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PUNKARUAIVITE, $LiTi_2[Si_4O_{11}(OH)](OH)_2{\bullet}H_2O$, A NEW MINERAL SPECIES FROM HYDROTHERMAL ASSEMBLAGES, KHIBINY AND LOVOZERO ALKALINE MASSIFS, KOLA PENINSULA, RUSSIA

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Abstract

Punkaruaivite, ideally $LiTi_2[Si_4O_{11}(OH)](OH)_2{\bullet}H_2O$, is a new species of Li titanosilicate [monoclinic, $C2/c$, a 26.688(2), b 8.7568(7), c 5.2188(5) Å, β 91.189(2)°, V 1219.4(2) Å^3, $Z = 4$], chemically and structurally related to lintisite. The mineral is found in two different hydrothermal veins, within the Khibiny and Lovozero alkaline massifs, Kola Peninsula, Russia. In the Lovozero massif, it occurs within an ussingite – aegirine – microcline vein in nepheline syenite at Mt. Punkaruaiv in association with anglesite, belovite-(Ce), chkalovite, epididymite, epistolite, eudialyte, ferronordite-(Ce), karnasurtite-(Ce), lamprophyllite, lorenzenite, manganoneptunite, manganonordite-(Ce), monazite-(Ce), murmanite, natrolite, pectolite, rhabdophane-(Ce), steenstrupine-(Ce), tainiolite, tugtupite and vitusite-(Ce). In the Khibiny massif, it is found in a natrolite–microcline vein in foyaite at Mt. Eveslogchorr in association with aegirine, albite, belovite-(La), chivruaiite, epididymite, kuzmenkoite-Mn, lamprophyllite, monazite-(La), murmanite, palygorskite, pectolite, safflorite, sphalerite and tugtupite. In both veins, it forms small (up to 3 mm long) tabular elongate crystals, which grew on the walls of voids within leached ussingite (Lovozero massif) or natrolite (Khibiny massif). The mineral is transparent, yellowish brown to colorless, with a vitreous luster and a white streak. It has a perfect cleavage on {100}, and the pattern of fractures is step-like. The Mohs hardness is 4–5. In transmitted light, the mineral is brownish yellow, with a faint pleochroism: Y light brownish yellow, X brownish yellow; no dispersion is observed. Punkaruaivite is biaxial (–), α 1.658(2), β 1.696(2), γ 1.726(5) (for $\lambda = 589$ nm), $2V_{meas}$ 85(5)°, $2V_{calc}$ 82°. The optical orientation is $X = b$, $Y \wedge c = 12°$. $D_{calc} = 2.55$ g.cm^{-3}, $D_{meas} = 2.60(5)$ g.cm^{-3}. The mean chemical composition determined with an electron microprobe is (wt.%): Li_2O 3.22 (flame photometry), Na_2O 0.29, K_2O 0.14, CaO 0.01, MnO 0.31, FeO 0.21, Al_2O_3 0.05, SiO_2 51.35, TiO_2 32.50, Nb_2O_5 1.06, H_2O 10.50 (Penfield method), total 99.64 wt.%. The empirical formula, calculated on the basis of Si + Ti + Nb + Fe + Mn + Al = 6 *apfu* and taking into account results of a single-crystal study, is $(Li_{1.02}Na_{0.04}K_{0.01})_{\Sigma 1.07}$ $\{(Ti_{1.92}Nb_{0.04}Mn_{0.02}Fe^{3+}{}_{0.01})_{\Sigma 1.99}$ $(OH)_{2.00}[Si_{4.03}O_{11.03}(OH)_{0.97}]\}{\bullet}1.26H_2O$. The simplified formula is $LiTi_2[Si_4O_{11}(OH)](OH)_2{\bullet}H_2O$. The strongest six reflections in the powder-diffraction pattern [d in Å(I)(hkl)] are: 13.3(100)(200), 6.23(80)(310), 4.38(60)(020), 3.50(80)(710), 3.01(70)(42) and 2.81(70)(910). The structure of punkaruaivite was refined to $R_1 = 0.084$ on the basis of 1347 unique observed reflections. It is similar to the structures of vinogradovite, lintisite, and kukisvumite, and based upon a 3D framework consisting of parallel chains of corner-sharing SiO_4 tetrahedra linked into a framework by chains of corner-sharing LiO_4 tetrahedra and edge-sharing TiO_6 octahedra. The framework contains large channels occupied by H_2O molecules. The mineral is named after its type locality at Mt. Punkaruaiv, in the Lovozero massif, Kola Peninsula, Russia. Punkaruaivite is a Na-free analogue of lintisite and related to it according to the substitution mechanism $Na^+ + O^{2-} \leftrightarrow \square + (OH)^-$.

Keywords: punkaruaivite, Li titanosilicate, new mineral species, crystal structure, Lovozero alkaline massif, Kola Peninsula, Russia.

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SOMMAIRE

La punkaruaivite, de compositon idéale $LiTi_2[Si_4O_{11}(OH)](OH)_2•H_2O$, est une nouvelle espèce de titanosilicate de lithium [monoclinique, *C*2/*c*, *a* 26.688(2), *b* 8.7568(7), *c* 5.2188(5) Å, β 91.189(2)°, *V* 1219.4(2) Å^3, *Z* = 4], chimiquement et structuralement apparentée à la lintisite. Nous avons découvert ce minéral dans des veines hydrothermales des massifs de Khibiny et de Lovozero, péninsule de Kola, en Russie. A Lovozero, on trouve la punkaruaivite dans une veine à ussingite – aegyrine – microcline dans une syénite néphélinique au mont Punkaruaiv, en association avec anglésite, bélovite-(Ce), chkalovite, epididymite, epistolite, eudialyte, ferronordite-(Ce), karnasurtite-(Ce), lamprophyllite, lorenzenite, manganoneptunite, manganonordite-(Ce), monazite-(Ce), murmanite, natrolite, pectolite, rhabdophane-(Ce), steenstrupine-(Ce), tainiolite, tugtupite et vitusite-(Ce). A Khibiny, on la trouve dans une veine de natrolite + microcline dans une foyaïte au mont Eveslogchorr, en association avec aegyrine, albite, bélovite-(La), chivruaiite, epididymite, kuzmenkoïte-Mn, lamprophyllite, monazite-(La), murmanite, palygorskite, pectolite, safflorite, sphalérite et tugtupite. Dans les deux cas, elle se présente en cristaux tabulaires atteignant une longueur de 3 mm, disposés sur les parois de cavités formées par dissolution de l'ussingite (Lovozero) ou natrolite (Khibiny). Il s'agit d'un minéral transparent, brun jaunâtre à incolore, avec un éclat vitreux et une rayure blanche. Il possède un clivage {100} parfait, et des fractures en escalier. La dureté de Mohs est dans l'intervalle 4–5. En lumière transmise, le minéral est jaune brunâtre, avec un léger pléochroïsme: *Y* jaune brunâtre pâle, *X* jaune brunâtre; aucune dispersion n'est observée. La punkaruaivite est biaxe (–), α 1.658(2), β 1.696(2), γ 1.726(5) (λ = 589 nm), $2V_{\text{mes}}$ 85(5)°, $2V_{\text{calc}}$ 82°. L'orientation optique est $X = b$, $Y \wedge c = 12°$. $D_{\text{calc}} = 2.55$ g.cm^{-3}, $D_{\text{mes}} = 2.60(5)$ g.cm^{-3}. La composition chimique, déterminée avec une microsonde électronique, est: Li_2O 3.22 (photométrie de flamme), Na_2O 0.29, K_2O 0.14, CaO 0.01, MnO 0.31, FeO 0.21, Al_2O_3 0.05, SiO_2 51.35, TiO_2 32.50, Nb_2O_5 1.06, H_2O 10.50 (méthode de Penfield), pour un total de 99.64% (poids). La formule chimique, calculée sur une base de Si + Ti + Nb + Fe + Mn + Al = six atomes par formule unitaire (*apfu*) et tenant compte des résultats de notre étude sur monocristal, est $(Li_{1.02}Na_{0.04}K_{0.01})_{\Sigma 1.07}$ $\{(Ti_{1.92}Nb_{0.04}Mn_{0.02}Fe^{3+}_{0.01})_{\Sigma 1.99}(OH)_{2.00}$ $[Si_{4.03}O_{11.03}(OH)_{0.97}]\}•1.26H_2O$. La formule simplifiée est $LiTi_2[Si_4O_{11}(OH)](OH)_2•H_2O$. Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å(I)(*hkl*)] sont: 13.3(100)(200), 6.23(80)(310), 4.38(60)(020), 3.50(80)(710), 3.01(70)(42) et 2.81(70)(910). La structure de la punkaruaivite a été affinée jusqu'à un résidu R_1 de 0.084 en utilisant 1347 réflexions uniques observées. Elle ressemble à la structure de la vinogradovite, de la lintisite, et de la kukisvumite; elle présente une trame tri-dimensionnelle faite de chaînes parallèles de tétraèdres SiO_4 interconnectées par des chaînes de tétraèdres LiO_4 à coins partagés et d'octaèdres TiO_6 à arêtes partagées. La charpente contient des canaux où logent des molécules H_2O. Le nom du minéral rappelle la localité type au mont Punkaruaiv, massif de Lovozero, péninsule de Kola, en Russie. La punkaruaivite est l'analogue de la lintisite dépourvu de Na, et serait liée à celle-ci selon le mécanisme de substitution $Na^+ + O^{2-} \leftrightarrow \square + (OH)^-$.

(Traduit par la Rédaction)

Mots-clés: punkaruaivite, titanosilicate de lithium, nouvelle espèce minérale, structure cristalline, complexe alcalin de Lovozero, péninsule de Kola, Russie.

INTRODUCTION

Punkaruaivite is a new member of the series of vinogradovite-related titanosilicates of the Khibiny–Lovozero alkaline complex. The others include vinogradovite itself, $Na_4(Na,K)Ti_4[Si_2O_6]_2[Si_3AlO_8]O_6•2H_2O$ (Rastsvetaeva *et al.* 1968), lintisite, $Na_3LiTi_2[Si_4O_{12}]O_2•2H_2O$ (Khomyakov *et al.* 1990), kukisvumite, $Na_3Zn_{0.5}Ti_2[Si_4O_{12}]O_2•2H_2O$ (Yakovenchuk *et al.* 1991), manganokukisvumite, $Na_3Mn_{0.5}Ti_2[Si_4O_{12}]O_2•2H_2O$ (Gault *et al.* 2004), and paravinogradovite, $(Na,\square)_2[(Ti,Fe)_4[Si_2O_6]_2[Si_3AlO_{10}](OH)_4]H_2O$ (Khomyakov *et al.* 2003). Crystal structures of these minerals are based upon pyroxene-like Si_2O_6 chains linked into a framework by TiO_6 octahedra and MO_4 tetrahedra (*M* = Li, Zn, Mn) (Rastsvetaeva & Andrianov 1984, Kalsbeek & Rønsbo 1992, Merlino *et al.* 1992, 2000). The framework cavities are occupied by Na^+ cations and H_2O molecules. All the species are rare late-stage hydrothermal minerals formed as a result of the alteration of earlier titanosilicates, *e.g.*, lorenzenite, lamprophyllite, lomonosovite, murmanite. Punkaruaivite was discovered during a systematic re-investigation of well-known mineral localities of the Khibiny and Lovozero massifs that was initiated by the "Apatite" mining company in 2000. Punkaruaivite was found within two separate veins previously described in detail by Semenov (1972, vein no. 71, Lovozero massif) and Yakovenchuk *et al.* (2005, vein no. 18, Khibiny massif). Another locality (Mt. Alluaiv, Lovozero massif) contains a phase that is intermediate between punkaruaivite and lintisite.

Punkaruaivite is named after one of its type localities, Mount Punkaruaiv, in the Lovozero massif, Kola Peninsula, Russia. The new mineral species and the name have been approved by the Commission on New Minerals and mineral Names of IMA (IMA 2008–018). Cotype material is housed in the collections of the Mineralogical Museum of the St. Petersburg State University (Russia) and the Geological and the Mineralogical Museum of the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences (Apatity, Russia, No. 6441). We here describe its mode of occurrence at its three type-localities, its properties, and its structure.

OCCURRENCE

In the Lovozero massif, punkaruaivite occurs within a ussingite – aegirine – microcline pegmatite in nepheline syenite at Mt. Punkaruaiv (type locality no. 1). It was found in a large (15 m diameter and up to 1.5 m thickness) lens with concentric zoning. The vein selvage (up to 30 cm thick) is composed of large pale-brown tabular crystals of microcline (up to 20 cm diameter), interstitial eudialyte (separate crystals up to 4 cm in diameter and their segregations, up to 15 cm in diameter), lorenzenite (crystals up to 8 mm long), aegirine (radiating aggregates up to 8 cm in diameter) and murmanite (sheaf-like aggregates up to 5 cm in diameter).

The intermediate zone of the lens is formed by radiating aggregates of aegirine cemented by dark violet ussingite. Large crystals of pectolite–serandite replaced by manganese hydroxides and dark red crystals of manganoneptunite grow inside ussingite from the aegirine spherulites. These spherulites are often hollow, and contain well-shaped needle-like crystals of aegirine incrusted by chabazite-Ca and heulandite-Ca. In ussingite, there are yellow prismatic crystals of belovite-(Ce), pale pink plates of gerasimovskite, pale yellow karnasurtite-(Ce) and pale brown catapleiite.

The core (about 0.5 m thick) is composed of pale to dark violet ussingite with relics of sodalite, aggregates of platy crystals of murmanite and epistolite, eudialyte crystals, colorless crystals of chkalovite partially replaced by fine-grained bright crimson tugtupite or white epididymite, manganoneptunite, thin plates of taeniolite, radiating aggregates of manganonordite-(Ce) and ferronordite-(Ce), grains and well-formed crystals of steenstrupine-(Ce), powder-like aggregates of rhabdophane-(Ce), and grains of galena, sphalerite and löllingite. Cerussite forms a fine-grained rim around galena crystals. In some cases, ussingite is replaced by fine-grained natrolite. The walls of voids in ussingite are encrusted by isometric and small crystals of gmelinite-Ca. Punkaruaivite usually occurs in voids as brownish yellow flattened prismatic crystals (up to 3 mm long, Fig. 1) in close association with chkalovite, manganonordite-(Ce), ferronordite-(Ce), manganoneptunite, belovite-(Ce), sphalerite and gmelinite-Ca. Rarely, it forms radiating aggregates (up to 2 mm diameter) in sodalite in association with an undefined powdery substance.

In the Khibiny massif, punkaruaivite was found in the natrolite–microcline hydrothermal assemblage in gneissose foyaite at Mt. Eveslogchorr (type locality no. 3). The hydrothermal assemblage forms an irregularly shaped lens (up to 1 m wide) with a concentric zoned structure. The selvages (10–15 cm) are composed of microcline and aegirine aggregates with scarce rounded clusters of golden-brown lamprophyllite (up to 2 cm in diameter).

An intermediate microcline-rich zone (up to 50 cm) contains radiating aggregates of brownish purple bladed crystals and lamellar segregations of murmanite, black sword-shaped crystals of altered pectolite, greenish yellow belovite-(La), bright crimson eudialyte and silvery white prismatic safflorite. In the interstices of the thickest part of the zone, there are irregularly shaped crimson grains of tugtupite, partially replaced by white fine-grained epididymite, aggregates of yellow bladed sphalerite, and small flattened prisms of lamprophyllite.

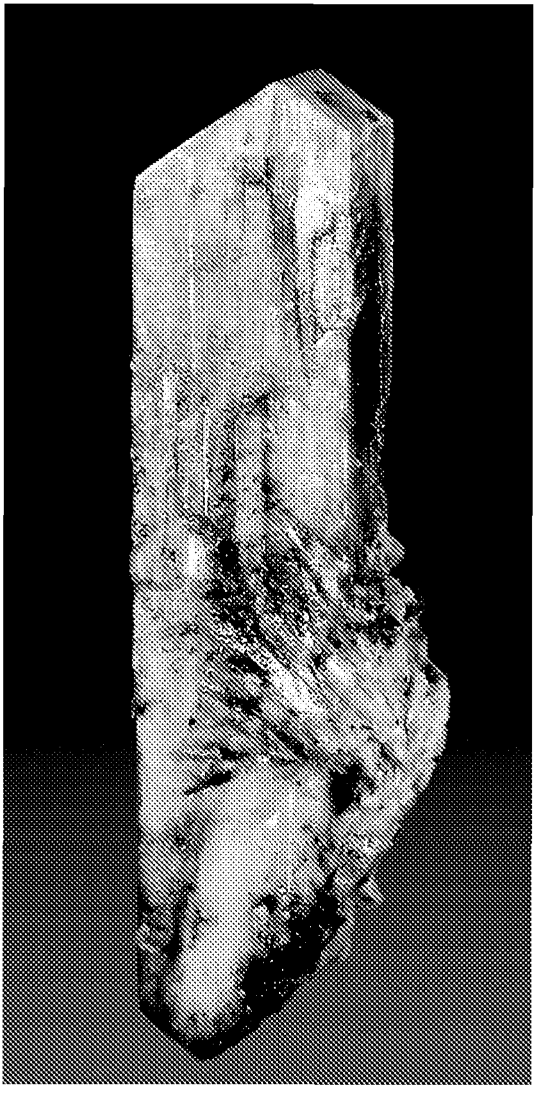

FIG. 1. Crystal of punkaruaivite from the ussingite – aegirine – microcline pegmatite in nepheline syenite at Mt. Punkaruaiv, Lovozero massif (type locality no. 1).

Kuzmenkoite-Mn forms small brown spherulites (up to 0.5 mm diameter) on microcline and aegirine crystals, in association with white disk-like crystals of epididymite and brown radiating aggregates of needle-like crystals of Mn-rich palygorskite and spherulites of colorless long-prismatic crystals of chivruaiite. Monazite-(La) also occurs here as brown fine-grained segregations (up to 8 mm diameter) in microcline.

The microcline–natrolite core (1 m in diameter and 15 cm thick) consists of cavernous fine-grained crystals of white natrolite, amongst which there are scarce tabular crystals of microcline, black sword-shaped crystals of altered pectolite, and greyish brown bladed crystals and spherulites of murmanite. Punkaruaivite occurs here as sheaf-like aggregates (up to 4 mm diameter, Fig. 2) of colorless flattened prismatic crystals in intimate association with murmanite, chivruaiite, kuzmenkoite-Mn, belovite-(La) and monazite-(La).

In locality no. 3, where we found the phase with composition intermediate between punkaruaivite and lintisite, the host rock is a microcline – sodalite – ussingite pegmatite in nepheline syenite of Mt. Alluaiv, in the Lovozero massif. It forms a large lens (up to 1 m thick) with a concentric zonal structure. The selvage of the lens consists of large crystals of microcline with interstitial nepheline, sodalite, eudialyte, generally replaced by catapleiite, lovozerite and zircon, keldyshite, aegirine, magnesioarfvedsonite, lorenzenite, lomonosovite and beta-lomonosovite, loparite-(Ce) and pyrochlore. The walls of the voids are covered by crystals of manganoneptunite, lamprophyllite and barytolamprophyllite, analcime, belovite-(Ce), murmanite, epistolite, catapleiite, vinogradovite, natrolite, phillipsite-Ca, chabazite-Ca, chabazite-K, and gmelinite-Ca. In some cases, the voids are filled with hydroxycancrinite, epididymite and beryllite. The punkaruaivite–lintisite phase forms small sheaf-like aggregates of elongate prismatic crystals (up to 5 mm long and 0.1 mm diameter) in close association with eudialyte, aegirine, arfvedsonite, zircon, belovite-(Ce), phillipsite-Ca and phillipsite-K (Fig. 3).

PHYSICAL AND OPTICAL PROPERTIES

Punkaruaivite forms well-shaped prismatic crystals flattened on (100) and elongate along [001] with dominant pinacoidal {100}, {001} and rhombic prismatic {011} forms. Usually, the crystals are arranged in sheaf-like and radiating aggregates. No twinning was observed. Macroscopically, punkaruaivite is brownish yellow to colorless with a vitreous luster. The mineral is transparent to translucent, with a white streak. Cleavage is perfect on {100}. Punkaruaivite is brittle and has a step-like fracture. The Mohs hardness is about 4½. The density determined by the float–sink method in Clerici solution is 2.60(5) g•cm^{-3}. This value is in good agreement with the calculated density, 2.55 g•cm^{-3}.

Punkaruaivite is biaxial negative, with indices of refraction α 1.658(2), β 1.696(2), γ 1.726(5) (for λ = 589 nm), $2V_{meas}$ 85(5)°, $2V_{calc}$ 82°. Optical orientation is $X = b$, $Y \wedge c$ =12°. In transmitted light, the mineral is brownish yellow, with a faint pleochroism: Y light

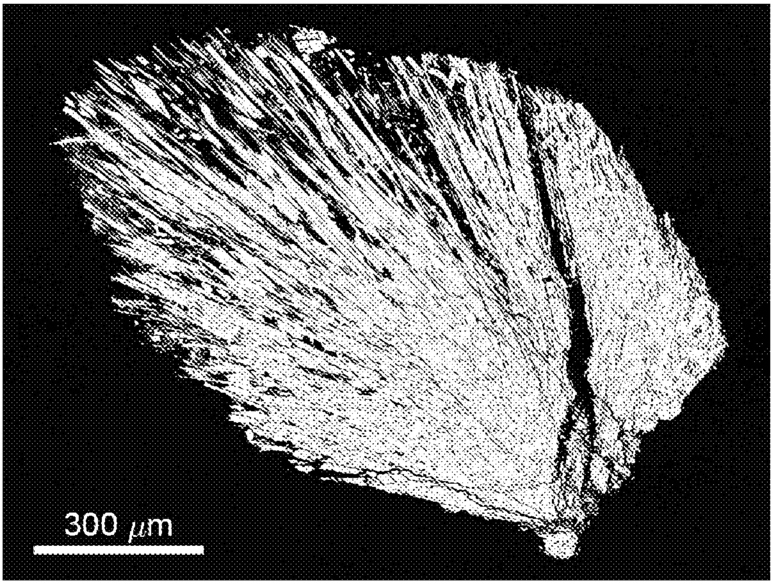

FIG. 2. Radiating aggregate of punkaruaivite from the natrolite–microcline hydrothermal assemblage in gneissose foyaite at Mt. Eveslogchorr, Khibiny massif (locality no. 2).

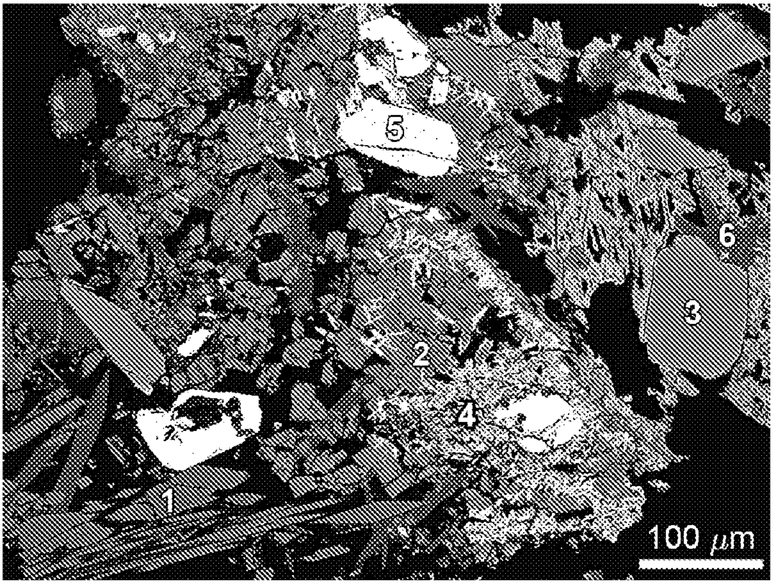

FIG. 3. BSE image of aggregate of punkaruaivite (1), eudialyte (2), aegirine (3), zircon (4), belovite-(Ce) (5) and phillipsite-Ca (6) from the microcline – sodalite – ussingite pegmatite in nepheline syenite at Mt. Alluaiv, in the Lovozero massif (locality no. 3).

brownish yellow, *X* brownish yellow. There is no dispersion. A Gladstone–Dale calculation provides a compatibility index of 0.049, which is regarded as good (Mandarino 1981).

CHEMICAL COMPOSITION

The chemical composition of punkaruaivite has been studied by wavelength-dispersion spectrometry using a Cameca MS–46 electron microprobe of the Geological Institute, Kola Science Centre of the Russian Academy of Sciences in Apatity, operating at 20 kV and 20–30 nA. The following standards were used: lorenzenite (Na, Ti), pyrope (Al), diopside (Si, Ca), wadeite (K), synthetic $MnCO_3$ (Mn), hematite (Fe) and metallic niobium (Nb). The H_2O and Li contents were determined by the Penfield and flame photometry methods, respectively, using purified material from type locality no. 1. Table 1 provides mean analytical results for five crystals of punkaruaivite from type locality no. 1 and a sheaf-like aggregate from locality no. 2. For comparison, we provide compositions of lintisite from the Lovozero massif (Mt. Alluaiv) and the phase from locality no. 3.

By analogy with lintisite and kukisvumite, the formula of punkaruaivite from locality no. 1 is calculated on the basis of Si + Ti + Nb + Fe + Mn + Al = 6 *apfu* as $(Na_{0.04}K_{0.01})_{\Sigma 0.05}Li_{1.02}\ (Ti_{1.92}Nb_{0.04}Mn_{0.02}Fe^{3+}{}_{0.01})_{\Sigma 1.99}\ [Si_{4.03}O_{11.03}(OH)_{0.97}](OH)_2{\bullet}1.26H_2O$. The composition of punkaruaivite from locality no. 2 corresponds to the empirical formula: $(Na_{0.04}K_{0.02}Ca_{0.02})_{\Sigma 0.08}\ Li_{1.00}(Ti_{1.96}Fe^{3+}{}_{0.02})_{\Sigma 1.98}\ [Si_{4.03}O_{11.12}(OH)_{0.88}](OH)_2{\bullet}\ 1.44H_2O$. The formula of the phase intermediate between punkaruaivite and lintisite (locality no. 3) is $(Na_{1.46}K_{0.03}Ca_{0.01})_{\Sigma 1.50}Li_{1.00}(Ti_{1.88}Al_{0.03}Nb_{0.02}Fe^{3+}{}_{0.02})_{\Sigma 1.95}\ [Si_{4.08}O_{12.60}(OH)_{1.40}]{\bullet}2.66H_2O$. The empirical formula of lintisite is $Na_{2.99}Li_{0.99}\ (Ti_{1.92}Nb_{0.05}\ Fe^{3+}{}_{0.02})_{\Sigma 1.99}\ [Si_{4.06}O_{12.10}]O_2{\bullet}2.01H_2O$ (Khomyakov *et al.* 1990). On the basis of the chemical data, punkaruaivite can be considered as a vacancy-bearing analogue of lintisite $Na_3LiTi_2[Si_4O_{12}]O_2{\bullet}2H_2O$ balanced according to the mechanism of substitution $Na^+ + O^{2-} \leftrightarrow \square + (OH)^-$. Its simplified formula can be written as $\square LiTi_2[Si_4O_{11}(OH)](OH)_2{\bullet}H_2O$.

CRYSTAL STRUCTURE

Experimental

The crystal of punkaruaivite selected for data collection was mounted on a STOE IPDS II Image-Plate-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic Mo$K\alpha$ X-radiation, with frame widths of 2° in ω, and with a 180 s count for each frame. The unit-cell parameters (Table 2) were refined using least-squares techniques. The intensity data were integrated and corrected for

Lorentz, polarization, and background effects using the STOE program X-AREA. The structure was solved by direct methods and refined to $R_1 = 0.0837$. The SHELXL program package was used for all structural calculations (Sheldrick 1997). The relatively high R_1 index, in our opinion, may be the result of the defect structure of the crystals of punkaruavite: at least part of the diffraction pattern showed diffuse scattering features that are indicative of certain structural defects, such as stacking faults and disorder. The presence of defects can be explained on the basis of the modular description of the vinogradovite family of minerals as proposed by Merlino & Pasero (1997) and Merlino *et al.* (2000). The final model included all atomic positional parameters, anisotropic displacement parameters for all atoms except Li and H_2O8, and a refinable weighting scheme of the structure factors. The final coordinates and anisotropic-displacement parameters of the atoms are given in Table 3, and selected interatomic distances, in Table 4. A list of observed and calculated structure-factors can be acquired from the Depository of Unpublished Data on the MAC website [document Punkaruaivite CM48_41].

TABLE 1. CHEMICAL COMPOSITION OF
THE PUNKARUAIVITE – LINTISITE SERIES OF MINERALS

	Punkaruaivite		Intermediate phase	Lintisite
	locality no. 1	locality no. 2	locality no. 3	Khomyakov *et al.* (1990)
Li_2O wt.%	3.22	3.19*	2.86*	2.68
Na_2O	0.29 ± 0.08	0.23	8.66	16.72
K_2O	0.14 ± 0.02	0.16	0.23	0.03
CaO	0.01 ± 0.01	0.19	0.14	–
MnO	0.31 ± 0.17	–	–	0.05
FeO	0.21 ± 0.11	0.24	0.24	0.28
Al_2O_3	0.05 ± 0.11	–	0.24	–
SiO_2	51.35 ± 0.74	51.62	46.94	44.03
TiO_2	32.50 ± 0.60	33.31	28.71	27.68
Nb_2O_5	1.06 ± 0.01	–	0.40	1.10
H_2O	10.50	11.06**	11.58**	6.55
Total	99.64	100.00	100.00	99.12
Li *apfu*	1.02	1.00	1.00	0.99
Na	0.04	0.04	1.46	2.99
K	0.01	0.02	0.03	–
Ca	–	0.02	0.01	–
Ti	1.92	1.96	1.88	1.92
Nb	0.04	–	0.02	0.05
Fe	0.01	0.02	0.02	0.02
Mn	0.02	–	–	–
Al	–	–	0.03	–
Si	4.03	4.03	4.08	4.06
H	5.49	5.76	6.72	4.02
O	15.26	15.44	16.66	16.11

* The amount of Li_2O is calculated to give Li = 1 *apfu*.
** The amount of H_2O is calculated to give a total of 100 wt.%.

TABLE 2. CRYSTALLOGRAPHIC DATA AND
REFINEMENT PARAMETERS FOR PUNKARUAIVITE

a (Å)	26.688(2)	Crystal size (mm)	0.12×0.24×0.06
b (Å)	8.7568(7)	Radiation	Mo*K*α
c (Å)	5.2188(5)	Total reflections	4586
β (°)	91.189(2)	Unique reflections	1502
V (Å^3)	1219.38(18)	Unique $\|F_o\| \geq 4\sigma_F$	1347
Space group	*C*2/*c*	R_1	0.0837
Z	4	wR_2	0.2609
D_{calc}(g/cm^3)	2.506	*S*	1.089

Results

The structure of punkaruaivite is similar to the structures of vinogradovite (Rastsvetaeva & Andrianov 1984, Kalsbeek & Rønsbo 1992), lintisite (Merlino *et al.* 1992), and kukisvumite (Merlino *et al.* 2000). It is based upon a 3D framework consisting of parallel chains of corner-sharing SiO_4 tetrahedra and chains of edge-sharing TiO_6 octahedra (Fig. 4). The Li^+ ions are in tetrahedral coordination. The LiO_4 tetrahedra share edges to form chains parallel to the chains of silicate and Ti-bearing octahedra. The framework contains channels occupied by H_2O molecules.

In terms of basic structural elements, the structure of punkaruaivite is very similar to the structure of lintisite (Merlino *et al.* 1992) and differs from the latter by the absence of Na. Electroneutrality is balanced by the above-mentioned mechanism of substitution, $Na^+ + O^{2-} \leftrightarrow \square + (OH)^-$. To invoke the structural nature of this mechanism, it is necessary to analyze availability of the O sites to protonation. The O3, O4, and O7 sites are bridging between adjacent SiO_4 tetrahedra and cannot be protonated. The O1 and O5 sites have coordinations (2Ti + Si) and (Ti + Si), which indicates their inability to form hydroxyl groups. The O2 site forms two O–Ti bonds and can possibly be protonated. The O6 site forms one O–Si and two O–Li bonds and, under certain circumstances, can also be available to protonation. Bond-valence analysis calculated using bond-valence parameters taken from Brown & Altermatt (1985) provides bond-valence sums of 4.19, 4.44, 4.07, and 1.10 valence units (*vu*) for the Ti, Si1, Si2, and Li sites, respectively. The bond-valence sums for the O1, O3, O4, O5, and O7 sites are 2.01, 1.99, 2.06, 2.05, and 2.07 *vu*, respectively. The O2 site receives 1.33 *vu* and can be unambigously assigned to a OH group. The bond-valence sum incident at the O6 site is 1.73 *vu*, which indicates that this site can be partially protonated. In order to obtain electroneutrality of the structural formula, the O6 site has been assigned the occupancy $O_{0.5}(OH)_{0.5}$. Thus, the structural formula can be written as $LiTi_2[Si_4O_{11}(OH)](OH)_2 \bullet H_2O$, in good agreement with the results of chemical analyses.

X-RAY POWDER DIFFRACTION

The powder X-ray-diffraction pattern of punkaruaivite from type locality no. 1 was obtained by means

TABLE 3. COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) OF ATOMS AND SITE-OCCUPATION FACTORS (SOF) FOR PUNKARUAIVITE

Atom	*x*	*y*	*z*	U_{iso}	SOF
Si1	0.08868(13)	0.6008(3)	0.5131(7)	0.0492(8)	Si
Si2	0.26853(6)	0.08447(18)	0.2283(3)	0.0110(5)	Si
Ti	0.16618(4)	0.10480(13)	0.8920(2)	0.0147(4)	Ti
Li	0	0.518(6)	0.25	0.090(11)	Li
O1	0.20759(16)	0.0690(5)	0.2160(8)	0.0124(9)	O
OH2	0.12949(18)	0.0614(6)	0.5811(9)	0.0180(10)	OH
O3	0.28699(18)	0.2594(5)	0.2216(9)	0.0166(9)	O
O4	0.29072(16)	-0.0061(5)	-0.0141(8)	0.0147(9)	O
O5	0.1214(2)	0.7493(6)	0.5087(12)	0.0289(12)	O
O6	0.0314(4)	0.6339(16)	0.507(4)	0.112(5)	$O_{0.5}(OH)_{0.5}$
O7	0.1012(5)	0.5048(15)	0.767(3)	0.101(4)	O
H_2O8	0.0323(16)	0.109(4)	0.520(8)	0.141(13)	$H_2O_{0.5}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	0.0467(17)	0.0424(16)	0.058(2)	0.0025(13)	0.0012(14)	-0.0087(12)
Si2	0.0147(8)	0.0107(8)	0.0077(8)	0.0002(5)	0.0009(6)	-0.0009(6)
Ti	0.0158(7)	0.0153(6)	0.0131(7)	0.0035(4)	0.0002(4)	0.0005(4)
O1	0.015(2)	0.0130(19)	0.0099(19)	0.0012(15)	0.0011(15)	-0.0003(15)
OH2	0.018(2)	0.020(2)	0.016(2)	-0.0047(18)	-0.0013(17)	0.0024(18)
O3	0.023(2)	0.014(2)	0.013(2)	0.0013(16)	-0.0006(17)	-0.0027(17)
O4	0.016(2)	0.019(2)	0.0093(18)	-0.0036(16)	0.0012(15)	0.0010(16)
O5	0.030(3)	0.025(3)	0.032(3)	0.006(2)	0.007(2)	-0.006(2)
O6	0.048(6)	0.092(8)	0.196(16)	-0.002(10)	0.018(8)	-0.009(6)
O7	0.112(10)	0.089(8)	0.104(9)	0.049(7)	0.015(8)	0.005(7)

TABLE 4. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF PUNKARUAIVITE

Si1–O6	1.555(12)	Ti–O3	1.833(5)
Si1–O5	1.567(6)	Ti–O5	1.861(5)
Si1–O7	1.598(12)	Ti–OH2	1.916(5)
Si1–O7	1.624(11)	Ti–OH2	2.023(5)
<Si1–O>	1.59	Ti–O1	2.025(4)
		Ti–O1	2.103(4)
Si2–O3	1.610(5)	<Ti–O>	1.96
Si2–O4	1.611(4)		
Si2–O4	1.616(4)	Li–O6	1.87(3) 2×
Si2–O1	1.632(5)	Li–O6	2.03(3) 2×
<Si2–O>	1.62	<Li–O>	2.20

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR PUNKARUAIVITE FROM TYPE LOCALITY NO. 1

I	d_{obs}	d_{calc}	*h k l*	*I*	d_{obs}	d_{calc}	*h k l*
100	13.3	13.3	2 0 0	10	2.412	2.419	4 0 2
80	6.23	6.24	3 1 0	20	2.349	2.350	8 2 1
30	4.56	4.56	5 1 0	40	2.13	2.128	7 3 $\bar{1}$
60	4.38	4.38	0 2 0	5	2.067	2.075	7 1 2
40	4.16	4.16	2 2 0	20	1.994	1.993	2 4 1
10	3.99	3.98	3 1 1	40	1.934	1.936	4 4 $\bar{1}$
80	3.50	3.49	7 1 0	20	1.841	1.843	6 4 $\bar{1}$
10	3.41	3.41	5 1 1			1.842	12 2 1
70	3.01	3.02	4 2 $\bar{1}$	10	1.766	1.766	11 3 $\bar{1}$
70	2.81	2.81	9 1 0	20	1.719	1.726	11 1 2
20	2.77	2.77	3 3 0			1.717	3 5 0
40	2.70	2.70	6 2 $\bar{1}$	10	1.692	1.691	10 4 0
40	2.665	2.661	6 2 1	20	1.667	1.674	3 1 3
		2.667	10 0 0			1.667	16 0 0
10	2.564	2.558	2 0 2	40	1.605	1.606	13 3 $\bar{1}$
10	2.539	2.539	1 3 $\bar{1}$	20	1.559	1.559	12 4 0

of the URS–1 instrument operated at 40 kV and 30 mA with X-ray a Debye–Scherrer camera 114.7 mm in diameter and Fe*K*α radiation (Table 5). Unit-cell parameters determined from powder patterns are in agreement with those obtained from single-crystal structure experiment: *a* 26.68(5), *b* 8.75(2), *c* 5.24(2) Å, β 91.2(3)°, *V* 1223.0(5) Å^3.

INFRARED SPECTROSCOPY

The infrared-absorption (IR) spectrum of purified punkaruaivite was obtained using a Specord M–80 spectrometer at the Institute of Chemistry and Technology of Rare Elements and Mineral Resources (Kola Science Center, Russian Academy of Sciences). The IR spectrum (Fig. 5) is similar to those of lintisite, kukisvumite and manganokukisvumite (Khomyakov *et al.* 1990, Yakovenchuk *et al.* 1991, Gault *et al.* 2004). The Si–O stretching vibration is seen as a doublet at 1000–1050 cm^{-1}, and a Si–O bending vibration as a medium-intensity band at 700 cm^{-1}. The strong triplet at 420–530 cm^{-1} is probably due to a Ti–O bending vibration. The O–H stretching vibration of H_2O and

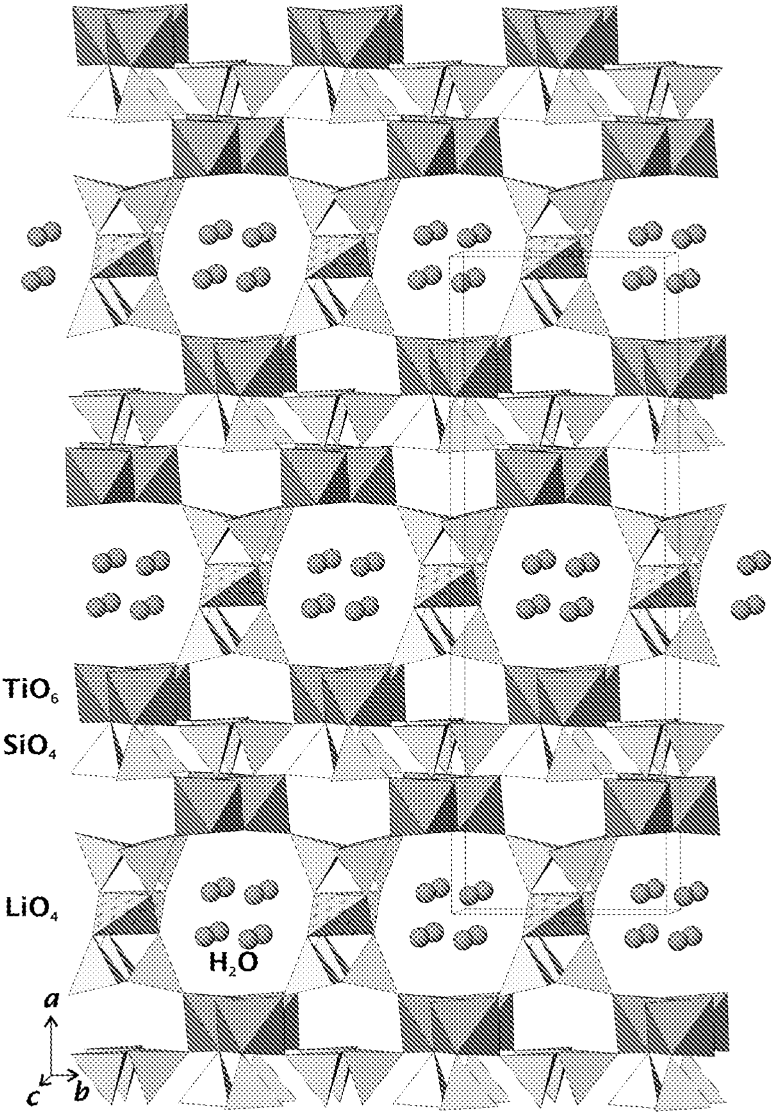

FIG. 4. The crystal structure of punkaruaivite, projected approximately parallel to the *c* axis, as consisting of framework of Siϕ_4, Liϕ_4, and Tiϕ_6 coordination polyhedra (ϕ: O^{2-}, OH^-).

$(OH)^-$ groups causes an intense broad band at 3360 cm^{-1}. A medium-strength band of H_2O bending vibration occurs at 1640 cm^{-1}.

DISCUSSION

A comparison of punkaruaivite, lintisite, kukisvumite and manganokukisvumite is given in Table 6. Merlino *et al.* (2000) mentioned a possibility to transform lintisite into kukisvumite by the coupled substitution in the tetrahedrally coordinated lithium position: $2Li^+ \leftrightarrow Zn^{2+}$. Gault *et al.* (2004) considered manganokukisvumite as a result of homovalent substitution of Mn^{2+} for Zn^{2+} in kukisvumite. Our data demonstrate that lintisite transforms into punkaruaivite by the partial or total removal of Na balanced according to the substitution mechanism: $Na^+ + O^{2-} \leftrightarrow \square + (OH)^-$. It is important to note that the overall topology of the

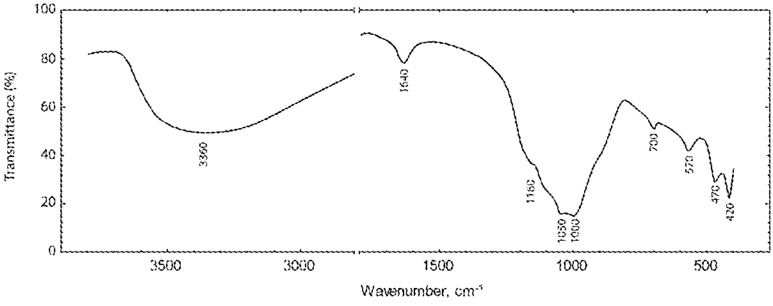

FIG. 5. Infrared spectrum of punkaruaivite.

TABLE 6. COMPARISON OF PUNKARUAIVITE, LINTISITE, KUKISVUMITE AND MANGANOKUKISVUMITE

Mineral	Punkaruaivite $LiTi_2[Si_4O_{11}(OH)](OH)_2 \cdot H_2O$	Lintisite $Na_3LiTi_2[Si_4O_{12}]O_2 \cdot 2H_2O$	Kukisvumite $Na_3Zn_{0.5}Ti_2[Si_4O_{12}]O_2 \cdot 2H_2O$	Manganokukisvumite $Na_3Mn_{0.5}Ti_2[Si_4O_{12}]O_2 \cdot 2H_2O$
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	*C2/c*	*C2/c*	*Pccn*	*Pccn*
a Å	26.68	28.58	28.89	29.05
b Å	8.75	8.60	8.60	8.61
c Å	5.24	5.22	5.22	5.22
β °	91.2	91.0	90.0	90.0
Z	4	4	4	4
Strongest lines	13.3(100), 6.23 (80), 4.38(60), 3.50(80), 3.01(70), 2.81(70)	14.29(100), 6.39 (50), 4.77(50), 3.69(50), 2.744 (50), 2.709(50)	14.49(90), 6.42 (60), 4.815(80), 4.302(47), 3.722 (65), 3.009(100)	14.47(100), 6.43 (20), 4.83(10), 3.743(10), 3.025 (40), 2.881(20)
Density g/cm³	2.60	2.77	2.90	2.86
Mohs hardness	4–5	5–6	5½–6	5½–6
Color	colorless to brownish yellow	silver-white	white	colorless
Opt. character	biaxial (–)	biaxial (–)	biaxial (–)	biaxial (–)
α	1.658	1.672	1.676	1.657
β	1.696	1.739	1.746	1.744
γ	1.726	1.803	1.795	1.792
2*V* °	85	85	77	70
Orientation	$X = b$, $Y \wedge c = 12°$	$Y = b$	$X = c$, $Z = a$	$X = a$, $Y = b$, $Z = c$
Dispersion	none observed	$r < v$, strong	none observed	none observed
Pleochroism	*X* brownish yellow *Y* light brownish yellow	none observed	none observed	none observed
Habit of crystals	elongate (on *c*), tabular (on *a*)	elongate (on *c*), tabular (on *a*)	elongate (on *c*), tabular (on *a*)	elongate (on *c*), tabular (on *a*)
Cleavage	{100} perfect	{100} perfect, {010} average	{100} perfect	none observed

framework is not changed during all these substitutions; we predict the existence of vacancy-bearing analogues of kukisvumite and manganokukisvumite with approximate formulae of $\square Zn_{0.5}Ti_2[Si_4O_{11}(OH)](OH)_2 \cdot H_2O$ and $\square Mn_{0.5}Ti_2 [Si_4O_{11}(OH)](OH)_2 \cdot H_2O$.

In their description of paravinogradovite, Khomyakov *et al.* (2003) indicated that this mineral can be considered as a transformation-induced mineral species formed from vinogradovite. The concept of transformation-induced mineral species has been introduced by Khomyakov (1990, 1995) and has been used to indicate mineral species developing through alteration of a corresponding protophase, from which the newly formed mineral inherits the principal features of its composition and structure. From this viewpoint, a protophase for punkaruaivite is lintisite, from which it possibly forms as a result of the removal of Na. Similar relationships (formation of a framework mineral from the protophase with the loss of Na) have been observed in the lovozerite group (the zirsinalite → lovozerite and kazakovite → tisinalite transformations). In that group, the removal of Na is accompanied by the protonation reactions and thus can be used as a sign of changing acidity of the hydrothermal solutions.

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