

**PARAERSHOVITE, Na₃K₃Fe³⁺₂(Si₄O₁₀OH)₂(OH)₂(H₂O)₄,
 A NEW MINERAL SPECIES FROM THE Khibina Alkaline Massif,
 Kola Peninsula, Russia: Description and Crystal Structure**

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ABSTRACT

Paraershovite, Na₃K₃Fe³⁺₂(Si₄O₁₀OH)₂(OH)₂(H₂O)₄, is a new silicate mineral species discovered in a hyperagpaitic pegmatite from Mount Yukspor, Khibina alkaline massif, Kola Peninsula, Russia. The mineral occurs as equant (100) platy and [001] elongate prismatic crystals up to 0.5–1 mm and aggregates up to 2–3 mm sporadically scattered in a pegmatite matrix. Associated minerals are sodalite, aegirine, arfvedsonite, pectolite, shcherbakovite, lamprophyllite, lomonosovite, shafranovskite, villiaumite and natrophosphate. Crystals of paraershovite are yellow with orange or pinkish shades, with a white streak and vitreous luster. The mineral is translucent or transparent, and non-fluorescent under 240–400 nm ultraviolet radiation. Paraershovite has a perfect {100} cleavage. It is brittle, has a step-like and splintery fracture, and a Mohs hardness of 3. Its observed and calculated densities (g/cm³) are 2.60(3) (by microvolumetric methods) and 2.584 (using the empirical formula), respectively. It is biaxial positive, with α 1.569(2), β 1.583(2), γ 1.602(2), $2V(\text{meas.}) = 80(3)^\circ$, $2V(\text{calc.}) = 82^\circ$, non-pleochroic, dispersion $r > v$ (weak), with $X \wedge c = 84^\circ$, $Y \wedge c = 66^\circ$, $Z \wedge c = 24^\circ$. Paraershovite is triclinic, space group $P\bar{1}$, a 10.1978(5), b 12.0155(6), c 5.2263(3) Å, α 103.439(1), β 96.020(1), γ 91.683(1)°, V 618.46(3) Å³, $Z = 1$. The strongest lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 11.778(100)(010), 4.390(70)($\bar{1}\bar{1}$, $0\bar{2}\bar{1}$), 3.012(70)(230, $\bar{3}\bar{2}0$), 2.606(70)($\bar{3}\bar{2}\bar{1}$, 131, $0\bar{1}\bar{2}$, $\bar{1}\bar{1}\bar{2}$), 4.109(60)($\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{2}\bar{1}$) and 2.730(60)($\bar{3}\bar{2}\bar{1}$, $\bar{1}\bar{4}\bar{1}$, $\bar{1}\bar{4}\bar{1}$, $3\bar{1}\bar{1}$, 221). A chemical analysis with an electron microprobe gave Na₂O 7.77, MgO 0.24, SiO₂ 49.67, Al₂O₃ 0.58, K₂O 14.07, Fe₂O₃ 11.29, MnO 0.73, TiO₂ 3.32, F 0.39, H₂O 10.98, O = F –0.16, sum 98.88 wt.%; the valence state of Fe was determined by Mössbauer spectroscopy, and the amount of H₂O was calculated from the crystal-structure refinement. The empirical formula based on 28 anions is (Na_{2.44}□_{1.56}Σ₄K_{2.91}(Fe³⁺_{1.38}Ti_{0.40}Al_{0.11}Mn²⁺_{0.10}Mg_{0.06}Σ_{2.05}Si_{8.05}O₂₀[(OH)_{3.80}F_{0.20}]_{Σ4}(H₂O)₄). The IR spectrum of the mineral has absorption bands at 1600 and 3500 cm⁻¹, showing the presence of H₂O and OH groups in the structure. The crystal structure of paraershovite was solved by direct methods and refined to an R_1 index of 4.28% (for 2134 observed [$F_o > 4\sigma F$] unique reflections measured with MoK α radiation on a Bruker $P4$ diffractometer with a CCD 4K APEX detector). The crystal structure of paraershovite is isostructural with that of ershovite, ideally Na₄K₃(Fe²⁺, Mn, Ti)₂(Si₄O₁₀OH)₂(OH)₂(H₂O)₄ (a 10.244, b 11.924, c 5.276 Å, α 103.491, β 96.960, γ 91.945°, V 620.8 Å³, space group $P\bar{1}$). Paraershovite is a Na-deficient, Fe³⁺-dominant analogue of ershovite. It can be considered an oxidized product of the epithermal alteration of ershovite. Paraershovite is chemically related to ershovite by the heterovalent substitution $\square + \text{Fe}^{3+}_2 \rightarrow \text{Na}^+ + \text{M}^{2.5+}_2$, where M^{2.5+} represents Fe²⁺, Mn²⁺ and Ti⁴⁺. The name *paraershovite*, derived from the Greek *para* (close by) and *ershovite*, recalls the close structural, chemical and genetic relations between paraershovite and ershovite.

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Keywords: paraershovite, new mineral species, crystal structure, Fe^{3+} silicate, ershovite, electron-microprobe analysis, Khibina, Kola Peninsula, Russia.

SOMMAIRE

Nous décrivons la paraershovite, $\text{Na}_3\text{K}_3\text{Fe}^{3+}_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$, nouvelle espèce minérale découverte dans une pegmatite hyperagpaitique au mont Yukspor, massif alcalin de Khibina, péninsule de Kola, en Russie. Le minéral se présente en cristaux équidimensionaux en plaquettes (100) allongées en prismes selon [001], atteignant une longueur de 0.5–1 mm ou en agrégats mesurant 2–3 mm, distribués éparsement dans la matrice pegmatitique. Lui sont associés sodalite, aegyrine, arfvedsonite, pectolite, shcherbakovite, lamprophyllite, lomonosovite, shafranovskite, villiamite et natrophosphate. Les cristaux de paraershovite sont jaunes avec teintes oranges ou rosâtres, avec une rayure blanche et un éclat vitreux. Le minéral est translucide ou transparent, et non fluorescent en lumière ultraviolette ayant une longueur d'onde dans l'intervalle 240–400 nm. La paraershovite possède un clivage {100} parfait. Elle est cassante, et se brise par fractures en échapes ou en escaliers; sa dureté est 3 sur l'échelle de Mohs. Les densités observée et calculée (g/cm^3) sont 2.60(3) (par méthodes microvolumétriques) et 2.584 (selon la formule empirique), respectivement. Elle est biaxe positive, avec α 1.569(2), β 1.583(2), γ 1.602(2), $2V(\text{mes.}) = 80(3)^\circ$, $2V(\text{calc.}) = 82^\circ$, non pléochroïte, dispersion $r > v$ (weak), with $X \wedge c = 84^\circ$, $Y \wedge c = 66^\circ$, $Z \wedge c = 24^\circ$. La paraershovite est triclinique, groupe spatial $P\bar{1}$, a 10.1978(5), b 12.0155(6), c 5.2263(3) Å, α 103.439(1), β 96.020(1), γ 91.683(1)°, V 618.46(3) Å³, $Z = 1$. Les six raies les plus intenses du spectre de diffraction, méthode des poudres [d en Å(I)(hkl)] sont: 11.778(100)(010), 4.390(70)($\bar{1}\bar{1}$, $0\bar{2}$), 3.012(70)(230, $\bar{3}20$), 2.606(70)($3\bar{2}$, 131, $0\bar{1}2$, $\bar{1}\bar{1}2$), 4.109(60)($\bar{1}\bar{1}$, $\bar{1}\bar{2}$) et 2.730(60)($\bar{3}\bar{2}$, $\bar{1}\bar{4}$, $\bar{1}\bar{4}$, $3\bar{1}$, $2\bar{1}$). Une analyse chimique a donné: Na_2O 7.77, MgO 0.24, SiO_2 49.67, Al_2O_3 0.58, K_2O 14.07, Fe_2O_3 11.29, MnO 0.73, TiO_2 3.32, F 0.39, H_2O 10.98, $O = F - 0.16$, pour une somme de 98.88%; la valence du fer a été établie par spectroscopie de Mössbauer, et la quantité de H_2O a été calculée par affinement de la structure cristalline. La formule empirique fondée sur 28 anions est $(\text{Na}_{2.44}\square_{1.56})\Sigma_4\text{K}_{2.91}(\text{Fe}^{3+}_{1.38}\text{Ti}_{0.40}\text{Al}_{0.11}\text{Mn}^{2+}_{0.10}\text{Mg}_{0.06})\Sigma_{2.05}\text{Si}_{8.05}\text{O}_{20}[(\text{OH})_{3.80}\text{F}_{0.20}]_{\Sigma 4}(\text{H}_2\text{O})_4$. Le spectre infrarouge possède des bandes d'absorption à 1600 et 3500 cm^{-1} , ce qui indique la présence de H_2O et de groupes OH dans la structure. Nous en avons résolu la structure cristalline par méthodes directes et nous l'avons affinée jusqu'à un résidu R_1 de 4.28% (pour 2134 réflexions uniques observées [$F_o > 4\sigma F$] mesurées avec rayonnement $\text{MoK}\alpha$ et un diffractomètre Bruker P4 muni d'un détecteur CCD 4K APEX). La structure de la paraershovite est celle de la ershovite, de stoechiométrie idéale $\text{Na}_4\text{K}_3(\text{Fe}^{2+}, \text{Mn}, \text{Ti})_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$ (a 10.244, b 11.924, c 5.276 Å, α 103.491, β 96.960, γ 91.945°, V 620.8 Å³, groupe spatial $P\bar{1}$). La paraershovite serait l'analogue déficitaire en Na et à dominance de Fe^{3+} de la ershovite. Elle résulterait d'une oxydation lors de l'altération épithermale de la ershovite. La paraershovite est chimiquement apparentée à la ershovite selon la substitution hétérovalente $\square + \text{Fe}^{3+}_2 \rightarrow \text{Na}^+ + \text{M}^{2.5+}_2$, dans laquelle $\text{M}^{2.5+}$ représente Fe^{2+} , Mn^{2+} et Ti^{4+} . Le nom *paraershovite*, dérivé du grec *para* (proche de) et *ershovite*, rappelle les liens structuraux, chimiques et génétiques entre la paraershovite et l'ershovite.

(Traduit ar la Rédaction)

Mots-clés: paraershovite, nouvelle espèce minérale, structure cristalline, silicate de Fe^{3+} , ershovite, analyse avec une microsonde électronique, Khibina, péninsule de Kola, Russie.

INTRODUCTION

The Khibina and Lovozero alkaline massifs in the Kola Peninsula, Russia, are a gigantic (about 2000 km²) complex of agpaitic nepheline syenites with associated large deposits of rare metals and phosphates. This complex is the type locality for about 180 minerals, and over 600 mineral species are known to occur there. The majority of the new and rare minerals, as well as the mineral in question, were identified there while investigating hyperagpaitic pegmatites, the extreme alkaline differentiates of nepheline-bearing syenitic magmas (Khomyakov 1995, 2008).

Here we describe a new silicate mineral that was collected by one of us (A.P.K.) in the Khibina massif about 20 years ago, but has remained poorly studied until now because of an extremely limited amount of material. Detailed study of this mineral, including electron-microprobe, single-crystal Mössbauer spectroscopy and X-ray powder and single-crystal X-ray diffraction analyses, shows that on the basis of some

features, in particular the type of chemical formula, ideally $\text{Na}_3\text{K}_3\text{Fe}^{3+}_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$, it is very similar to ershovite, ideally $\text{Na}_4\text{K}_3(\text{Fe}^{2+}, \text{Mn}, \text{Ti})_2(\text{Si}_8\text{O}_{20})(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ (Khomyakov *et al.* 1993), with a structural formula $[\text{Na}_3\text{K}_3(\text{H}_2\text{O})_4]\{[\text{M}_2(\text{OH})_2][(\text{Si}_8\text{O}_{20})(\text{OH})_2]\}$, where $\text{M} = \text{Fe}^{2+}, \text{Mn}, \text{Ti}, \text{Mg}$ (Rastsvetaeva *et al.* 1991). According to our data, paraershovite can be regarded as the Na-deficient Fe^{3+} -analogue of ershovite, satisfying the criteria for a distinct mineral species (Nickel & Grice 1998). The name *paraershovite* [from the Greek *para* (close by) and *ershovite*] recognizes the close structural and chemical relations between the new mineral and its closest analogue.

The new mineral species and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, IMA 2009–025. The holotype specimen of paraershovite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia (catalogue number 3793).

OCCURRENCE AND ASSOCIATED MINERALS

Paraershovite was found in the Mount Yukspor area of the Khibina massif, in waste material from an adit driven through a series of strongly mineralized bodies of hyperagpaitic pegmatite occurring in ijolite-urtite. The mineral was identified in only one hand specimen of pegmatite, where it occurs as equant (100) platy and [001] elongate prismatic crystals up to 0.5–1 mm and aggregates up to 2–3 mm, sporadically scattered in the pegmatite matrix. Associated minerals are sodalite, aegirine, arfvedsonite, pectolite, shcherbakovite, lamprophyllite, lomonosovite, shafranovskite, villiaumite and natrophosphate.

PHYSICAL AND OPTICAL PROPERTIES

The main properties of paraershovite are presented in Table 1, where they are compared to those for ershovite. Crystals of paraershovite are yellow with orange or pinkish shades, with a white streak and a vitreous luster. The mineral is translucent or transparent, and non-fluorescent under 240–400 nm ultraviolet radi-

ation. Paraershovite has a perfect {100} cleavage. It is brittle, has a step-like and splintery fracture, and a Mohs hardness of 3. Its observed and calculated densities (in g/cm³) are 2.60(3) (by microvolumetric methods) and 2.584 (using the empirical formula), respectively. The mineral is biaxial positive with α 1.569(2), β 1.583(2), γ 1.602(2) (λ 589 nm), $2V(\text{meas.}) = 80(3)^\circ$, $2V(\text{calc.}) = 82^\circ$, non-pleochroic, dispersion $r > v$ (weak), and with an orientation as follows: $X \wedge c = 84^\circ$, $Y \wedge c = 66^\circ$, $Z \wedge c = 24^\circ$. A Gladstone–Dale calculation gives a compatibility index of 0.024, which is rated as excellent (Mandarino 1981).

The infrared spectrum of paraershovite has absorption bands at 1600 and 3500 cm⁻¹, showing the presence of H₂O and OH groups in the structure (Fig. 1). Paraershovite readily decomposes at room temperature in a ceramic container with 50% HCl and HNO₃ solution.

CHEMICAL COMPOSITION

Mössbauer spectroscopy

Transmission Mössbauer spectroscopy measurements were done at room temperature (RT) using a ⁵⁷Co(Rh) point source. A metallic Fe foil was used for the calibration of the spectrometer, and spectra were collected in the velocity range of ± 4 mm/s.

Figure 2 shows the RT Mössbauer spectrum of a single crystal of paraershovite (~400 μm in size). It is fit with one Fe³⁺ site, with a single Gaussian component, using a Voigt-based method of distribution of quadrupole splitting implemented in the program suite RECOL. No Fe²⁺ was found. To account for the asymmetry in the spectrum, produced by the orientation of the crystal, the intensity ratio of the low-velocity peak to the high-velocity peak was allowed to vary during the fitting routine. The average center shift, CS, is equal to 0.39(1) mm/s, and the average quadrupole splitting, QS,

TABLE 1. COMPARISON OF PARAERSHOVITE WITH ERSHOVITE

	Paraershovite*	Ershovite**
Formula	Na ₂ K ₂ Fe ³⁺ ₂ (Si ₄ O ₁₀ OH) ₂ (OH) ₂ (H ₂ O) ₄	Na ₂ K ₂ (Fe ²⁺ , Mn, Ti) ₂ (Si ₄ O ₁₀ OH) ₂ (OH) ₂ (H ₂ O) ₄
System	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.1978(5)	10.244
<i>b</i>	12.0155(6)	11.924
<i>c</i>	5.2263(3)	5.276
α (°)	103.439(1)	103.491
β	96.020(1)	96.960
γ	91.683(1)	91.945
<i>V</i> (Å ³)	618.46(3)	620.8
<i>Z</i>	1	1
<i>D</i> _{meas} (g/cm ³)	2.60	2.75
Strongest lines in the powder pattern	11.778(100) 4.390(70) 3.012(70) 2.606(70)	11.57(100) 2.992(28) 2.598(26) 2.716(22)
<i>d</i> _{meas} (Å)	4.109(60) 2.730(60)	3.006(21) 3.386(19)
Optical character	biaxial positive	biaxial positive
<i>n</i> _{α}	1.569	1.569
<i>n</i> _{β}	1.583	1.574
<i>n</i> _{γ}	1.602	1.590
<i>n</i> _{α} - <i>n</i> _{γ}	0.033	0.021
$2V$ (°)	80	58
Orientation		
$X \wedge c$	84°	86°
$Y \wedge c$	66°	73°
$Z \wedge c$	24°	17°
Color	yellow	olive green
Pleochroism		
X	pale yellow	pale green
Y	honey yellow	pale green
Z	pinkish brown	dark green

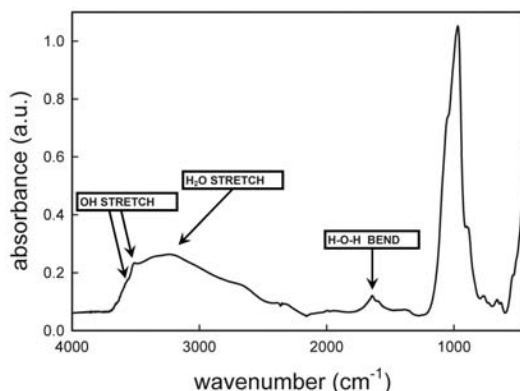
* This work; ** Rastsvetaeva *et al.* (1991), Khomyakov *et al.* (1993).

FIG. 1. IR spectrum of paraershovite.

is 0.33(1) mm/s. The value of the CS is characteristic of Fe^{3+} in octahedral coordination.

Electron-microprobe analysis

The chemical composition of paraershovite was determined by electron-microprobe analysis (Table 2). The analysis (12 points) was done using a Cameca SX-100 in wavelength-dispersion mode with an accelerating voltage of 15 kV, a sample current of 10 nA, and a beam diameter of 20 μm . We used the following standards (spectral line, analyzing crystal): albite ($\text{NaK}\alpha$ TAP), orthoclase ($\text{KK}\alpha$ LPET), forsterite ($\text{MgK}\alpha$ LTAP), spessartine ($\text{MnK}\alpha$ LLIF), fayalite ($\text{FeK}\alpha$ LLiF), andalusite ($\text{AlK}\alpha$ TAP), diopside ($\text{SiK}\alpha$ TAP), titanite ($\text{TiK}\alpha$ LLiF), and F-bearing riebeckite ($\text{FK}\alpha$ LTAP). The data were reduced and corrected with the PAP method of Pouchou & Pichoir (1985). We did not determine H_2O directly because of insufficient material; it was calculated by stoichiometry from the crystal-structure analysis. The presence of OH and H_2O groups in the crystal structure was confirmed by infrared spectroscopy (see above). On the basis of 28 (O + F) anions *pfu* (per formula unit), the empirical formula for paraershovite is $(\text{Na}_{2.44}\square_{1.56})_{\Sigma 4}\text{K}_{2.91}(\text{Fe}^{3+}_{1.38}\text{Ti}_{0.40}\text{Al}_{0.11}\text{Mn}^{2+}_{0.10}\text{Mg}_{0.06})_{\Sigma 2.05}\text{Si}_{8.05}\text{O}_{20}[(\text{OH})_{3.80}\text{F}_{0.20}]_{\Sigma 4}(\text{H}_2\text{O})_4$, $Z = 1$. The simplified formula is $\text{Na}_3\text{K}_3\text{Fe}^{3+}_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$. The silicate ribbon in paraershovite has the same bond-topology as the corresponding ribbon in the amphibole structure

(Figs. 3a,b), but differs in having a silanol group as part of its ribbon. We write this ribbon as $(\text{Si}_4\text{O}_{10}\text{OH})$ in order to emphasize that the translational repeat of the ribbon has the formula $(\text{Si}_4\text{O}_{10}\text{OH})$ [*cf.* $(\text{Si}_4\text{O}_{11})$ ribbons in amphibole and vlasovite and $(\text{Si}_8\text{O}_{20})$ ribbon in fenaksite: Belov (1976)]. Paraershovite is chemically related to ershovite, $\text{Na}_4\text{K}_3(\text{Fe}^{2+}, \text{Mn}, \text{Ti})_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$, by the heterovalent substitution $\square + \text{Fe}^{3+}_2 \rightarrow \text{Na}^+ + \text{M}^{2.5+}_2$, where $\text{M}^{2.5+} = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ti}^{4+}$.

TABLE 2. CHEMICAL COMPOSITION* OF PARAERSHOVITE

oxide	wt. %	range	cation	<i>apfu</i>
Na_2O	7.77	7.18 – 8.16	Na	2.44
K_2O	14.07	13.86 – 14.19	K	2.91
MgO	0.24	0.16 – 0.30	Mg	0.06
MnO	0.73	0.54 – 0.93	Mn	0.10
$\text{Fe}_2\text{O}_3^{**}$	11.29	9.96 – 13.125	Fe^{3+}	1.38
Al_2O_3	0.58	0.42 – 0.72	Al	0.11
SiO_2	49.67	48.86 – 50.39	Si	8.05
TiO_2	3.32	1.58 – 4.68	Ti	0.40
F	0.39	0.24 – 0.54	F	0.20
H_2O	10.98		H	11.80
O=F	–0.16			
Total	98.88			

* CaO , Nb_2O_5 and BaO were sought but not detected. Cations were recalculated on the basis of 28 atoms of O + F.

** determined by Mössbauer spectroscopy.

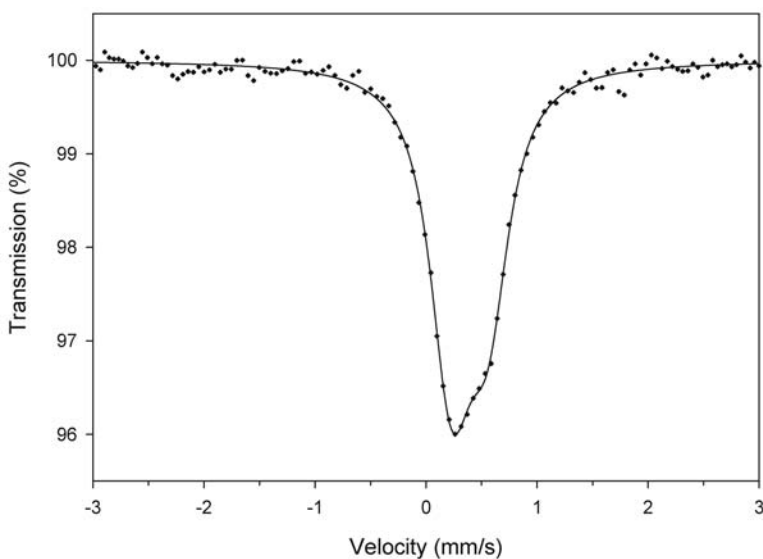


FIG. 2. Room-temperature Mössbauer spectrum of paraershovite single crystal fitted with one site due to Fe^{3+} . The center shift [CS = 0.39(1) mm/s] is typical of octahedral Fe^{3+} . Interestingly, it has a very small quadrupole splitting [QS = 0.33(1) mm/s].

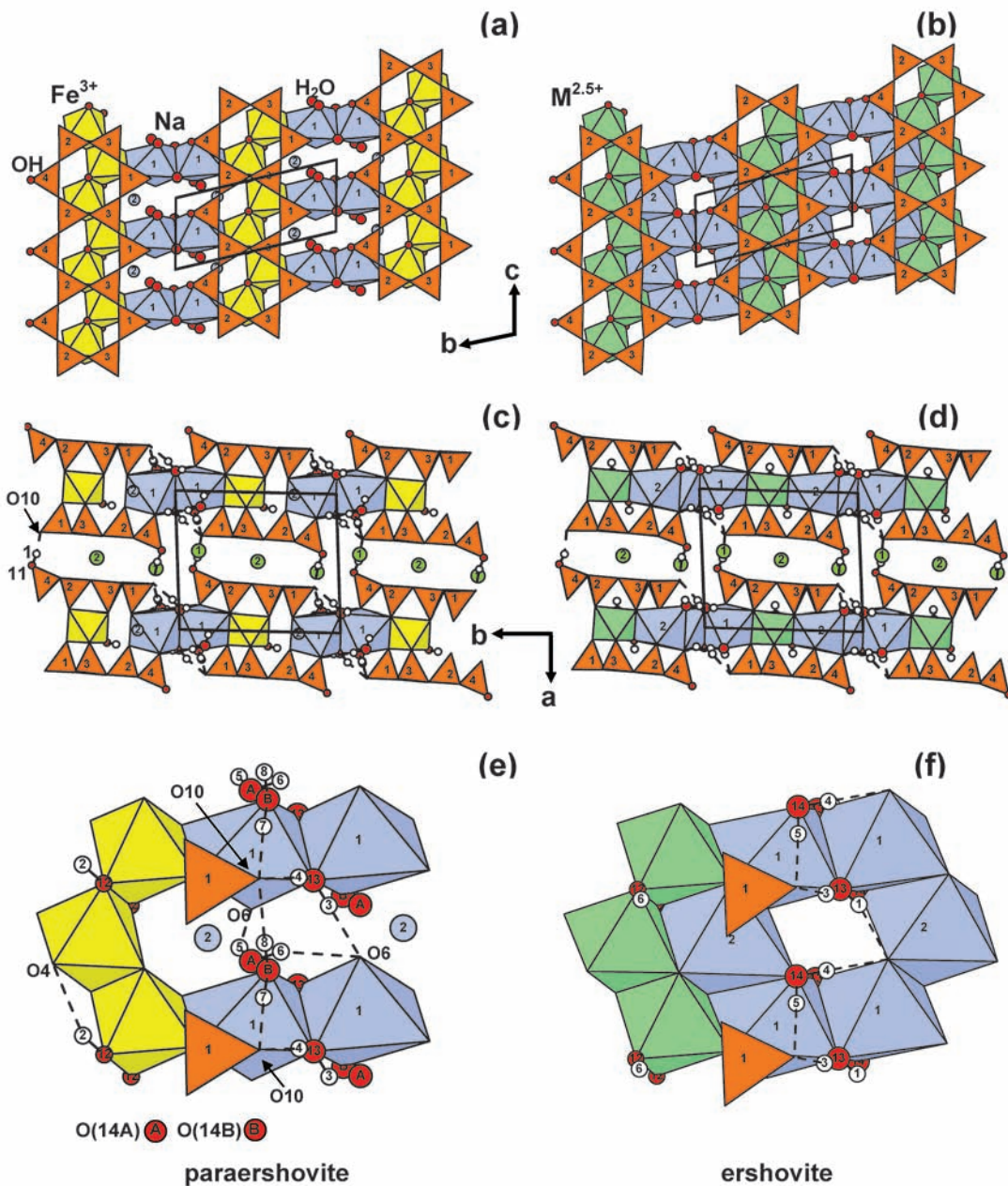


FIG. 3. Details of the crystal structure of paraershovite and ershovite [after Rastsvetaeva et al. (1991)]: linkage of an (100) interrupted O sheet, ideally $\text{Na}_3\text{[Si}_2\text{Fe}^{3+}_2\text{O}_8(\text{OH})_2(\text{H}_2\text{O})_4]$ in paraershovite and $\text{Na}_4\text{[M}_2\text{O}_8(\text{OH})_2(\text{H}_2\text{O})_4]$ in ershovite and an amphibole-like $(\text{Si}_4\text{O}_{10}\text{OH})$ ribbon in paraershovite (a) and ershovite (b); general view of the structure projected onto (001), paraershovite (c), ershovite (d); hydrogen bonding in paraershovite (e) and ershovite (f). In (e,f), the H atoms are shown only above the plane of the interrupted O sheet. The (SiO_4) tetrahedra are shown in orange, labels 1–8 (on orange) correspond to Si(1)–Si(4) tetrahedra; Fe^{3+} and M octahedra are yellow and green, Na octahedra are navy blue, labels 1 and 2 (on blue) correspond to Na(1) and Na(2) polyhedra. For paraershovite, partly occupied Na(2) sites are shown as navy blue spheres; K atoms are shown as large green spheres, which are labeled 1 and 2. The OH and H_2O groups are shown as small and large red spheres; they are labeled 12 and 13, 14A, 14B in (e), 12 and 13, 14, in (f). The H atoms are shown as small white spheres, they are labeled 2–8 in (e) and 1, 3–6 in (f). The bonds O (donor)–H and hydrogen bonds O(acceptor)⋯H are shown as solid and dashed lines, respectively. Acceptor oxygen atoms are labeled as O4, O6 and O10 (cf. Table 8). Hydrogen bonding involving the silanol group, O(11)–H(1)⋯O(10), is shown in (c).

CRYSTAL STRUCTURE

Data collection and structure refinement

A single crystal of paraershovite was mounted on a Bruker *P4* automated four-circle diffractometer equipped with graphite-filtered MoK α X-radiation and a CCD 4K APEX detector. The intensities of 10977 reflections with $-11 < h < 12$, $-14 < k < 14$, $-6 < l < 6$ were collected to 50.37° 2 θ using 30 s per 0.1° frame, and an empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 1) were obtained from 6520 reflections with $I > 10\sigma I$. The crystal structure of paraershovite was refined to an R_1 index of 4.28% (Sheldrick 1997; Table 3) using atom coordinates of the ershovite structure (Rastsvetaeva *et al.* 1991). Site occupancies were refined for the *M* site (occupied mainly by Fe³⁺), two *Na* sites, two *K* sites and one (H₂O) site [O(14)] with scattering curves of Fe, Na, K and O, respectively. The refinement showed that the O(14) site splits into two sites, O(14A) and O(14B), with approximately 50% occupancy and separated by 0.64 Å. For subsequent refinement, the site occupancies for the O(14A) and O(14B) sites were fixed at 0.5, and anisotropic displacement parameters were constrained to be equal. In the last stages of the refinement, two H atoms of two (OH) groups [O(11) and O(12)] and six H atoms of three (H₂O) groups [O(13) and O(14A) + O(14B) = O(14)] were found in the difference-electron-density map (D-map) and included in the refinement with two types of constraints: (1) the distances O (donor)–H were fixed to have the distances taken from the D-map; (2) the distances H–H for H₂O groups were fixed at 1.55 and 1.50 Å for the O(14A) and O(14B) sites; (3) the isotropic-displacement factor for an H atom was constrained to be 1.5 times larger than the displacement parameter of the O atom of associated (OH) and (H₂O) groups. The H(5,6) and H(7,8)

atoms belonging to two central O atoms of H₂O groups, O(14A) and O(14B), were included in the refinement with 50% occupancy. Final atom coordinates and displacement parameters are given in Table 4, selected interatomic distances and angles are listed in Table 5, refined site-scattering values and assigned populations for cation sites are given in Table 6, Table 7 gives the bond valences, and Table 8 gives details of hydrogen bonding for paraershovite. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data on the MAC website [document Paraershovite CM48_279].

DESCRIPTION OF THE STRUCTURE

We describe the crystal structure of paraershovite and compare it with that of ershovite (Rastsvetaeva *et al.* 1991).

Cation sites

The Si sites: There are four *Si* sites occupied solely by Si. Three sites, Si(1–3), are coordinated by a tetrahedral array of O atoms, with $\langle \text{Si–O} \rangle = 1.622$ Å, and one site, Si(4), is coordinated by three O atoms and an OH group, with $\langle \text{Si(4)–}\phi \rangle = 1.620$ Å, where ϕ represents an unspecified anion (Table 5), as in ershovite.

The M, Na and K sites: There is one *M* site, coordinated by a distorted octahedral array of four O atoms and two (OH) groups, with a $\langle \text{M–}\phi \rangle$ distance of 2.021 Å (Table 5). The *M* site is occupied by (Fe³⁺_{1.38}Ti_{0.40}Mn²⁺_{0.10}Al³⁺_{0.08}Mg_{0.04}) (Table 6), which ideally gives Fe³⁺₂ *pfu*. The ideal composition of the *M* site (charge of 6+) adequately describes its refined occupancy (charge 6.26+). In ershovite, the *M* site is occupied by (Fe²⁺_{0.87}Mn²⁺_{0.68}Ti_{0.38}Mg_{0.07}) (Table 6) (with a total charge of 4.76+), which ideally gives M^{2.5+}₂ *pfu*. The *Na*(1) and *Na*(2) sites are coordinated by octahedral arrangements of four O atoms and two H₂O groups and four O atoms, one OH and one H₂O group, with $\langle \text{Na(1)–}\phi \rangle$ and $\langle \text{Na(2)–}\phi \rangle$ equal to 2.39 and 2.46 Å, respectively (Table 5). The *Na*(1) and *Na*(2) sites are partly occupied by Na (Table 5) at 81 and 41% occupancy (Table 6). The total refined scattering at the *Na*(1) and *Na*(2) sites is 27.3 *epfu*, which corresponds to 2.44 *apfu* Na. There is a close agreement between the observed and calculated mean bond-lengths for the *Na*(1) site, 2.39 *versus* 2.40 Å. For the *Na*(2) site, there is a mismatch between observed and calculated mean bond-lengths, 2.46 *versus* 2.39 Å. This mismatch is possibly due to vacancy–*Na*(2) order, where the positions of O atoms can vary significantly depending on the local occupancy of the *Na*(2) site. In ershovite, the *Na*(1) and *Na*(2) sites are fully occupied by Na, with $\langle \text{Na(1)–}\phi \rangle$ and $\langle \text{Na(2)–}\phi \rangle = 2.393$ and 2.409 Å (Table 6), respectively, with a total content of *Na* = *Na*₄ *pfu*. The two *K* sites, *K*(1) and *K*(2), are occupied by K atoms at 96 and 100% occu-

TABLE 3. MISCELLANEOUS DATA CONCERNING THE REFINEMENT OF PARAERSHOVITE

Absorption coefficient (mm ⁻¹)	1.22
<i>F</i> (000)	468.00
<i>D</i> _{calc} (g/cm ³)	2.584
Crystal size (mm)	0.08 × 0.18 × 0.18
Radiation/filter	MoK α / graphite
2 θ upper limit for data collection (°)	50.37
<i>R</i> (int) (%)	2.53
Reflections collected	10977
Independent reflections	2226
<i>F</i> _o > 4 σ [<i>F</i>]	2134
Refinement method	Full-matrix least squares on <i>F</i> ² , fixed weights proportional to 1/ σ <i>F</i> _o ²
Goodness of fit on <i>F</i> ²	1.246
Final <i>R</i> (obs) (%) [<i>F</i> _o > 4 σ [<i>F</i>]]	4.28
<i>R</i> indices (all data) (%)	
<i>R</i> ₁	4.50
<i>wR</i> ₂	10.07
<i>GooF</i>	1.246

TABLE 4. FINAL COORDINATES AND DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN PARAERSHOVITE

Atom	x	y	z	Occu- pancy	Anion spec.	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M	0.00552(9)	0.42473(9)	0.70056(19)	1.0		0.0085(6)	0.0140(6)	0.0119(6)	0.0012(4)	0.0001(4)	0.0019(4)	0.0118(4)
Na(1)	0.9757(4)	0.8611(3)	0.4609(8)	0.81		0.024(2)	0.023(2)	0.045(3)	0.0043(17)	-0.0027(17)	-0.0001(15)	0.0318(15)
Na(2)	0.9901(7)	0.7410(7)	0.8855(15)	0.41		0.027(5)	0.035(5)	0.034(5)	0.011(3)	0.016(3)	0.009(3)	0.031(3)
Si(1)	0.73752(17)	0.28343(15)	0.4291(3)	1.0		0.0103(9)	0.0144(9)	0.0118(9)	0.0024(7)	0.0021(7)	0.0014(7)	0.0122(5)
Si(2)	0.71648(17)	0.67365(15)	0.1360(4)	1.0		0.0099(9)	0.0152(9)	0.0148(9)	0.0033(7)	0.0017(7)	0.0032(7)	0.0133(5)
Si(3)	0.73373(16)	0.41941(15)	0.9938(3)	1.0		0.0088(9)	0.0137(9)	0.0117(9)	0.0016(7)	0.0017(7)	0.0014(7)	0.0116(5)
Si(4)	0.67806(19)	0.81252(16)	0.7010(4)	1.0		0.0191(10)	0.0167(10)	0.0157(10)	0.0027(7)	0.0034(7)	0.0035(7)	0.0172(5)
K(1)	0.56870(19)	0.13502(14)	0.8203(3)	0.96		0.0437(12)	0.0226(10)	0.0181(10)	0.0041(7)	0.0014(7)	-0.0025(8)	0.0285(7)
K(2)	½	½	½	1.0		0.0355(14)	0.0427(15)	0.0279(13)	0.0125(11)	0.0082(10)	0.0247(12)	0.0339(7)
O(1)	0.6735(4)	0.3522(4)	0.6954(9)	1.0	O	0.009(2)	0.023(3)	0.015(2)	0.004(2)	0.0024(18)	0.0022(19)	0.0159(10)
O(2)	0.8952(4)	0.2965(4)	0.4822(9)	1.0	O	0.011(2)	0.021(2)	0.016(2)	0.0016(19)	0.0014(18)	0.0020(18)	0.0166(10)
O(3)	0.6525(5)	0.7284(5)	0.8982(10)	1.0	O	0.018(3)	0.034(3)	0.023(3)	0.013(2)	0.001(2)	0.005(2)	0.0241(12)
O(4)	0.8735(4)	0.6832(4)	0.1747(9)	1.0	O	0.010(2)	0.021(2)	0.022(2)	0.006(2)	0.0008(18)	0.0018(18)	0.0176(10)
O(5)	0.8919(4)	0.4392(4)	0.0176(8)	1.0	O	0.009(2)	0.021(2)	0.010(2)	0.0021(18)	0.0011(17)	-0.0005(18)	0.0134(10)
O(6)	0.8233(5)	0.8724(5)	0.7639(12)	1.0	O	0.019(3)	0.037(3)	0.039(3)	-0.001(3)	0.003(2)	-0.003(2)	0.0334(14)
O(7)	0.6602(4)	0.5397(4)	0.0558(10)	1.0	O	0.011(2)	0.017(2)	0.029(3)	0.003(2)	0.0024(19)	0.0033(19)	0.0193(11)
O(8)	0.6503(5)	0.7323(4)	0.4004(10)	1.0	O	0.018(3)	0.029(3)	0.018(3)	-0.001(2)	0.004(2)	0.004(2)	0.0228(12)
O(9)	0.6832(4)	0.3468(4)	0.1941(9)	1.0	O	0.012(2)	0.027(3)	0.014(2)	0.006(2)	0.0006(18)	0.0015(19)	0.0179(11)
O(10)	0.6773(5)	0.1541(4)	0.3523(10)	1.0	O	0.017(2)	0.019(3)	0.023(3)	0.002(2)	0.003(2)	-0.001(2)	0.0202(11)
O(11)	0.5653(5)	0.9052(4)	0.7303(10)	1.0	OH	0.020(3)	0.019(3)	0.031(3)	0.002(2)	0.002(2)	0.003(2)	0.0238(12)
O(12)	0.8933(4)	0.5458(4)	0.5733(9)	1.0	OH	0.015(2)	0.019(2)	0.017(2)	0.002(2)	0.0033(19)	0.0053(19)	0.0171(10)
O(13)	0.8581(8)	0.9925(6)	0.2831(18)	1.0	H ₂ O	0.057(5)	0.040(4)	0.083(6)	-0.012(4)	-0.026(4)	0.020(3)	0.066(3)
O(14A)	0.889(2)	0.156(2)	0.904(5)	0.5	H ₂ O	0.040(12)	0.058(14)	0.059(14)	0.018(10)	0.012(9)	0.005(8)	0.051(4)
O(14B)	0.856(2)	0.113(2)	0.822(5)	0.5	H ₂ O	0.040(12)	0.058(14)	0.059(14)	0.018(10)	0.012(9)	0.005(8)	0.051(4)
H(1)	0.481(3)	0.875(7)	0.692(17)	1.0		0.03566(0)						
H(2)	0.882(8)	0.603(5)	0.714(10)	1.0		0.02569(0)						
H(3)	0.847(15)	0.953(11)	0.111(10)	1.0		0.09960(0)						
H(4)	0.789(9)	1.038(11)	0.31(3)	1.0		0.09960(0)						
H(5)	0.969(12)	0.179(18)	1.01(4)	0.5		0.07653(0)						
H(6)	0.86(2)	0.079(8)	0.91(6)	0.5		0.07653(0)						
H(7)	0.786(18)	0.13(2)	0.664(19)	0.5		0.07653(0)						
H(8)	0.799(17)	0.13(2)	0.98(2)	0.5		0.07653(0)						

pancy (Table 6). The K(1) site is coordinated by six O atoms, three OH and one H₂O groups, with $\langle K(1)-\phi \rangle = 2.96$ Å; the K(2) site is coordinated by twelve O atoms, with $\langle K(2)-O \rangle = 3.098$ Å (Table 5). The total content of K is 2.91 *apfu*. In ershovite, the total content of K is 3 *apfu* (Table 6).

Anion sites

In paraershovite, atoms O(1)–O(10) coordinate Si in tetrahedra; they receive bond valence in the range 1.88–2.13 *vu* (valence units) [except for O(6), 1.57 *vu*; this issue will be addressed later in the text] (Table 7), and they are O atoms. An H₂O group and OH groups occur at the O(13) and O(11) and O(12) sites, respectively; O(11)=OH is a silanol group, part of the Si(4) tetrahedron (Table 7). The anion speciation for O(1)–O(13) is exactly the same as in ershovite. The only difference in the anion arrangement in paraershovite and ershovite results from different stereochemistry of the O(14) site. In paraershovite, the O(14) site splits into two, O(14A) and O(14B) (Table 4). Each site is occupied by H₂O at 50% occupancy (Tables 4, 7). In ershovite, O(14) is the central atom of an H₂O group,

and the O(14) site does not split. For paraershovite, the sum of the anions listed above gives O₂₀(OH)₄(H₂O)₄ *pfu*, as in ershovite.

Structure topology

In the structure of paraershovite, Fe³⁺-dominant M polyhedra share common edges to form a brookite-like [M₂O₆(OH)₂] chain along [001] (Fig. 3a). These chains share common edges with Na(1) and Na(2) octahedra to constitute an interrupted O (octahedral) sheet (Fig. 3a). As the Na(2) site is occupied by Na at 50%, only half of the Na(2) sites (shown as navy blue spheres in Fig. 3a) are occupied. Therefore two Na sites give Na₃□ *pfu*. In paraershovite, the composition of the sheet is [Na₃□₂Fe³⁺₂O₈(OH)₂(H₂O)₄], where □₂ is the sum of the vacancy characteristic of the topology of the interrupted sheet (as in ershovite, Fig. 3b) and a vacancy due to partial occupancy of the Na(2) site. In ershovite, the composition of the interrupted sheet is [Na₄□₂M^{2.5+}₂O₈(OH)₂(H₂O)₄]. Note that vacancy–Na(2) order in paraershovite can result in two types of sheets, one being Na-dominant as in ershovite (Fig. 3b) and the other being vacancy-dominant [Fig. 3a, omitting

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR PARAERSHOVITE

<i>M</i> – O(2)a	1.938(5)	Na(1) – O(13)H ₂ O	2.314(8)	Na(2) – O(4)h	2.236(9)
<i>M</i> – O(12)b OH	1.940(5)	Na(1) – O(6)	2.318(7)	Na(2) – O(2)e	2.316(9)
<i>M</i> – O(4)b	1.987(5)	Na(1) – O(2)e	2.393(6)	Na(2) – O(14B)f H ₂ O	2.44(2)
<i>M</i> – O(12)a OH	2.063(5)	Na(1) – O(4)	2.439(6)	Na(2) – O(6)	2.487(9)
<i>M</i> – O(5)b	2.097(4)	Na(1) – O(14A)e H ₂ O	2.45(3)	Na(2) – O(12) OH	2.624(9)
<i>M</i> – O(5)c	2.098(4)	Na(1) – O(14B)e H ₂ O	2.44(3)	Na(2) – O(5)e	2.632(9)
< <i>M</i> – φ>	2.021	Na(1) – O(13) H ₂ O	2.452(9)	<Na(2) – φ>	2.46
		<Na(1) – φ>	2.39		
Si(1) – O(10)	1.599(5)	Si(2) – O(4)	1.590(5)	Si(3) – O(5)h	1.611(5)
Si(1) – O(2)	1.600(5)	Si(2) – O(8)	1.622(5)	Si(3) – O(9)h	1.623(5)
Si(1) – O(9)	1.647(5)	Si(2) – O(3)g	1.624(5)	Si(3) – O(1)	1.629(5)
Si(1) – O(1)	1.654(5)	Si(2) – O(7)	1.636(5)	Si(3) – O(7)h	1.629(5)
<Si(1) – O>	1.625	<Si(2) – O>	1.618	<Si(3) – O>	1.623
Si(4) – O(6)	1.595(6)	Si(1) – O(1) – Si(3)	134.7(3)		
Si(4) – O(11)OH	1.618(5)	Si(2)h – O(3) – Si(4)	146.0(4)		
Si(4) – O(8)	1.632(5)	Si(2) – O(7) – Si(3)g	132.3(3)		
Si(4) – O(3)	1.636(5)	Si(2) – O(8) – Si(4)	145.2(3)		
<Si(4) – φ>	1.620	Si(1) – O(9) – Si(3)g	142.1(3)		
K(1) – O(11)l OH	2.690(5)	K(2) – O(1)	2.824(4)	×2	
K(1) – O(10)h	2.838(5)	K(2) – O(9)	2.982(5)	×2	
K(1) – O(10)	2.842(5)	K(2) – O(7)	3.091(5)	×2	
K(1) – O(14B) H ₂ O	2.95(3)	K(2) – O(7)h	3.106(5)	×2	
K(1) – O(9)h	2.948(5)	K(2) – O(3)	3.270(5)	×2	
K(1) – O(11)j OH	2.963(6)	K(2) – O(8)	3.317(5)	×2	
K(1) – O(11)b OH	2.979(6)	<K(2) – O>	3.098		
K(1) – O(1)	3.026(5)				
K(1) – O(8)b	3.064(5)	Na(2) – O(14A)f H ₂ O	1.81(2)		
K(1) – O(3)j	3.120(5)	O(14A) H ₂ O – O(14B) H ₂ O	0.64(2)		
K(1) – O(14A) H ₂ O	3.24(2)				
<K(1) – φ>	2.96				

a = *x* – 1, *y*, *z*; b = –*x* + 1, –*y* + 1, –*z* + 1; c = *x* – 1, *y*, *z* + 1; d = –*x* + 2, –*y* + 2, –*z* + 1; e = –*x* + 2, –*y* + 1, –*z* + 1; f = –*x* + 2, –*y* + 1, –*z* + 2; g = *x*, *y*, *z* – 1; h = *x*, *y*, *z* + 1; i = *x*, *y* – 1, *z*; j = –*x* + 1, –*y* + 1, –*z* + 2. φ: unspecified anion, *i.e.*, O, OH, H₂O.

The two sites, O(14A) and O(14B), are 50% occupied by H₂O groups: (1) for the Na(1) and K(1) polyhedra, a contribution from O(14A) and O(14B) atoms is considered as ½, (2) for the Na(2) octahedron, only a contribution from the O(14B) atom is considered as 1.0 (see discussion in the text).

TABLE 6. REFINED SITE-SCATTERING (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR PARAERSHOVITE

Site	Refined site-scattering	Site population	Calculated site-scattering	<X–φ> _{calc} * (Å)	<X–φ> _{obs} (Å)
<i>M</i>	46.3(3)	1.38 Fe ³⁺ + 0.40 Ti + 0.10 Mn ²⁺ + 0.08 Al + 0.04 Mg 0.87 Fe ²⁺ + 0.68 Mn ²⁺ + 0.38 Ti + 0.07 Mg	48.7	2.013	2.021 2.071
Na(1)	18.1(3)	1.62 Na + 0.38 □ 2.0 Na	17.8	2.40	2.39 2.393
Na(2)	9.2(3)	1.18 □ + 0.82 Na 2.0 Na	9.0	2.39	2.46 2.409
¹⁰ K(1)	36.7(3)	1.91 K + 0.09 □ 2.0 K	36.3	2.96	2.96 2.944
¹² K(2)	19.0	1.0 K 1.0 K	19.0	3.02	3.098 3.100

* X: cation, φ: anion; atomic radii are from Shannon (1976); <X–φ>_{calc} = *r*_{cat} + <*r*_{anion}>, where <*r*_{anion}> for an individual polyhedron has been calculated taking into account that all O atoms are [4]-coordinated except for [3]-coordinated O(6) and O(10); coordination numbers are shown for non-octahedral sites; second line of each entry corresponds to data for ershovite (Rastsvetaeva *et al.* 1991).

TABLE 7. BOND-VALENCE (νu)* TABLE FOR PARAERSHOVITE

Atom	Si(1)	Si(2)	Si(3)	Si(4)	M	Na(1)	Na(2)	K(1)	K(2)	H(1)	H(2)	H(3)	H(4)	H(5) [§]	H(6) [§]	H(7) [§]	H(8) [§]	Σ	
O(1)	0.92		0.99					0.07	0.14 ^{*2} ₁										2.12
O(2)	1.05				0.63	0.17	0.10												1.95
O(3)		0.99		0.96				0.06	0.04 ^{*2} ₁										2.05
O(4)		1.09			0.55	0.16	0.11				0.06								1.91
O(5)			1.03		0.40		0.06												1.89
					0.40														
O(6)				1.07		0.19	0.07					0.18		0.03	0.03				1.57
O(7)		0.96	0.98							0.06 ^{*2} ₁									2.00
										0.06 ^{*2} ₁									
O(8)		1.00		0.97				0.07	0.03 ^{*2} ₁										2.07
O(9)	0.94		1.00					0.10	0.09 ^{*2} ₁										2.13
O(10)	1.04							0.13		0.26			0.18				0.07	0.04	1.88
								0.13											
O(11)				1.01				0.22		0.74									2.15
								0.09 ^{*2} ₁											
O(12)					0.62		0.06				0.94								2.06
					0.44														
O(13)						0.20						0.82	0.82						1.99
						0.15													
O(14A) [§]						0.08		0.02						0.47	0.47				1.04
O(14B) [§]						0.08	0.08	0.05									0.43	0.46	1.10
Aggregate charge	3.98	4.04	4.00	4.01	3.04	1.03	0.48	1.03	0.84	1.0	1.0	1.0	1.0	0.5	0.5	0.5	0.5		
Total	4.00	4.00	4.00	4.00	3.13	0.81	0.41	1.0	1.0	1.0	1.0	1.0	1.0	0.5	0.5	0.5	0.5		

* The bond-valence parameters are from Brown (1981) and Brown & Altermatt (1985); [§] 50% occupied.

TABLE 8. HYDROGEN BONDING IN PARAERSHOVITE

Donor (D) species	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	\angle DHA (°)	\angle HOH (°) H...H (Å)
OH	O(11) - H(1)...O(10)a	0.91(2)	1.62(3)	2.519(7)	169(9)	
OH	O(12) - H(2)...O(4)b	0.90(2)	2.39(4)	3.222(6)	154(7)	
H ₂ O	O(13) - H(3)...O(6)c	0.91(2)	1.83(2)	2.74(1)	180(17)	109(10)
	O(13) - H(4)...O(10)d	0.91(2)	1.82(4)	2.706(8)	166(15)	1.48(4)
H ₂ O	O(14A) - H(5)...O(6)e	0.93(3)	2.49(10)	3.32(3)	149(18)	111(4)
	O(14A) - H(6)...O(6)f	0.97(5)	2.43(9)	3.34(2)	157(26)	1.56(9)
H ₂ O	O(14B) - H(7)...O(10)	1.10(7)	1.95(6)	3.04(3)	172(15)	101(4)
	O(14B) - H(8)...O(10)b	1.05(4)	2.38(4)	3.42(3)	177(16)	1.66(10)

a = -x + 1, -y + 1, -z + 1; b = x, y, z + 1; c = x, y, z - 1; d = x, y + 1, z; e = -x + 2, -y + 1, -z + 2; f = x, y - 1, z.

the Na(2) atoms]. In ershovite, there is only one (Na-dominant) sheet (Fig. 3b). In paraershovite (and ershovite), the Si(1)-Si(4) tetrahedra share their vertices to form an amphibole-like (Si₄O₁₀OH) ribbon along [001] (Figs. 3a, b). The repeat distance along this ribbon corresponds to the *c* cell-parameter 5.2263(3) Å. In the structure of paraershovite, linkage of the amphibole-like ribbon and the interrupted O sheet occurs *via* common vertices of tetrahedra of the ribbon and octahedra of

the sheet: each Fe³⁺ octahedron shares three common vertices with three Si tetrahedra. Rastvetaeva *et al.* (1991) gave a detailed comparison of the amphibole-like (Si₄O₁₀OH) ribbon in ershovite and an amphibole (Si₄O₁₁) ribbon, and discussed the stacking of those ribbons with chains of M octahedra in both structures. Figures 3c and 3d show linkage of the amphibole-like (Si₄O₁₀OH) ribbons and a sheet in paraershovite and ershovite, respectively. In paraershovite, two

amphibole-like ribbons, $2(\text{Si}_4\text{O}_{10}\text{OH})$, and an interrupted sheet, $\text{Na}_3\text{□}_2\text{Fe}^{3+}_2\text{O}_8(\text{OH})_2(\text{H}_2\text{O})_4$, constitute the structural unit $\text{Na}_3\text{□}_2\text{Fe}^{3+}_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$, ideally with a charge of 3^- (note that being common for two chains and the sheet, eight O anions have been counted once as anions of the amphibole-like ribbon). Along [100], structural units $\text{Na}_3\text{□}_2\text{Fe}^{3+}_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$ connect (1) through interstitial atoms K(1) and K(2) with a total content of ~ 3 apfu and a charge of 3^+ , and (2) via hydrogen bonds between the silanol group $\text{O}(11)=\text{OH}$ and the oxygen atom O(10) belonging to the Si(1) tetrahedron (Fig. 3e and Fig. 1f for ershovite).

Hydrogen bonding

Details of hydrogen bonding in paraershovite are given in Table 8. Figures 3e and 3f show the arrangement of hydrogen bonds [except for a hydrogen bond $\text{O}(11)-\text{H}(1)\dots\text{O}(10)$ shown in Fig. 3c]. The H(1) and H(2) atoms of the OH groups at the O(11) and O(12) sites form strong and weak hydrogen bonds 1.62 and 2.39 \AA in length, respectively (Table 8, Figs. 3c, e). The H(3) and H(4) atoms belong to an (H_2O) group at the O(13) site, and they form strong hydrogen bonds $\sim 1.83 \text{ \AA}$ in length in the plane of the interrupted sheet [$A = \text{O}(6)$] and with the O(10) atom of the amphibole-like ribbon, respectively. The geometry of hydrogen bonding at the O(11) (= OH) and at the O(13) (= H_2O) sites is identical to that in ershovite (Figs. 3d, f). However, the geometry of hydrogen bonding of the OH group at the O(12) site is different: in ershovite, the H(6) atom occurs just above the O(12) site (Fig. 3f) and does not form any hydrogen bond (Rastvetaeva *et al.* 1991); in paraershovite, the H(2) atom has shifted toward the position of the Na(2) atom (59% vacant) and forms a weak hydrogen bond with O(4) (Fig. 3e). Inclination of the OH vector toward the vacant sites occurs in other minerals, such as the dioctahedral micas (Beran 2002).

Effect of vacancy–Na(2) order on the hydrogen bonding

In paraershovite, the O(14) site splits into the O(14A) and O(14B) sites, each 50% occupied by H_2O . The O(14a) and Na(2) sites (the latter occupied at 41% occupancy) are separated by a short distance, 1.81 \AA , and can be only partly occupied. We suggest that vacancy–Na(2) order results in a splitting of the O(14) site. Where the Na(2) site is vacant, the H(5) and H(6) atoms of an (H_2O) group at the O(14A) site form weak hydrogen bonds $\sim 2.46 \text{ \AA}$ in length with two O(6) atoms. Where the Na(2) site is occupied, the H(7) and H(8) atoms of an (H_2O) group at the O(14B) site form hydrogen bonds 1.95 and 2.38 \AA in length with two O(10) atoms. Note that the O(6) atom receives a low incident bond-valence sum of 1.57 *vu* (Table 7).

We suggest that this is due to the vacancy–Na(2) order, where positions of O and H atoms change; it is difficult to determine their positional parameters accurately from the structure refinement. In ershovite, the Na(2) site is fully occupied by Na, and the geometry of the hydrogen bonding around O(14) is similar to that around O(14B) in paraershovite. To conclude, vacancy–Na(2) order results in a split of the O(14A) site and a flip of H_2O groups at the site in accord with the occupancy of the Na(2) site.

ORIGIN OF PARAERSHOVITE

Khomyakov (1980) established that in zones of epithermal and supergene alteration of hyperagpaitic pegmatites, many highly alkaline primary minerals are replaced extensively by moderately alkaline secondary species. He developed the concept of “transformation mineral species” (Khomyakov 1995, 1996). Such a transformation mineral develops by alteration of the corresponding precursor phase, from which the newly formed mineral inherits its principal compositional and structural features. Gaft *et al.* (1982) carried out a fluorimetric analysis of a representative collection of minerals from the Khibina and Lovozero hyperagpaitic pegmatites. They found that the primary and secondary mineralization formed in reducing and oxidizing environments, respectively, which resulted in the substantial predominance of ferrous iron in highly alkaline minerals and of ferric iron in moderately alkaline minerals.

In interpreting our paraershovite data from the standpoint of the above concept, considering its occurrence in freshly exposed pegmatites virtually unaffected by weathering and its close similarity to ershovite based on composition, structure and properties, we consider it most likely that paraershovite is a product of transformation of ershovite, a secondary phase that replaced the pre-existing higher-temperature primary phase (ershovite) during the epithermal stage of pegmatite formation.

So far, the most detailed work on transformation mineral species has been done on titanosilicates and zirconosilicates belonging to the following families: lomonosovite (lomonosovite \rightarrow murmanite), vuonnemite (vuonnemite \rightarrow epistolite), lovozerite (zirsinalite \rightarrow lovozerite, kazakovite \rightarrow tisinialite) and keldyshite (parakeldyshite \rightarrow keldyshite \rightarrow species M34). This one-to-one relation between primary and secondary minerals in these series suggests the possibility of reconstructing the primary mineralogy of rocks and ores from products of their alteration. This type of transformation relation between the primary and secondary iron-bearing silicates compositionally similar to ershovite and paraershovite at Khibina was established earlier (Khomyakov 1995) for the series “iron-rich shafranovskite” (species M20), $(\text{Na},\text{K})_6\text{Fe}^{2+}_3\text{Si}_9\text{O}_{24}\cdot 6\text{H}_2\text{O} \rightarrow$ species M21, $(\text{Na},\text{K})_3\text{Fe}^{3+}_3\text{Si}_9\text{O}_{24}\cdot n\text{H}_2\text{O}$. As shown in the work cited,

the secondary mineral of this series actively develops from the primary phase by loss of alkalis. To compensate for the loss of a positive charge, oxidation of Fe^{2+} takes place. It is highly possible that the oxidation of Fe^{2+} simplifies the reaction, as it helps to keep the topology of the structure approximately the same. The ease of transformation under atmospheric conditions (no Fe^{2+} oxidation) has been demonstrated experimentally and documented both by chemical analysis and by infrared spectroscopy (Khomyakov *et al.* 1978). It has been established that up to half the Na and K is leached out by distilled water at room temperature (and at 100°C), with simultaneous oxidation of an equivalent amount of divalent iron to the trivalent state.

There is an analogy between paraershovite – ershovite and paravinogradovite, ideally $(\text{Na}, \square)_2 [(\text{Ti}^{4+}, \text{Fe}^{3+})_4 \{\text{Si}_2\text{O}_6\}_2 \{\text{Si}_3\text{AlO}_{10}\}(\text{OH})_4] \text{H}_2\text{O}$, (Khomyakov *et al.* 2003) – vinogradovite, ideally $\text{Na}_5 \text{Ti}^{4+}_4 (\text{Si}_7\text{Al}) \text{O}_{26} (\text{H}_2\text{O})_3$ (Kalsbeek & Rønso 1992, Rastsvetaeva & Andrianov 1984). Paravinogradovite is chemically related to vinogradovite by the substitution $\square_3 + \text{Fe}^{3+} + (\text{OH})^-_4 + (\text{H}_2\text{O})_2 \rightarrow \text{Na}_3 + \text{Ti}^{4+} + \text{O}^{2-}_4 + \square_2$ (*cf.* paraershovite \rightarrow ershovite, $\square + \text{Fe}^{3+}_2 \rightarrow \text{Na}^+ + \text{M}^{2.5+}_2$). It is apparent that both transformations, ershovite \rightarrow paraershovite and vinogradovite \rightarrow paraevinogradovite, are accompanied by loss of Na^+ and oxidation of Fe^{2+} to Fe^{3+} .

CONCLUSIONS

There is a close structural relation between paraershovite and ershovite:

(1) Paraershovite and ershovite are isostructural.

(2) Paraershovite is chemically related to ershovite by the heterovalent substitution $\square + \text{Fe}^{3+}_2 \rightarrow \text{Na}^+ + \text{M}^{2.5+}_2$, where $\text{M}^{2.5+} = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ti}^{4+}$.

(3) We write the ideal formulae of paraershovite and ershovite as $\text{Na}_3\text{K}_3\text{Fe}^{3+}_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$ and $\text{Na}_4\text{K}_3(\text{Fe}^{2+}, \text{Mn}, \text{Ti})_2(\text{Si}_4\text{O}_{10}\text{OH})_2(\text{OH})_2(\text{H}_2\text{O})_4$. These formulae tell us exactly about the type of Si–O radical, and which H_2O groups are ligands of the cations in the interrupted O sheet, not interstitial species. Previously, the ideal formula and structural formulae of ershovite were written as $\text{Na}_4\text{K}_3(\text{Fe}^{2+}, \text{Mn}, \text{Ti})_2 (\text{Si}_8\text{O}_{20}) (\text{OH})_4 \cdot 4\text{H}_2\text{O}$ (Khomyakov *et al.* 1993) and $[\text{Na}_3\text{K}_3(\text{H}_2\text{O})_4] \{[\text{M}_2(\text{OH})_2] [(\text{Si}_8\text{O}_{20}) (\text{OH})_2]\}$, where $\text{M} = \text{Fe}^{2+}, \text{Mn}, \text{Ti}, \text{Mg}$ (Rastsvetaeva *et al.* 1991).

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