refinement of perraultite in space group $C\bar{1}$: 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 are given in Table 7, and details of hydrogen bonding are given in Table 8. A Crystallography Information File (CIF) for perraultite (space group $C\bar{1}$) may be obtained from The Depository of Unpublished Data on the MAC website (documents perraultite CM59, 20-00066)[1].

Site-population assignment

O sheet. In perraultite, the aggregate refined scattering for the five M^{O} sites is 98.16 *epfu* (Table 6). We assign the following cations, which are available from the chemical analyses [Table 2, analysis (3)]: $Mn_{2.52}Fe^{2+}_{1.20}Fe^{3+}_{0.08}Zn_{0.08}Mg_{0.04}Al_{0.02}Zr_{0.02}$ *apfu*, with a total calculated-scattering value of 100.22 *epfu* (Table 6). The aggregate refined site-scattering value for the five M^{O} sites is in close accord with that composition. The refined site-scattering values at the five M^{O} sites vary from 24.18 to 25.10 electrons per site (normalized per one atom *pfu*). The mean bond-lengths around these sites are very similar (Tables 5 and 6), indicating disorder of cations over the five M^{O} sites.

H sheet. In TS-block minerals, the Ti- and Nb-dominant M^{H} sites are always fully occupied (Sokolova 2006, Sokolova & Cámara 2013). In perraultite, the aggregate refined scattering at these sites is 47.06 *epfu* (Table 6). For the M^{H} sites, the following cations are available from Table 2: $Ti_{1.84}Nb_{0.16}Ta_{0.01}$ *apfu*, with calculated site-scattering of 47.77 *epfu*. Hence, in accord with individual refined site-scattering values, we assign $Ti_{1.84}Nb_{0.16}$ *apfu*, with calculated site-scattering of 47.04 *epfu* to the M^{H} sites (Table 6).

***I** block*. The refined site-scattering values at the $^{[10]}A^{P}$(1) site (per one atom) and mean bond-lengths $<A^{P}(1)–\varphi>$ (where φ is an unspecified anion) are 55.82 *epfu* and 2.908 Å (Table 6), and they are consistent with the atomic number and the ionic radius of Ba ($^{[10]}r = 1.52$ Å, Shannon 1976). Therefore, we assign Ba to the A^{P}(1) site in perraultite (Table 6). The $^{[13]}A^{P}$(2) site is disordered off the inversion center at ½00, and the two points of the A^{P}(2) site are 0.99 Å apart in perraultite (Table 5). Hence, the A^{P}(2) site can only be 50% occupied. In perraultite, the refined site-scattering value at the A^{P}(2) site is 13.82 *epfu* (Table 6). The latter value is higher than can be provided by 0.39 K *apfu* available from the chemical analysis, with calculated site-scattering of 7.41 *epfu*. Therefore, we assign $(K_{0.39}Ba_{0.0.08}Rb_{0.03})_{\Sigma 0.50}$ *apfu* (calculated scattering of 13.00 *epfu*) to the A^{P}(2) site.

The refined site-scattering values for the B^{P}(1) and B^{P}(2) sites (0.5 multiplicity) are 6.68 and 6.82 *epfu*; the empirical formula gives $Na_{0.71}Ca_{0.28}$ *apfu* (see above), and we assign $(Na_{0.37}Ca_{0.13})_{\Sigma 0.50}$ and $(Na_{0.34}Ca_{0.15}\square_{0.01})_{\Sigma 0.50}$ *pfu* to these two sites, with calculated site-scattering of 6.67 and 6.74 *epfu* (Table 6). The values of U_{eq} (equivalent displacement parameters) for the B^{P}(1) and B^{P}(2) atoms are 0.013 and 0.012 Å^{2}, respectively (Table 4); mean distances are 2.624 and 2.633 Å (Tables 5 and 6). There is no order of Ca at the B^{P}(1,2) sites.

Description of the structure

Topology of the structure. The general topology of the perraultite structure is in accord with the recent work on jinshajiangite by Jin *et al*. (2018). In the perraultite structure, there is one type of TS (Titanium-Silicate) block and one type of **I** (Intermediate) block; they alternate along **c** (Fig. 1a). The TS block consists of HOH sheets (H – heteropolyhedral, O – octahedral). The topology of the TS block is as in the bafertisite group of TS-block minerals where Ti (+ Nb) = 2 *apfu*: Si_2O_7 groups link to two $(M^{O})^{2+}$ octahedra of the O sheet adjacent along $\mathbf{t_2}$. In the O sheet, there are five $^{[6]}M^{O}$ sites occupied mainly by the divalent cations Mn and Fe^{2+}. In the H sheet, two $^{[6]}M^{H}$ sites are occupied mainly by Ti (+ Nb). The M^{H} octahedra and Si_2O_7 groups constitute the H sheet (Fig. 1b). The TS blocks

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[1] Supplementary Data are available from the Depository of Unpublished Data on the MAC website (http://mineralogicalassociation.ca/), documents "Perraultite, CM59, 20-00066".

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TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN PERRAULTITE AND SURKHOBITE*, SPACE GROUP $C\bar{1}$

	Perraultite		Surkhobite	
M$^{\mathrm{O}}$(1)–X$^{\mathrm{O}}_{\mathrm{A}}$(1)a	2.127(2)	×2	2.130(5)	×2
M$^{\mathrm{O}}$(1)–O(11)b	2.182(2)	×2	2.173(4)	×2
M$^{\mathrm{O}}$(1)–X$^{\mathrm{O}}_{\mathrm{M}}$(1)a	2.237(2)	×2	2.232(4)	×2
<M$^{\mathrm{O}}$(1)–φ>	2.182		2.178	
M$^{\mathrm{O}}$(2)–O(12)b	2.062(2)	×2	2.055(4)	×2
M$^{\mathrm{O}}$(2)–X$^{\mathrm{O}}_{\mathrm{A}}$(2)	2.129(2)	×2	2.132(5)	×2
M$^{\mathrm{O}}$(2)–X$^{\mathrm{O}}_{\mathrm{M}}$(2)b	2.477(2)	×2	2.470(4)	×2
<M$^{\mathrm{O}}$(2)–φ>	2.223		2.219	
M$^{\mathrm{O}}$(3)–X$^{\mathrm{O}}_{\mathrm{A}}$(2)b	2.105(2)		2.092(3)	
M$^{\mathrm{O}}$(3)–X$^{\mathrm{O}}_{\mathrm{M}}$(1)k	2.125(2)		2.112(3)	
M$^{\mathrm{O}}$(3)–O(11)c	2.219(2)		2.212(4)	
M$^{\mathrm{O}}$(3)–O(13)	2.223(2)		2.218(4)	
M$^{\mathrm{O}}$(3)–O(13)l	2.242(2)		2.244(4)	
M$^{\mathrm{O}}$(3)–O(12)	2.253(2)		2.253(5)	
<M$^{\mathrm{O}}$(3)–φ>	2.195		2.188	
M$^{\mathrm{O}}$(4)–X$^{\mathrm{O}}_{\mathrm{A}}$(1)d	2.122(2)		2.113(3)	
M$^{\mathrm{O}}$(4)–X$^{\mathrm{O}}_{\mathrm{M}}$(2)	2.143(2)		2.133(3)	
M$^{\mathrm{O}}$(4)–O(11)	2.205(2)		2.205(5)	
M$^{\mathrm{O}}$(4)–O(14)b	2.237(2)		2.238(4)	
M$^{\mathrm{O}}$(4)–O(14)e	2.239(2)		2.232(4)	
M$^{\mathrm{O}}$(4)–O(12)c	2.262(2)		2.251(4)	
<M$^{\mathrm{O}}$(4)–φ>	2.201		2.195	
M$^{\mathrm{O}}$(5)–X$^{\mathrm{O}}_{\mathrm{A}}$(1)	2.118(2)		2.119(5)	
M$^{\mathrm{O}}$(5)–O(13)	2.120(2)		2.111(4)	
M$^{\mathrm{O}}$(5)–O(14)b	2.123(2)		2.115(4)	
M$^{\mathrm{O}}$(5)–X$^{\mathrm{O}}_{\mathrm{A}}$(2)b	2.141(2)		2.138(5)	
M$^{\mathrm{O}}$(5)–X$^{\mathrm{O}}_{\mathrm{M}}$(2)	2.241(2)		2.239(4)	
M$^{\mathrm{O}}$(5)–X$^{\mathrm{O}}_{\mathrm{M}}$(1)b	2.464(2)		2.462(4)	
<M$^{\mathrm{O}}$(5)–φ>	2.201		2.197	
M$^{\mathrm{H}}$(1)–X$^{\mathrm{O}}_{\mathrm{M}}$(1)	1.795(2)		1.803(3)	
M$^{\mathrm{H}}$(1)–O(4)	1.938(2)		1.947(3)	
M$^{\mathrm{H}}$(1)–O(3)	1.947(2)		1.951(3)	
M$^{\mathrm{H}}$(1)–O(1)a	1.999(2)		2.010(3)	
M$^{\mathrm{H}}$(1)–O(2)f	2.005(2)		2.010(3)	
M$^{\mathrm{H}}$(1)–X$^{P}_{\mathrm{M}}$	2.095(2)		2.094(3)	
<M$^{\mathrm{H}}$(1)–φ>	1.963		1.969	
M$^{\mathrm{H}}$(2)–X$^{\mathrm{O}}_{\mathrm{M}}$(2)	1.791(2)		1.794(3)	
M$^{\mathrm{H}}$(2)–O(5)	1.945(2)		1.949(3)	
M$^{\mathrm{H}}$(2)–O(6)	1.945(2)		1.948(3)	
M$^{\mathrm{H}}$(2)–O(8)	2.001(2)		1.999(3)	
M$^{\mathrm{H}}$(2)–O(7)	2.005(2)		2.007(3)	
M$^{\mathrm{H}}$(2)–(X$^{P}_{\mathrm{M}}$)g	2.093(2)		2.096(3)	
<M$^{\mathrm{H}}$(2)–φ>	1.963		1.966	
Si(1)–O(5)	1.617(2)		1.615(3)	
Si(1)–O(1)	1.620(2)		1.612(3)	
Si(1)–O(11)	1.626(2)		1.624(4)	
Si(1)–O(9)h	1.642(2)		1.635(4)	
<Si(1)–O>	1.625		1.622	
Si(2)–O(2)	1.616(2)		1.611(3)	
Si(2)–O(6)	1.617(2)		1.616(3)	
Si(2)–O(12)	1.630(2)		1.625(4)	
Si(2)–O(10)h	1.638(2)		1.635(4)	
<Si(2)–O>	1.625		1.622	
Si(3)–O(3)	1.616(2)		1.613(3)	
Si(3)–O(7)f	1.618(2)		1.611(3)	
Si(3)–O(13)f	1.625(2)		1.625(4)	
Si(3)–O(9)	1.637(2)		1.640(4)	
<Si(3)–O>	1.624		1.622	
Si(4)–O(4)	1.617(2)		1.610(3)	
Si(4)–O(8)a	1.618(2)		1.615(3)	
Si(4)–O(14)	1.625(2)		1.623(4)	
Si(4)–O(10)	1.640(2)		1.643(4)	
<Si(4)–O>	1.625		1.623	
Si(1)i–O(9)–Si(3)	134.5(1)		134.8(2)	
Si(2)i–O(10)–Si(4)	133.9(1)		133.9(2)	
<Si–O–Si>	134.2		134.4	
A^{P}(1)–O(8)a	2.846(2)	×2	2.848(3)	×2
A^{P}(1)–O(7)a	2.851(2)	×2	2.856(3)	×2
A^{P}(1)–O(2)i	2.852(2)	×2	2.854(3)	×2
A^{P}(1)–O(1)g	2.859(2)	×2	2.857(3)	×2
A^{P}(1)–(X$^{P}_{\mathrm{M}}$)a	3.133(2)	×2	3.143(3)	×2
<A^{P}(1)–φ>	2.908		2.912	
A^{P}(2)–O(10)	2.949(2)		2.969(4)	
A^{P}(2)–O(10)j	2.960(2)		2.923(4)	
A^{P}(2)–O(9)j	2.972(2)		2.929(4)	
A^{P}(2)–O(9)	2.977(2)		3.011(4)	
A^{P}(2)–O(6)g	3.015(2)		3.048(4)	
A^{P}(2)–O(5)g	3.020(2)		3.042(4)	
A^{P}(2)–O(3)	3.035(3)		3.115(5)	
A^{P}(2)–O(4)	3.039(2)		3.115(4)	
A^{P}(2)–X$^{P}_{\mathrm{M}}$	3.292(3)		3.362(3)	
A^{P}(2)–O(6)i	3.730(3)		3.695(4)	
A^{P}(2)–O(5)i	3.743(3)		3.709(4)	
A^{P}(2)–O(3)j	3.751(3)		3.664(5)	
A^{P}(2)–O(4)j	3.764(3)		3.683(5)	
<A^{P}(2)–φ>	3.250		3.251	
A^{P}(2)–A^{P}(2)j	0.990(2)		0.841(4)	
B^{P}(1)–O(5)a	2.381(2)	×2	2.378(3)	×2
B^{P}(1)–O(4)	2.403(2)	×2	2.402(3)	×2
B^{P}(1)–X$^{P}_{\mathrm{M}}$	2.710(2)	×2	2.706(3)	×2
B^{P}(1)–O(8)a	2.806(2)	×2	2.804(4)	×2
B^{P}(1)–O(1)a	2.853(2)	×2	2.843(3)	×2
<B^{P}(1)–φ>	2.631		2.627	
B^{P}(2)–O(3)	2.396(2)	×2	2.396(3)	×2
B^{P}(2)–O(6)g	2.400(7)	×2	2.399(3)	×2
B^{P}(2)–X$^{P}_{\mathrm{M}}$	2.700(2)	×2	2.696(3)	×2
B^{P}(2)–O(2)g	2.823(7)	×2	2.815(3)	×2
B^{P}(2)–O(7)g	2.825(7)	×2	2.815(4)	×2
<B^{P}(2)–φ>	2.629		2.624	

* Data for surkhobite are from Sokolova *et al.* (2020); φ – unspecified anion: O, OH, F.

Symmetry operators: a: $x - {}^{1}/_{2}$, $y - {}^{1}/_{2}$, z; b: $-x + 1$, $-y + 1$, $-z + 1$; c: $-x + 1$, $-y + 2$, $-z + 1$; d: $-x + {}^{3}/_{2}$, $-y + {}^{3}/_{2}$, $-z + 1$; e: $x + {}^{1}/_{2}$, $y + {}^{1}/_{2}$, z; f: $x + {}^{1}/_{2}$, $y - {}^{1}/_{2}$, z; g: $-x + 1$, $-y + 1$, $-z$; h: x, $y + 1$, z; i: x, $y - 1$, z; j: $-x + 1$, $-y$, $-z$; k: $x - {}^{1}/_{2}$, $y + {}^{1}/_{2}$, z; l: $-x + {}^{1}/_{2}$, $-y + {}^{3}/_{2}$, $-z + 1$.

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TABLE 6. REFINED SITE-SCATTERING AND ASSIGNED SITE-POPULATIONS FOR PERRAULTITE, SPACE GROUP $C\bar{1}$

Site*	Refined site-scattering (*epfu*)	Assigned site-population (*pfu*)	Calculated site-scattering (*epfu*)	$<Ct–\varphi>_{obs.}$ (Å)	Ideal composition (*apfu*)
		Perraultite			
$M^O(1)$	12.09(5)			2.182	
$M^O(2)$	12.55(5)			2.223	
$M^O(3)$	24.47(6)	$Mn_{2.52}Fe^{2+}_{1.20}Fe^{3+}_{0.08}Zn_{0.08}Mg_{0.04}$		2.195	
$M^O(4)$	24.34(7)	$Al_{0.02}Zr_{0.02}\square_{0.04}$		2.201	
$M^O(5)$	24.71(8)			2.201	
ΣM^O	98.16		100.22		Mn_4
$M^H(1)$	23.51(6)	$Ti_{1.84}Nb_{0.16}$		1.963	
$M^H(2)$	23.55(6)			1.963	
ΣM^H	47.06		47.04		Ti_2
$^{[10]}A^P(1)$	27.91(5)	$Ba_{0.50}$	28.00	2.908	
$^{[13]}A^P(2)$	13.82(6)	$K_{0.39}Ba_{0.08}Rb_{0.03}\square_{0.50}$	13.00	3.250	
ΣA^P	41.73	$Ba_{0.58}K_{0.39}Rb_{0.03}$	41.00		Ba
$^{[10]}B(1)$	6.68(4)	$Na_{0.37}Ca_{0.13}$	6.67	2.631	$Na_{0.5}$
$^{[10]}B(2)$	6.82(4)	$Na_{0.34}Ca_{0.15}\square_{0.01}$	6.74	2.629	$Na_{0.5}$
ΣB	13.60	$Na_{0.71}Ca_{0.28}\square_{0.01}$	13.41		Na
$(^{[3]}X^O{}_A)_2$		$(OH)_{1.69}F_{0.31}$			$(OH)_2$
$^{[6]}X^P{}_M$		$F_{1.0}$			F
		Surkhobite, holotype (from Sokolova *et al.* 2020)			
$M^O(1)$	12.40(8)			2.178	
$M^O(2)$	12.53(9)			2.219	
$M^O(3)$	25.1(1)	$Mn_{1.83}Fe^{2+}_{1.77}Fe^{3+}_{0.24}Mg_{0.03}Al_{0.03}\square_{0.10}$		2.188	
$M^O(4)$	25.0(1)			2.195	
$M^O(5)$	25.4(2)			2.197	
ΣM^O	100.43		98.76		Mn_4
$M^H(1)$	22.9(1)	$Ti_{1.82}Nb_{0.10}Zr_{0.08}$		1.969	
$M^H(2)$	22.6(1)			1.966	
ΣM^H	45.5		47.42		Ti_2
$^{[10]}A^P(1)$	27.15(8)	$Ba_{0.49}Sr_{0.01}$	27.82	2.912	
$^{[13]}A^P(2)$	14.92(9)	$K_{0.38}Ba_{0.10}Cs_{0.02}\square_{0.50}$	13.92	3.251	
ΣA^P	42.07	$Ba_{0.59}K_{0.38}Cs_{0.02}Sr_{0.01}$	41.74		Ba
$^{[10]}B(1)$	7.12(6)	$Na_{0.30}Ca_{0.19}\square_{0.01}$	7.10	2.627	$Na_{0.5}$
$^{[10]}B(2)$	7.19(6)	$Na_{0.29}Ca_{0.20}\square_{0.01}$	7.19	2.624	$Na_{0.5}$
ΣB	14.31	$Na_{0.59}Ca_{0.39}\square_{0.02}$	14.29		Na
$(^{[3]}X^O{}_A)_2$		$(OH)_{1.79}F_{0.21}$			$(OH)_2$
$^{[6]}X^P{}_M$		$F_{1.0}$			F

* Coordination numbers are shown for non-[6]-coordinated cations and non-[4]-coordinated anions; Ct – cation; φ – unspecified anion.

link *via* common vertices of M^H octahedra, *i.e.*, M^H–$X^P{}_M$–M^H bridges. In the **I** block, there are $A^P(1)$ and $A^P(2)$ sites, occupied mainly by Ba and K, respectively, and two Na-dominant $B^P(1,2)$ sites (Fig. 1b–e).

Sokolova & Cámara (2016) described two rings of polyhedra in the H sheet of TS-block minerals with double t_1 and t_2 translations: (1) the six-membered A^P ring consists of six polyhedra: four SiO_4 tetrahedra [two Si_2O_7 groups] and two M^H octahedra, and (2) the four-membered B^P ring consists of four polyhedra: two SiO_4 tetrahedra and two M^H octahedra. In perraultite-type minerals, the six-membered $A^P(1)$ ring is shortened along $\mathbf{t}_2$ and the six-membered $A^P(2)$ ring is elongated along $\mathbf{t}_2$ (Fig. 1b). Sokolova & Cámara (2016) showed that this distortion of rings of polyhedra is necessary to satisfy bond-valence requirements at the $X^P{}_M$ anions, where $X^P{}_M$ = F, O.

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

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TABLE 7. BOND-VALENCE VALUES* FOR SELECTED ANIONS IN PERRAULTITE, SPACE GROUP $C\bar{1}$

Atom**	$M^O(1)$	$M^O(2)$	$M^O(3)$	$M^O(4)$	$M^O(5)$	$M^H(1)$	$M^H(2)$	$A^P(1)$	$A^P(2)$	$B^P(1)$	$B^P(2)$	Σ
						Perraultite						
$X^O{}_M(1)$	0.29		0.39		0.17	1.03						1.88
$X^O{}_M(2)$		0.17		0.37	0.29		1.04					1.87
$^{[3]}X^O{}_A(1)$	0.39			0.40	0.40							1.19
$^{[3]}X^O{}_A(2)$		0.39	0.41		0.38							1.18
$^{[6]}X^P{}_M$						0.33	0.33	0.11	0.06	0.09	0.09	1.01

* Bond-valence parameters (*vu*) are from Brown (1981); $M^O(1–5) = Mn$; $M^H(1,2) = Ti$; $A^P(1) = Ba$; $A^P(2) = K$; $B^P(1,2) = Na$; $^{[6]}X^P{}_M = F$; $X^O{}_M(1,2) = O$; $X^O{}_A(1,2) = OH$; ** Coordination numbers are shown for non-[4]-coordinated anions.

which occur in the **I** block. In accord with Sokolova (2006), we label the X anions as follows: $X^O{}_M$ = a common anion for three M^O and one M^H cations; $X^O{}_A$ = a common anion for three M^O cations located approximately under the A^P site; $X^P{}_M$ = an apical anion of an M^H cation at the periphery of the TS block (a bridge anion between two M^H cations) (Fig. 1a, b).

In the O sheet of perraultite, there are five Mn-dominant M^O sites (Table 6). The $M^O(1,2,5)$ atoms are coordinated by four O atoms and two monovalent $X^O{}_A$ anions, with $<M^O–\varphi> = 2.182–2.201$ Å. The $M^O(3,4)$ atoms are coordinated by five O atoms and a monovalent $X^O{}_A$ anion, with $<M^O–\varphi> = 2.195$ and 2.201 Å (Tables 5 and 6). There is no discernible order of Fe^{2+} and Mn at the $M^O(1–5)$ sites in the O sheet of perraultite. In perraultite, Mn-dominant M^O sites give ideally Mn_4 *apfu* (Table 6) (*cf.* surkhobite, Tables 5 and 6).

In the H sheets of perraultite, two Ti-dominant M^H sites are coordinated by five O atoms and an $X^P{}_M$ anion (Fig. 1a, b), with $<M^H–\varphi> = 1.963$ Å (Tables 5 and 6). The M^H sites of the two H sheets ideally give Ti_2 *apfu* (*cf.* surkhobite, Tables 5 and 6). The four tetrahedrally coordinated *Si* sites are occupied by Si, with $<Si–O> = 1.625$ Å (Table 5).

The peripheral A^P and B^P sites are shifted from the H sheets of the TS block and occur in the **I** block (Fig. 1a, b). In perraultite, the $A^P(1)$ site is fully occupied by Ba (Table 6). The $A^P(1)$ site is coordinated by eight O atoms and two F atoms ($X^P{}_M$ site), with $<A^P(1)–\varphi> = 2.908$ Å (Fig. 1c, Tables 5 and 6). As mentioned above, the $^{[13]}A^P(2)$ site is disordered off the inversion center at ½00, and the two points of the $A^P(2)$ site are 0.99 Å apart (Fig. 1b, d). In perraultite, the $A^P(2)$ site is 50% occupied by $K_{0.39}Ba_{0.08}Rb_{0.03}$ *pfu* (Table 6). The $A^P(2)$ site is coordinated by 12 O atoms and one F atom ($X^P{}_M$ site), with $<A^P(2)–\varphi> = 3.250$ Å (Fig. 1d; Tables 5 and 6). Inspection of Table 5 shows that for perraultite, there are nine short bonds $A^P(2)–\varphi = 2.949–3.292$ Å and four long bonds $A^P(2)–\varphi = 3.730–3.764$ Å. Figure 1e shows the $A^P(2)$ cage in which the four long bonds are to the right of the central $A^P(2)$ atom. The four long bonds are necessary to complete the coordination sphere of the $A^P(2)$ atom. In perraultite, the aggregate content of the two A^P sites is $Ba_{0.58}K_{0.39}Rb_{0.03}$ *apfu*, ideally Ba *apfu* ($Z = 4$) (*cf.* surkhobite, Tables 5 and 6).

In perraultite, the $B^P(1,2)$ sites are occupied by Na and Ca, where Na > Ca (Table 6). The $B^P(1,2)$ sites are coordinated by eight O atoms and two F atoms at the $X^P{}_M$ sites (Fig. 1e) with mean distances of 2.631 and 2.629 Å (Tables 5 and 6). There is no order of Na and Ca at the $B^P(1,2)$ sites in perraultite. In perraultite, the ideal composition of the $B^P(1)$ and $B^P(2)$ sites is $Na_{0.5}$ and $Na_{0.5}$ *apfu*, respectively, and the ideal composition of the $B^P(1) + B^P(2)$ sites is $Na_{1.0}$ *apfu*.

In surkhobite, the refined site-scattering values for the $B^P(1)$ and $B^P(2)$ sites are 7.12(6) and 7.19(6) *epfu*; the empirical formula gives $Na_{0.59}Ca_{0.39}$ *apfu* (see above), and Sokolova *et al.* (2020) assigned $Na_{0.30}Ca_{0.19}\square_{0.01}$ and $Na_{0.29}Ca_{0.20}\square_{0.01}$ *pfu* to these two sites, with calculated site-scattering values of 7.10 and 7.19 *epfu* (Table 6). The values of U_{eq} (equivalent displacement parameters) for the $B^P(1)$ and $B^P(2)$

TABLE 8. HYDROGEN BONDING IN PERRAULTITE, SPACE GROUP $C\bar{1}$

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠ DHA (°)
		Perraultite		
$X^O{}_A(1)OH–H(1)\cdots O(7)$	0.98(1)	2.58(3)	3.291(3)	130(3)
$X^O{}_A(1)OH–H(1)\cdots O(8)$	0.98(1)	2.66(3)	3.343(3)	128(3)
$X^O{}_A(2)OH–H(2)\cdots O(9)$	0.98(1)	2.46(3)	3.060(3)	120(2)
$X^O{}_A(2)OH–H(2)\cdots O(10)$	0.98(1)	2.38(3)	3.023(3)	123(2)

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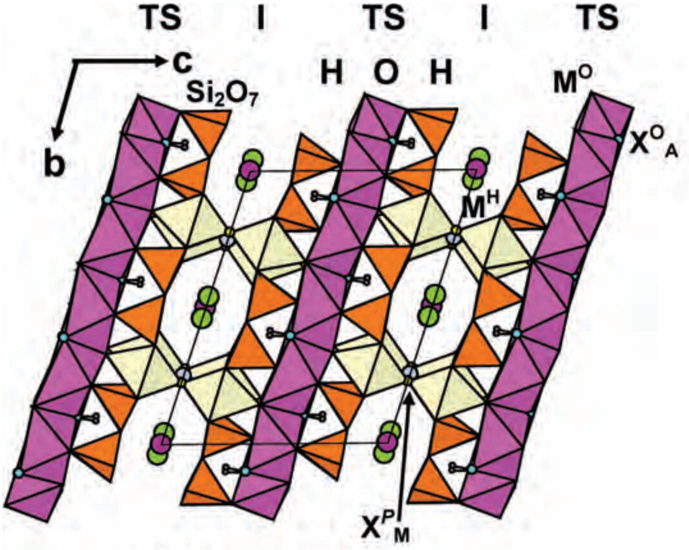
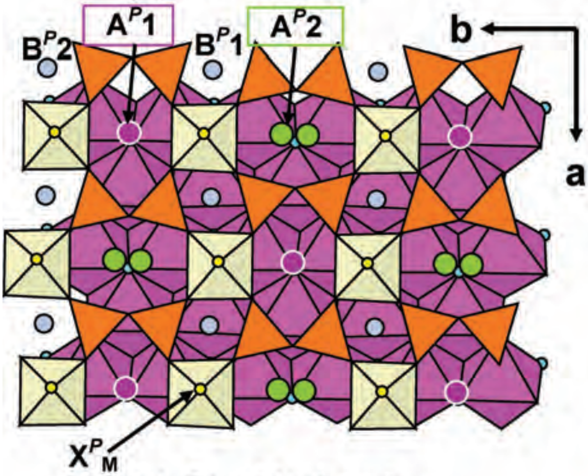
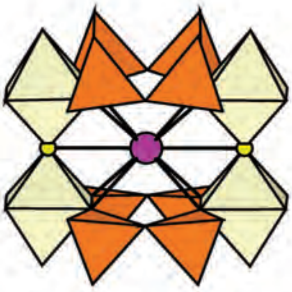


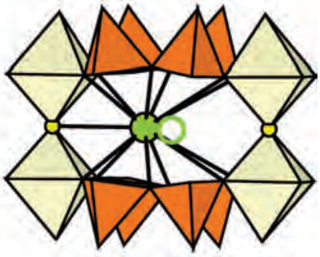
(a) Perraultite



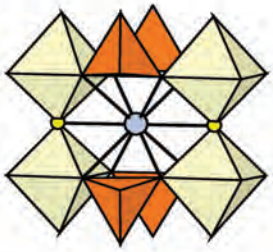
(b) O + H sheets



(c) Cage A^P1



(d) Cage A^P2



(e) Cage B^P1

FIG. 1. A general view of the crystal structure of perraultite, which consists of (a) TS and **I** blocks; (b) details of the TS block: the close-packed O sheet of Mn-dominant M^O octahedra and the H sheet of Ti-dominant M^H octahedra and Si_2O_7 groups with the **I** block of Ba, K, and Na atoms at the $A^P(1)$, $A^P(2)$, and $B^P(1,2)$ sites superimposed on the O sheet; (c) the $A^P(1)$ cage with [10]-coordinated $A^P(1)$ atom; (d) the $A^P(2)$ cage with the [13]-coordinated $A^P(2)$ atom at one point of the $A^P(2)$ site, the vacant position at the second point of the $A^P(2)$ site is shown by a white circle with a green rim; (e) the $B^P(1)$ cage with [10]-coordinated $B^P(1)$ atom. SiO_4 tetrahedra are orange; Ti- and Mn-dominant octahedra are pale yellow and fuchsia; Ba and K atoms at the A^P sites and Na atoms at the B^P sites in the **I** block are shown as large raspberry and green spheres and medium navy-blue spheres; O and H atoms of OH groups at the X^O_A sites are shown as turquoise and small grey spheres and O–H bonds are shown as black lines in (a); F atoms at the X^P_M sites are shown as yellow spheres. Unit cell is shown by thin black lines in (a).

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atoms are 0.012 and 0.010 Å^2, respectively (Table 4, Sokolova *et al*. 2020); mean distances are 2.627 and 2.624 Å (Tables 5 and 6). There is no dominance of Ca at either of the $B^P(1,2)$ sites, and therefore there is no order of Ca at the $B^P(1,2)$ sites. In surkhobite, the ideal composition of the $B^P(1)$ and $B^P(2)$ sites is $Na_{0.5}$ and $Na_{0.5}$ *apfu,* respectively, and the ideal composition of the $B^P(1) + B^P(2)$ sites is $Na_{1.0}$ *apfu* (Tables 5 and 6).

We write the cation part of the structural formula of perraultite (= surkhobite) as the sum of the following cations: (a) NaBa (B^PA^P) + (b) Mn_4 ($M^O{}_4$) + (c) Ti_2 ($M^H{}_2$); ideally $NaBaMn_4Ti_2$, with a total charge of 19^+.

In perraultite, there are 14 anions, O(1–14) (Table 4), that coordinate the Si atoms and hence they are O atoms. Two $X^O{}_M(1,2)$ anions are ligands of three M^O cations and an M^H cation (Table 5) and they are O atoms, with bond-valence sums of 1.88 to 1.87 *vu* (valence units) (Table 7). Two $X^O{}_M(1,2)$ sites ideally give O_2 *apfu*. The $X^O{}_A(1,2)$ sites are occupied by $[(OH)_{1.69}F_{0.31}]$ *pfu* (Table 6). Therefore, the $X^O{}_A(1,2)$ sites are occupied mainly by O atoms of OH groups, with bond-valence sums of 1.19 and 1.18 *vu* (Table 7). The H(1,2) atoms are involved in weak hydrogen bonds with O atoms that coordinate the polyhedra of the H sheets (Table 8). Two $X^O{}_A(1,2)$ sites ideally give $(OH)_2$ *pfu*. The $X^P{}_M$ anion is a bridging anion for two M^H atoms (mainly Ti) and two B^P atoms (Na > Ca); plus, the $X^P{}_M$ anion is bonded to one Ba atom [$A^P(1)$ site] and one $A^P(2)$ atom [either Ba or K at the $A^P(2)$ site] (Fig. 1). Hence the coordination number of the $X^P{}_M$ anion is [6]. In perraultite, occurrence of F at the $X^P{}_M$ site is in accord with the bond-valence sums of 1.01 *vu* at an $X^P{}_M$ anion (Table 7). The ideal composition of the $X^P{}_M$ site is F *apfu* (Table 6).

We write the anion part of the formulae of perraultite as the sum of the following anions: $(Si_2O_7)_2$ + O_2 $(X^O{}_M)_2$ + $(OH)_2$ $(X^O{}_A)_2$ + F $(X^P{}_M)$, ideally $(Si_2O_7)_2O_2(OH)_2F$, with a total charge of 19^-.

In accord with the perraultite-type general formula, $B^PA^PM^O{}_4M^H{}_2(Si_2O_7)_2X^O{}_4X^P{}_M$ (Sokolova 2006), we write the ideal structural formula of perraultite as $NaBaFe^{2+}{}_4Ti_2(Si_2O_7)_2O_2(OH)_2F$ (*cf*. identical ideal formula of surkhobite in Sokolova *et al*. (2020)].

DISCREDITATION OF SURKHOBITE

In the monoclinic structure of surkhobite with $c \sim 21$ Å, space group *C*2 (Rastsvetaeva *et al*. 2008), there are three [10]-coordinated sites occupied by Na and Ca: *Na*(1), *Na*(2), and *Ca*, with mean distances of 2.61, 2.62, and 2.624 Å, respectively. The empirical formula of surkhobite calculated on 76 anions (Rastsvetaeva *et al*. 2008) is as follows: $Na_{2.60}Ca_{1.60}Sr_{0.09}K_{1.41}Ba_{2.58}(Mn_{8.17}Fe^{2+}{}_{6.88}Fe^{3+}{}_{0.94}Mg_{0.115}Al_{0.01})_{\Sigma16.115}(Ti_{7.17}Nb_{0.57}Zr_{0.10})_{\Sigma7.84}Si_{16.06}(OH)_{4.61}F_{5.49}O_{70.51}$, $Z = 2$; hence the empirical formula gives $Na_{2.60}Ca_{1.60}Sr_{0.09}$ *apfu* to assign to those three sites. The site-populations of the *Na*(1), *Na*(2), and *Ca* sites (Rastsvetaeva *et al*. 2008) are as follows (*apfu*): *Na*(1): $Na_{1.0}$; *Na*(2): $Na_{1.0}$; *Ca*: $Ca_{1.60}Na_{0.30}Sr_{0.10}$; they sum to $Ca_{1.60}Na_{2.30}Sr_{0.10}$ *apfu*. Total assigned $Na_{2.30}$ *apfu* is less than $Na_{2.60}$ *apfu* (available from the empirical formula); hence, and without any reason given, $Na_{0.30}$ *apfu* was not assigned to any site in the structure. Therefore, there is an inconsistency between structure-refinement results and chemical composition of the (Na,Ca) sites in the monoclinic structure of surkhobite (Rastsvetaeva *et al*. 2008). Moreover, they refined a centrosymmetric structure in a non-centrosymmetric space group, and it is well-known that doing this frequently produces spurious results due to high variable correlation interacting with systematic errors such as absorption and extinction.

It is difficult to make a conclusion on the dominant cation at the *B* site in a perraultite-type structure based on mean distances, as these distances depend not only on the composition of the particular site, but on the chemical composition of the whole structure. In bobshannonite, the B^P sites are occupied solely by Na, with mean distances of 2.658 Å. In the astrophyllite-supergroup minerals, which have the [10]-coordinated B^P site of the same topology as that in perraultite-type minerals, the Ca-dominant sites of the compositions $Ca_{0.62}Na_{0.38}$ *apfu* (tarbagataite, Stepanov *et al*. 2012) and $Ca_{0.62}Na_{0.38}$ *apfu* (bulgakite, Agakhanov *et al*. 2016) have mean distances of 2.593 Å.

The value of the refined scattering for the site in question is a more reliable determinant for site-population assignment, especially where elements have different number of electrons: 20 for Ca and 11 for Na.

In the triclinic perraultite-type structure with $c \sim 11$ Å (after Jin *et al*. 2018), space group $C\bar{1}$, there are two [10]-coordinated $B^P(1)$ and $B^P(2)$ sites.

In perraultite, the refined site-scattering values for the $B^P(1)$ and $B^P(2)$ sites (0.5 multiplicity) are 6.68 and 6.82 *epfu* (electron per formula unit); the empirical formula gives $Na_{0.71}Ca_{0.28}$ *apfu* (see above), and we assign $Na_{0.37}Ca_{0.13}$ and $Na_{0.34}Ca_{0.15}\square_{0.01}$ *pfu* to these two sites, with calculated site-scattering values of 6.67 and 6.74 *epfu* (Table 6). The values of U_{eq} (equivalent displacement parameters) for the $B^P(1)$ and $B^P(2)$ atoms are 0.013 and 0.012 Å^2, respectively (Table 4); mean distances are 2.624 and 2.633 Å (Tables 5 and 6). There is no order of Ca at the $B^P(1,2)$ sites. The ideal composition of these two sites is $Na_{1.0}$ *apfu*.

In surkhobite, the refined site-scattering values for the $B^P(1)$ and $B^P(2)$ sites are 7.12 and 7.19 *epfu*; the

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empirical formula gives $Na_{0.59}Ca_{0.39}$ *apfu* (see above), and we assign $Na_{0.30}Ca_{0.19}\square_{0.01}$ and $Na_{0.29}Ca_{0.20}\square_{0.01}$ *pfu* to these two sites, with calculated site-scattering of 7.10 and 7.19 *epfu* (Table 6). The values of U_{eq} (equivalent displacement parameters) for the $B^P(1)$ and $B^P(2)$ atoms are 0.012 and 0.010 Å², respectively (Sokolova *et al.* 2020); mean distances are 2.627 and 2.624 Å (Tables 5 and 6). There is no dominance of Ca at either of the $B^P(1)$ sites, therefore there is no order of Ca at the $B^P(1,2)$ sites. The ideal composition of these two sites is $Na_{1.0}$ *apfu*.

We conclude that the stoichiometries of the B^P sites in perraultite and surkhobite are identical (our work). Perraultite, ideally $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$; and surkhobite, ideally $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, have the same chemical composition. Perraultite and surkhobite are isostructural: Mn > Fe^{2+} in the O sheet, Ti is dominant at the M^H sites in the H sheet, **I** block: Na > Ca at the B^P sites, there is no order of Ca at the B^P sites; Ba > K at the A^P sites. Hence perraultite and surkhobite are identical, and surkhobite has been discredited (IMA 20-A).

SUMMARY

(1) Rastsvetaeva *et al.* (2008) (IMA 07-A) redefined surkhobite as a "Mn-analogue of jinshajiangite and an ordered derivative of perraultite, with Ca ordered at one of the interstitial sites" in the **I** block; however, they ignored the pervasive twinning that is always present in this group of minerals (Jin *et al.* 2018, Sokolova *et al.* 2020). Rastsvetaeva *et al.* (2008) related surkhobite to perraultite from the Oktyabr'skii massif using a sample from which the crystal structure of perraultite was solved in monoclinic symmetry by Yamnova *et al.* (1998).

(2) We refined the crystal structure of perraultite from Oktyabr'skii massif, Ukraine [a = 10.741(6), b = 13.841(8), c = 11.079(6) Å, α = 108.174(6), β = 99.186(6), γ = 89.99(1)°, V = 1542.7(2.7) Å³, space group $C\bar{1}$, R_1 = 2.08 %] (this work) and the crystal structure of surkhobite (holotype, Fersman Mineralogical Museum, Moscow, Russia, registration # 2882/1) from the Darai-Pioz massif, Tajikistan [a = 10.728(6), b = 13.845(8), c = 11.072(6) Å, α = 108.185(6), β = 99.219(5), γ = 90.001(8)°, V = 1540.0(2.5) Å³, space group $C\bar{1}$, R_1 = 2.85%] (Sokolova *et al.* 2020). Perraultite and surkhobite are isostructural. However, there is no order of Ca at the $B^P(1,2)$ sites in surkhobite.

(3) We write the following ideal formulae as follows: perraultite, $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, $Z = 4$ [in accord with Sokolova (2006) and Sokolova & Cámara (2017)]; surkhobite, $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, Z = 4 (Sokolova *et al.* 2020) [*cf.* current IMA formula $KBa_3Ca_2Na_2Mn_{16}Ti_8(Si_2O_7)_8O_8(OH)_4(F,O,OH)_8$, $Z = 2$].

We consider surkhobite, ideally $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, chemically and structurally identical to perraultite, ideally $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$. Surkhobite was redefined in 2008 as a Ca-ordered analogue of perraultite. We have shown that there is no order of Ca in surkhobite.

(4) The definition of surkhobite as "an ordered derivative of perraultite, with Ca ordered at one of the interstitial sites" (Rastsvetaeva *et al.* 2008) is not correct. It is obvious that surkhobite is not a valid mineral species: surkhobite and perraultite have the same formula, $NaBaMn_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, $Z = 4$, they are isostructural, perraultite was described by Chao (1991), surkhobite was reinstated by (Rastsvetaeva *et al.* 2008) as a Ca-ordered derivative of perraultite; hence perraultite takes precedence over surkhobite. Our proposal "Discreditation of surkhobite" was approved by the CNMNC IMA and surkhobite was discredited (IMA 20-A).

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REFERENCES

AGAKHANOV, A.A., PAUTOV, L.A., SOKOLOVA, E., ABDU, Y.A., & KARPENKO, V.YU. (2016) Two astrophyllite-supergroup minerals, bulgakite and nalivkinite: Bulgakite, a new mineral from the Darai-Pioz alkaline massif, Tajikistan and revision of the crystal structure and chemical formula of nalivkinite. *Canadian Mineralogist* **54**, 33–48.

BROWN, I.D. (1981) The bond valence method: An empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York City, New York, United States (1–30).

CÁMARA, F., SOKOLOVA, E., & HAWTHORNE, F.C. (2016) From structure topology to chemical composition. XXII. Titanium silicates: Revision of the crystal structure of jinshajiangite, $NaBaFe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F$, a Group-II TS-block mineral. *Canadian Mineralogist* **54**, 1187–1204.

CHAO, G.Y. (1991) Perraultite, a new hydrous Na-K-Ba-Mn-Ti-Nb silicate species from Mont Saint-Hilaire, Quebec. *Canadian Mineralogist* **29**, 355–358.

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Eskova, E.M., Dusmatov, V.D., Rastsvetaeva, R.K., Chukanov, N.V., & Voronkov, A.A. (2003) Surkhobite $(Ca,Na)(Ba,K)(Fe^{3+},Mn)_4Ti_2(Si_4O_{14})O_2(F,OH,O)_3$. The new mineral (The Alai Ridge, Tadjikistan). *Zapiski Vserossiiskogo Mineralogicheskogo Obchshestva* **132(2)**, 60–67 (in Russian).

Hong, W. & Fu, P. (1982) Jinshajiangite, a new Ba-Mn-Fe-Ti-bearing silicate mineral. *Geochemistry (China)* **1**, 458–464.

Jin, S., Xu, H., Lee, S., & Fu, P. (2018) Jinshajiangite: Structure, twinning, and pseudosymmetry. *Acta Crystallographica* **B74**, 525–336.

Pekov, I.V., Belovitskaya, Yu.V., Kartashov, P.M., Chukanov, N.V., Yamnova, N.A., & Egorov-Tismenko, Yu.K. (1999) The new data on perraultite (The Azov sea region). *Zapiski Vserossiskogo Mineralogicheskogo Obshchetstva* **128(3)**, 112–120 (in Russian).

Pouchou, J.L. & Pichoir, F. (1985) "PAP" φ(ρZ) procedure for improved quantitative microanalysis. *In* Microbeam analysis (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California, United States (104–106).

Rastsvetaeva, R.K., Eskova, E.M., Dusmatov, V.D., Chukanov, N.V., & Schneider, F. (2008) Surkhobite: Revalidation and redefinition with the new formula, $(Ba,K)_2CaNa(Mn,Fe^{2+},Fe^{3+})_8Ti_4(Si_2O_7)_4O_4(F,OH,O)_6$. *European Journal of Mineral*ogy **20**, 289–295.

Rozenberg, K.A., Rastsvetaeva, R.K., & Verin, I.A. (2003) Crystal structure of surkhobite: New mineral from the family of titanosilicate micas. *Crystallography Reports* **48**, 384–389.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica* **A32**, 751–767.

Sheldrick, G.M. (2015) Crystal Structure refinement with *SHELX*. *Acta Crystallographica* **C71**, 3–8.

Sokolova, E. (2006) From structure topology to chemical composition. I. Structural hierarchy and stereochemistry in titanium disilicate minerals. *Canadian Mineralogist* **44,** 1273–1330.

Sokolova, E. (2010) Predictive crystal-chemical relations in Ti-silicates based on the TS block. *Geology of Ore Deposits* **52**, 410–427.

Sokolova, E. & Cámara, F. (2013) From structure topology to chemical composition. XVI. New developments in the crystal chemistry and prediction of new structure topologies for titanium disilicate minerals with the TS block. *Canadian Mineralogist* **51**, 861–891.

Sokolova, E. & Cámara, F. (2016) From structure topology to chemical composition. XXI. Understanding the crystal chemistry of barium in TS-block minerals. *Canadian Mineralogist* **54**, 79–95.

Sokolova, E. & Cámara, F. (2017) The seidozerite supergroup of TS-block minerals: Nomenclature and classification, with change of the following names: rinkite to rinkite-(Ce), mosandrite to mosandrite-(Ce), hainite to hainite-(Y) and innelite-1*T* to innelite-1*A*. *Mineralogical Magazine* **81**, 1457–1484.

Sokolova, E., Cámara, F., Abdu, Y.A., Hawthorne, F.C., Horváth, L., & Pfenninger-Horváth, E. (2015) Bobshannonite, $Na_2KBa(Mn,Na)_8(Nb,Ti)_4(Si_2O_7)_4O_4(OH)_4(O,F)_2$, a new TS-block mineral from Mont Saint-Hilaire, Québec, Canada: Description and crystal structure. *Mineralogical Magazine* **79**, 1791–1811.

Sokolova, E., Hawthorne, F.C., Cámara, F., Della Ventura, G., & Uvarova, Yu.A. (2020) From structure topology to chemical composition. XXVII. Revision of the crystal chemistry of the perraultite-type minerals of the seidozerite supergroup: Jinshajiangite, surkhobite, and bobshannonite. *Canadian Mineralogist* **58**, 19–43.

Stepanov, A.V., Bekenova, G.K., Levin, V.L., Sokolova, E., Hawthorne, F.C., & Dobrovol'skaya, E.A. (2012) Tarbagataite, $(K,\square)_2(Ca,Na)(Fe^{2+},Mn)_7Ti_2(Si_4O_{12})_2(OH)_4(OH,F)$, a new astrophyllite-group mineral from the Verkhnee Espe Deposit, Akjailyautas Mountains, Kazakhstan: Description and crystal structure. *Canadian Mineralogist* **50**, 159–168.

Wilson, A.J.C., Ed. (1992) *International Tables for Crystallography. Volume C: Mathematical, Physical, and Chemical Tables*. Kluwer Academic Publishers, Dordrecht, Netherlands.

Yamnova, N.A., Egorov-Tismenko, Yu.K., & Pekov, I.V. (1998) Crystal structure of perraultite from the coastal region of the Sea of Azov. *Crystallography Reports* **43**, 401–410.

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