

Ivanyukite-Na-T, ivanyukite-Na-C, ivanyukite-K, and ivanyukite-Cu: New microporous titanosilicates from the Khibiny massif (Kola Peninsula, Russia) and crystal structure of ivanyukite-Na-T

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ABSTRACT

Ivanyukite-Na-T, $\text{Na}_3[\text{Ti}_4(\text{OH})\text{O}_3(\text{SiO}_4)_3] \cdot 7\text{H}_2\text{O}$, ivanyukite-Na-C, $\text{Na}_2[\text{Ti}_4\text{O}_2(\text{OH})_2(\text{SiO}_4)_3] \cdot 6\text{H}_2\text{O}$, ivanyukite-K, $\text{K}_2[\text{Ti}_4(\text{OH})_2\text{O}_2(\text{SiO}_4)_3] \cdot 9\text{H}_2\text{O}$, and ivanyukite-Cu, $\text{Cu}[\text{Ti}_4(\text{OH})_2\text{O}_2(\text{SiO}_4)_3] \cdot 7\text{H}_2\text{O}$, are new microporous titanosilicates found in a natrolitized microcline-aegirine-sodalite lens in the orthoclase-bearing urtite at the Koashva Mountain (Khibiny Massif, Kola Peninsula, Russia). The minerals occur as well-shaped colorless (ivanyukite-Na-T), pale-orange (ivanyukite-Na-C), pale-blue (ivanyukite-K), and green (ivanyukite-Cu) cubic crystals (up to 1.5 mm in diameter) grown on microcline, vinogradovite, sazykinaite-(Y), natrolite, and djerfisherite. The minerals have vitreous luster and white streak. They are transparent and non-fluorescent. The Mohs hardness is estimated as ~4. The minerals are brittle. Cleavage is perfect on {100} (ivanyukite-Na-C, ivanyukite-K, and ivanyukite-Cu) or on {10 $\bar{1}$ 1} (ivanyukite-Na-T), fracture is stepped. Density, measured by the sink/float method in heavy liquids, ranges from 2.60 (ivanyukite-Na-C) to 2.70 g/cm³ (ivanyukite-Na-T, ivanyukite-K, and ivanyukite-Cu), whereas calculated densities are: 2.58 (ivanyukite-Na-T), 2.39 (ivanyukite-Na-C), 2.69 (ivanyukite-K), and 2.46 g/cm³ (ivanyukite-Cu). Ivanyukite-Na-T is uniaxial (+), $n_w = 1.76(1)$, $n_e = 1.85(9)$ (589 nm), and the other minerals are isotropic, $n = 1.73(1)$. Chemical analysis by electron microprobe gave (wt% for ivanyukite-Na-T, ivanyukite-Na-C, ivanyukite-K, and ivanyukite-Cu, respectively): Na₂O 7.46, 5.19, 0.27, and 0.17; Al₂O₃ 0.07, 0.21, 0.18, and 0.07; SiO₂ 23.75, 25.47, 23.16, and 24.80; SO₃ 0.00, 0.00, 0.00, and 0.20; K₂O 5.89, 6.34, 7.09, and 6.81; CaO 0.21, 0.14, 0.95, and 0.23; TiO₂ 38.89, 37.81, 36.14, and 38.36; MnO 0.05, 0.33, 0.68, and 0.28; FeO 0.54, 2.17, 0.37, and 0.73; CuO 0.00, 0.00, 2.21, and 6.81; SrO 0.00, 0.00, 0.00; Nb₂O₅ 2.99, 2.90, 3.62, and 3.02; BaO 0.14, 0.00, 0.00, and 0.00; H₂O (by the Penfield method) 19.00, 19.15, 25.00, and 21.50; total 98.99, 99.71, 99.86, and 98.97. The empirical formulae (based on Si+Al = 3 apfu) are (Na_{1.82}K_{0.95}Ca_{0.03}Ba_{0.01})_{Σ2.81}[(Ti_{3.68}Nb_{0.17}Fe_{0.06}Mn_{0.01})_{Σ3.92}(Si_{2.99}Al_{0.01})_{Σ3.00}O_{14.59}(OH)_{1.37}]·7.29H₂O (ivanyukite-Na-T), (Na_{1.17}K_{0.94}Ca_{0.03})_{Σ2.14}[(Ti_{3.32}Fe_{0.21}Nb_{0.15}Mn_{0.03})_{Σ3.71}(Si_{2.97}Al_{0.03})_{Σ3.00}O_{12.89}(OH)_{2.87}]·6.01H₂O (ivanyukite-Na-C), (K_{1.16}Cu_{0.21}Ca_{0.13}Na_{0.07}Sr_{0.01})_{Σ1.58}[(Ti_{3.49}Nb_{0.21}Mn_{0.07}Fe_{0.04})_{Σ3.81}(Si_{2.97}Al_{0.03})_{Σ3.00}O_{13.19}(OH)_{2.75}]·9.32H₂O (ivanyukite-K), and (Cu_{0.62}K_{0.43}Na_{0.04}Ca_{0.03})_{Σ1.12}[(Ti_{3.48}Nb_{0.16}Fe_{0.07}Mn_{0.03})_{Σ3.74}(Si_{2.99}Al_{0.01})_{Σ3.00}O_{12.88}(OH)_{2.88}(SO₄)_{0.02}]·7.21H₂O (ivanyukite-Cu). Ivanyukite-Na-T is trigonal, *R*3*m*, $a = 10.94(2)$, $c = 13.97(4)$ Å, $Z = 3$. Other minerals are cubic, *P*43*m* $a = 7.856(6)$ (ivanyukite-Na-C), 7.808(2) (ivanyukite-K), and 7.850(7) Å (ivanyukite-Cu); $Z = 1$. The strongest lines in the powder X-ray diffraction pattern [d_{obs} (Å) (I_{obs}) *hkl*] are: 7.88(100) (011), 3.277(60)(014), 3.175(80)(212), 2.730(50)(220), 2.607(70)(303), 2.471(50)(124), 1.960(60)(044), 1.916(50) (135) (ivanyukite-Na-T); 7.88(100)(100), 4.53(30)(111), 3.205(80)(211), 2.774(30)(220), 2.622(40)(221, 300), 2.478(40)(310), 1.960(30)(400), 1.843(30)(330, 411) (ivanyukite-Na-C); 7.85(100)(100), 3.91(20)(200), 3.201(80) (211), 2.765(20)(220), 2.602(30)(221, 300), 2.471(40)(310), 1.951(30)(400), 1.839(30)(330, 411) (ivanyukite-K); 7.87(100)(100), 3.94(20)(200), 3.205(80)(211), 2.774(20)(220), 2.616(30)(221, 300), 2.481(30)(310), 1.960(30) (400), 1.843(30)(330, 411) (ivanyukite-Cu). The crystal structure of ivanyukite-Na-T [trigonal, *R*3*m*, $a = 10.921(3)$, $c = 13.885(4)$ Å, $V = 1434.2(7)$ Å³] has been solved from highly mosaic crystal and refined to $R_1 = 0.147$ on the basis of 723 unique observed reflections. The crystal structures of ivanyukite-group minerals are based upon a 3-dimensional framework of the pharmacosiderite type, consisting of four edge-sharing TiO₆-octahedra interlinked by SiO₄ tetrahedra. The framework has a 3-dimensional system of channels defined by 8-membered rings with an effective channel width of 3.5 Å (calculated as the distance between O atoms across the channels minus 2.7 Å). The channels are occupied by Na⁺ and K⁺ cations and H₂O molecules. The infrared spectra of the ivanyukite group minerals show 14 absorption bands caused by vibrations of Si-O and Ti-O bonds, molecular water, and (OH)⁻ groups. Ivanyukite-

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Na-*T* formed as a late-stage, hydrothermal phase of ultra-agpaitic hydrothermalites; ivanyukite-Na-*C* is produced by partial hydration of ivanyukite-Na-*T*, and both ivanyukite-K and ivanyukite-Cu are produced by partial hydration of ivanyukite-Na-*T* and natural cation exchange of Cu for Na near dissolved djerfisherite and chalcopyrite grains. Nomenclature of the ivanyukite group is based on the dominant extraframework cation and symmetry of the crystal structure. The minerals are named in honor of Gregory Yur'evich Ivanyuk, Russian mineralogist and petrologist, head of the Laboratory of Self-Organized Mineral Systems in the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, for his contributions to the petrology and mineralogy of banded iron-formations, alkaline, and alkaline-ultrabasic massifs.

Keywords: Ivanyukite-Na-*T*, ivanyukite-Na-*C*, ivanyukite-K, ivanyukite-Cu, new mineral, microporous titanosilicate, crystal structure, ultra-alkaline hydrothermalite, cation exchange, Khibiny massif, Kola Peninsula

INTRODUCTION

The Khibiny massif is the world's largest intrusion of nepheline syenite and foidolite. Igneous rocks, pegmatites, and hydrothermalites of the massif consist of more than 510 species including 104 minerals found there for the first time. Recently discovered microporous titanosilicates of Na, K, and Ca attract the special attention of scientists because of their strong cation exchange properties. Synthetic analogues of zorite, chuvruaitite, umbite, sitinakite, and other minerals are promising materials for a wide range of industrial applications, including gas separation, catalysis, radioactive waste management, etc. (Rocha and Anderson 2000; Ferraris and Merlino 2005; Krivovichev 2008).

One of the most important microporous cation-exchangers of the titanosilicate family are synthetic analogues of pharmacosiderite, first obtained by Chapman and Roe (1990), including Cs, Rb, and exchanged protonated phases. Behrens et al. (1996), Behrens and Clearfield (1997), and Dadachov and Harrison (1997) provided data on preparation, crystal structures and properties of $A_3H[Ti_4O_4(SiO_4)_3](H_2O)_n$ ($A = H, Na, K, Cs$). Structures and ion-exchanged properties of $HA_3[M_4O_4(XO_4)_3](H_2O)_4$ ($A = K, Rb, Cs; M = Ti, Ge; X = Si, Ge$) were reported by Behrens et al. (1998). These compounds were considered as prospective materials for the selective removal of Cs and Sr from waste water solutions. However, no natural titanosilicates with pharmacosiderite topology have been reported so far. In this article, we report for the first time the occurrence of four pharmacosiderite-type titanosilicates in nature.

All four minerals were found in a natrolitized microcline-aegirine-sodalite lens in orthoclase-bearing urtite at Mt. Koashva (within the Koashva Quarry) and named in honor of Gregory Yur'evich Ivanyuk, Russian mineralogist and petrologist, head of the Laboratory of Self-Organized Mineral Systems in the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, for his contributions to the petrology and mineralogy of banded iron-formations, and alkaline and alkaline-ultrabasic massifs (Goryainov and Ivanyuk 2001; Ivanyuk et al. 2002; Yakovenchuk et al. 2005, etc.). All the minerals and mineral names have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposals 2007-041, 2007-042, and 2007-043). The holotype specimens of ivanyukite group minerals have been deposited in the Geological and Mineralogical Museum of the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, Apatity, Russia, numbers 6353 (ivanyukite-Na-*T*), 6354 (both ivanyukite-K and ivanyukite-Cu), and 6355 (ivanyukite-Na-*C*).

OCCURRENCE

The Khibiny massif lies in the western part of the Kola Peninsula, at the contact between Archean granite-gneisses of the Kola-Norwegian megablock and the Imandra-Varzuga Proterozoic green-stone belt. The age of the massif is about 380 million years (Kramm and Kogarko 1994). The dominant rock is foyaite (about 70 vol%), and the intrusion is divided into two approximately equal parts by a conical fault (the Central Ring). The fault is thick with melteigite-urtite (foidolite) and apatite-nepheline rock, and foyaite near the contact is enriched by orthoclase and kalsilite. The final stages of the complex formation include phonolite and melanephelinite dikes, monchikite and carbonatite pipes, and pegmatite and hydrothermal veins, located within and near the Central Ring (Yakovenchuk et al. 2005).

The largest in the Khibiny massif Koasva deposit is a fractal cluster of apatite-nepheline rock, which spreads over more than 3 km. Its strike is northeast, 330–340°, and the dip is 30–40°. The thickness of the ore zone decreases with depth from 200–300 m to several millimeters. The host rock is feldspar-bearing urtite that contains numerous ultraagpaitic pegmatites and hydrothermalites (Yakovenchuk et al. 2005), including a natrolitized microcline-aegirine-sodalite vein with ivanyukite group minerals.

This vein consists of few swellings with some different mineralization. The upper, larger swelling no. 1 (1.5 × 2.5 m) has unclear concentric zoning. A marginal aegirine-microcline zone (up to 40 cm thick) consists of large tabular crystals of microcline (up to 15 cm diameter) and black prismatic crystals of aegirine (up to 10 cm long) with minor arfvedsonite and eudialyte. An intermediate zone (up to 30 cm thick) consists of a sodalite aggregate with inclusions of nepheline (grains up to 2 cm diameter), aegirine (crystals up to 6 cm long), villiamite (crystals up to 1 cm diameter), chkalovite (crystals up to 10 cm diameter), fluorapatite (fine-grained segregations up to 8 cm diameter), catapleiite (pseudomorphs after eudialyte up to 1 cm diameter), pectolite (crystals up to 6 cm long), and mangan-nep-tunite (granular aggregates up to 1 cm diameter). The core of the swelling (1 m diameter) consists of a coarse-grained aggregate of natrolite (forming after sodalite) and contains numerous voids with well-formed natrolite crystals (up to 15 cm long). Within the voids, there are long-prismatic vinogradovite crystals (up to 3 mm long), rhombohedral sazykinaite-(Y) crystals (up to 2 mm diameter), orange prismatic crystals of a labuntsovite group mineral (up to 0.5 mm long), rounded grains of sphalerite and galena (up to 2 cm), and granular leached segregations (up to 3 cm diameter) of djerfisherite, chalcopyrite, chalcocite, and pyrite. Solid organic material forms black spherules growing on all the

above-mentioned minerals. Ivanyukite-Na-*T* crystals occur in voids within the intermediate zone and core as colorless to pale pink pseudocubic crystals (up to 2 mm diameter). Sometimes such crystals are abundantly included within transparent natrolite crystals. Ivanyukite-Na-*C* forms pale-orange cubic crystals (up to 1 mm) around spherules of solid organic matter. Ivanyukite-K and ivanyukite-Cu occur as pale-blue (ivanyukite-K) to bright-green (ivanyukite-Cu) cubic crystals (up to 1.5 mm) growing on leached grains of djerfisherite, chalcopyrite, and chalcocite.

Swelling no. 2 (0.8 × 1.5 m) lies about 7 m lower and has similar zoning. The marginal zone (up to 30 cm thick) consists of an aegirine-microcline-sodalite aggregate with large (up to 15 cm) lamprophyllite segregations. The natrolitized sodalite core (up to 1 m diameter) contains numerous voids (up to 15 cm diameter) incrustated by well-formed natrolite crystals (up to 3 cm long), aegirine needles (up to 3 mm long), prismatic pectolite crystals (up to 4 cm long), and pseudomorphs of acicular vinogradovite after unknown prismatic minerals (up to 2 cm long). Ivanyukite-Na-*T* occurs here as brown marginal zones (up to 0.5 mm thick) around short-prismatic sitinakite crystals (up to 1.5 mm long) in close association with small (up to 1.5 mm diameter) spherulites of lucasite-(Ce).

PHYSICAL AND OPTICAL PROPERTIES

Within swelling no. 1, ivanyukite group minerals form mosaic (pseudo)cubic crystals up to 2 mm in diameter (Fig. 1) grown on microcline, vinogradovite, sazykinaite-(Y), and natrolite. Within swelling no. 2, ivanyukite-Na-*T* occurs as thin rims (up to 0.5 mm) around crystals and polycrystalline aggregates of sitinakite (Fig. 2) grown on aegirine and vinogradovite needles. The crystals always have mosaic microstructure and are composed from blocks with misorientations of 3–8° relative to each other (Fig. 3). No twinning was observed in the cubic members of the ivanyukite group, whereas there are polysynthetic {0001} twins by merohedry in the crystals of ivanyukite-Na-*T*.

In ivanyukite-Na-*T*, cleavage is perfect on {10 $\bar{1}$ 1}, and in the rest minerals of the ivanyukite group it is perfect on {100}. All the minerals are brittle and have a stepped fracture. Mohs hardness is about 4. The density determined by the float-and-sink method in Clerici solution varies from 2.6 to 2.7 g/cm³, and density calculated on the basis of the empirical formulae and X-ray powder diffraction data ranges from 2.39 g/cm³ in ivanyukite-Na-*C* to 2.69 g/cm³ in ivanyukite-K (Table 1). The densities of ivanyukite group minerals could not be determined more correctly owing to their extremely strong ion-exchange properties. Thus, ivanyukite-Na includes in its composition up to 57 wt% Ti₂O derived from Clerici solution during 12 h treatment at ambient temperature (Yakovenchuk et al. 2008), whereas sorption of Ti⁺ by partially decationized species (cubic members of the ivanyukite group) is much faster.

Color is distinct for each ivanyukite-group mineral (see Table 1): colorless (swelling no. 1) or pale-brown (swelling no. 2) for ivanyukite-Na-*T*, pale-orange for ivanyukite-Na-*C*, pale-blue for ivanyukite-K, and bright-green for ivanyukite-Cu. Luster of crystals is vitreous (for all minerals) or matte (ivanyukite-Cu), luster of fragments is vitreous. Ivanyukite-Na is transparent; ivanyukite-K and ivanyukite-Cu are translucent. Streak is from white (ivanyukite-Na and ivanyukite-K) to

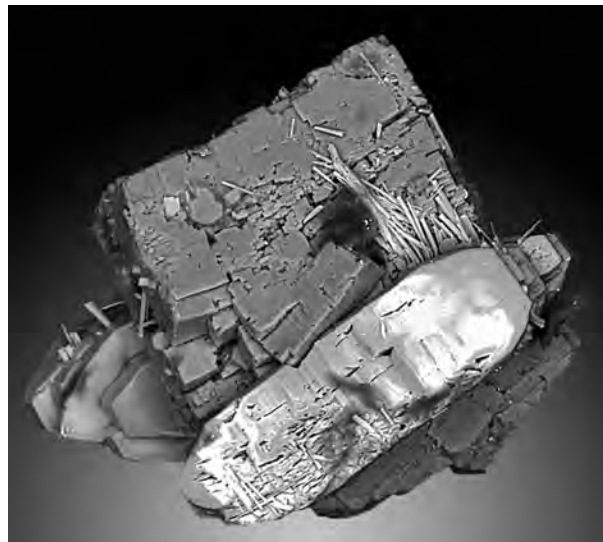


FIGURE 1. BSE-image of a mosaic crystal of ivanyukite-Na-*T* (250 μm diameter), with vinogradovite, from the selvage no. 1 of a natrolitized microcline-aegirine-sodalite vein in orthoclase-bearing urtite of Mt. Koashva.

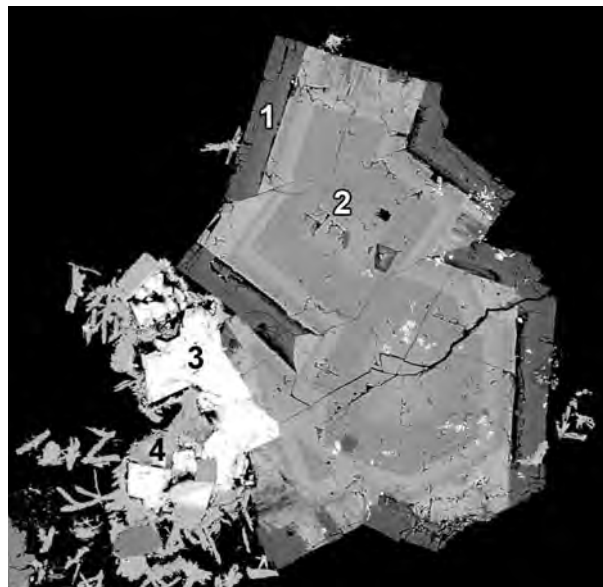


FIGURE 2. BSE-image of ivanyukite-Na-*T* rims (1), up to 60 μm thick, around zoned sitinakite crystals (2), with sazykinaite-(Y) (3) and lucasite-(Ce) (4), from selvage no. 2 of a natrolitized microcline-aegirine-sodalite vein in orthoclase-bearing urtite of Mt. Koashva.

pale-green (ivanyukite-Cu).

Ivanyukite-Na-*T* is uniaxial (+), $n_o = 1.76(1)$, $n_e = 1.85(9)$ (589 nm), whereas all other ivanyukite-group minerals are isotropic, $n = 1.73(1)$. In transmitted light, the minerals are colorless, without pleochroism and dispersion. Refractive indices of the ivanyukite-group minerals, especially partially decationized ones, are difficult to measure because of their strong ion-exchange capacities. The refractive index of ivanyukite-K increases in methylene iodide from 1.73 to 1.74 during 15 min.

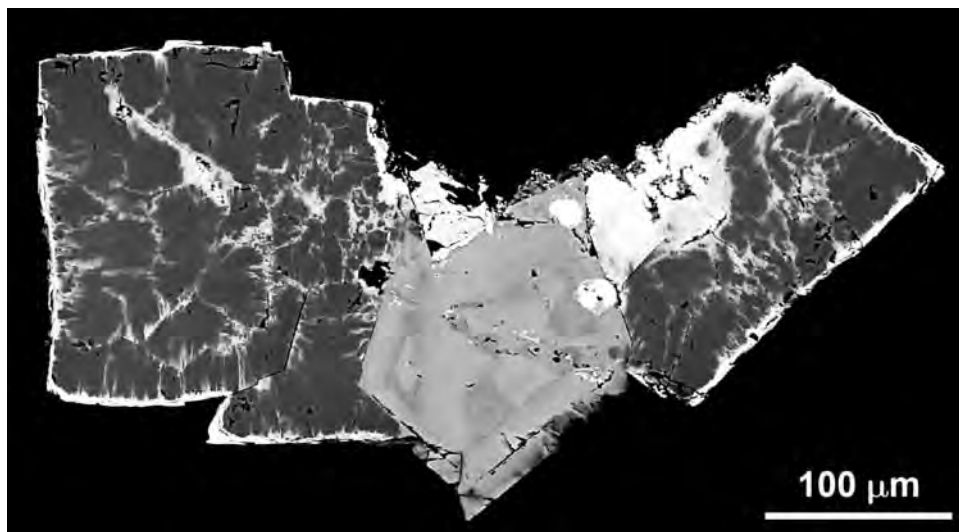


FIGURE 3. BSE-image of mosaic crystals of ivanyukite-Na-C growing on sazykinaite-(Y). Margins of separate blocks show Cs enrichment due to the Na → Cs substitution after ion-exchange experiments.

Besides, the mineral consists of very small (<1 μm) chaotically oriented blocks.

The Gladstone–Dale relationship (Mandarino 1981) provides a compatibility index of −0.004, superior (ivanyukite-Na-T); −0.007, superior (ivanyukite-Na-C); 0.118, poor (ivanyukite-K); and 0.034, excellent (ivanyukite-Cu). The poor compatibility constant for ivanyukite-K arises from high level of its decationization and, consequently, strong (and rapid) changing of all physical properties of this mineral during the measurements.

CHEMICAL COMPOSITION

The chemical composition of the ivanyukite-group minerals has been studied by wavelength dispersion spectrometry using a Cameca MS-46 electron microprobe (Geological Institute, Kola Science Center of the Russian Academy of Sciences, Apatity) operating at 20 kV and 20–30 nA. Analyses were performed with the probe defocused up to 20 μm, and by continuous movement of the sample to minimize mineral damage and Na, K, and water loss during 10 s counting time. The following standards were used: lorenzenite (Na, Ti), pyrope (Al), diopside (Si, Ca),

wadeite (K), synthetic MnCO₃ (Mn), hematite (Fe), celestine (Sr), metallic niobium (Nb), barite (Ba, S), and metallic copper (Cu). Water content was determined by the Penfield method for purified material. Table 2 provides compositions of four ivanyukite-group minerals (means from 3–5 analyses of different crystals of each mineral, and each analysis is the average of 6–10 points on each crystal). Empirical formulae were calculated on the basis of Si+Al = 3 apfu.

The compositions of ivanyukite group minerals correspond to the following empirical formulae:

(Na_{1.82} K_{0.95} Ca_{0.03} Ba_{0.01})_{Σ2.81}[(Ti_{3.68} Nb_{0.17} Fe_{0.06} Mn_{0.01})_{Σ3.92} (Si_{2.99} Al_{0.01})_{Σ3.00} O_{14.59}(OH)_{1.37}]·7.29H₂O—ivanyukite-Na-T;

(Na_{1.17} K_{0.94} Ca_{0.03})_{Σ2.14}[(Ti_{3.32} Fe_{0.21} Nb_{0.15} Mn_{0.03})_{Σ3.71} (Si_{2.97} Al_{0.03})_{Σ3.00} O_{12.89}(OH)_{2.87}]·6.01H₂O—ivanyukite-Na-C;

(K_{1.16} Cu_{0.21} Ca_{0.13} Na_{0.07} Sr_{0.01})_{Σ1.58}[(Ti_{3.49} Nb_{0.21} Mn_{0.07} Fe_{0.04})_{Σ3.81} (Si_{2.97} Al_{0.03})_{Σ3.00} O_{13.19}(OH)_{2.75}]·9.32H₂O—ivanyukite-K;

(Cu_{0.62} K_{0.43} Na_{0.040} Ca_{0.03})_{Σ1.12}[(Ti_{3.48} Nb_{0.16} Fe_{0.07} Mn_{0.03})_{Σ3.74} (Si_{2.99} Al_{0.01})_{Σ3.00} O_{12.88}(OH)_{2.88}(SO₄)_{0.02}]·7.21H₂O—ivanyukite-Cu. Simplified formulae can be written as:

Na₃[Ti₄(OH)O₃(SiO₄)₃]·7H₂O—ivanyukite-Na-T;

Na₂[Ti₄(OH)₂O₂(SiO₄)₃]·6H₂O—ivanyukite-Na-C;

K₂[Ti₄(OH)₂O₂(SiO₄)₃]·9H₂O—ivanyukite-K;

Cu[Ti₄(OH)₂O₂(SiO₄)₃]·7H₂O—ivanyukite-Cu.

Relations between chemical compositions of these minerals are shown in Figure 4 in coordinates of Na, K, and Cu. The Na content in ivanyukite-Na-T is higher than in ivanyukite-Na-C. Dadachov and Harrison (1997) noted the same feature in synthetic Na₄(TiO)₄(SiO₄)₃·6H₂O and explained it by the selective position of an additional Na atom, located on the threefold symmetry axis in the structure of the trigonal mineral.

CRYSTAL STRUCTURE

Structural studies of ivanyukite-group minerals are very difficult due to the scarcity of material and high mosaicity of their crystals (see Fig. 3). We were able to find few small fragments of ivanyukite-Na-T with more or less interpretable diffraction

TABLE 1. Properties of the ivanyukite group minerals

Properties	Ivanyukite-Na-T	Ivanyukite-Na-C	Ivanyukite-K	Ivanyukite-Cu
Crystal system	trigonal	cubic	cubic	cubic
Space group	<i>R</i> 3 <i>m</i>	<i>P</i> 43 <i>m</i>	<i>P</i> 43 <i>m</i>	<i>P</i> 43 <i>m</i>
<i>a</i> (Å)	10.921(3)	7.856(6)	7.808(2)	7.850(7)
<i>c</i> (Å)	13.885(4)			
<i>V</i> (Å ³)	1434.2(7)	484.8(9)	476(3)	483.7(9)
<i>Z</i>	3	1	1	1
Color	Colorless to pale-brown	Pale-orange	Pale-blue	Green
Density meas. (g/cm ³)	2.7	2.6	2.7	2.7
Density calc. (g/cm ³)	2.384	2.39	2.69	2.46
Hardness	4	4	4	4
Indicatrix	uniaxial (+)	isotropic	isotropic	isotropic
Refractive indices	<i>n</i> _ω = 1.76(1) <i>n</i> _ε = 1.85(9)	1.73(1)	1.73(1)	1.73(1)
(589 nm)				

TABLE 2. Chemical composition of the ivanyukite group minerals (wt%)

	Mean composition \pm standard deviation			
	Ivanyukite-Na-T	Ivanyukite-Na-C	Ivanyukite-K	Ivanyukite-Cu
Na ₂ O	7.46 \pm 1.71	5.19 \pm 0.25	0.27 \pm 0.25	0.17 \pm 0.10
Al ₂ O ₃	0.07 \pm 0.06	0.21 \pm 0.15	0.18 \pm 0.12	0.07 \pm 0.06
SiO ₂	23.75 \pm 1.11	25.47 \pm 1.99	23.16 \pm 0.71	24.80 \pm 1.10
SO ₃	—	—	—	0.20 \pm 0.11
K ₂ O	5.89 \pm 0.18	6.34 \pm 0.12	7.09 \pm 1.31	2.80 \pm 0.33
CaO	0.21 \pm 0.24	0.14 \pm 0.09	0.95 \pm 0.42	0.23 \pm 0.03
TiO ₂	38.89 \pm 1.31	37.81 \pm 1.16	36.14 \pm 2.73	38.36 \pm 1.47
MnO	0.05 \pm 0.09	0.33 \pm 0.15	0.68 \pm 0.43	0.28 \pm 0.06
FeO	0.54 \pm 0.30	2.17 \pm 1.19	0.37 \pm 0.11	0.73 \pm 0.16
CuO	—	—	2.21 \pm 1.40	6.81 \pm 1.11
SrO	—	—	0.19 \pm 0.11	—
Nb ₂ O ₅	2.99 \pm 1.01	2.90 \pm 0.67	3.62 \pm 0.72	3.02 \pm 0.10
BaO	0.14 \pm 0.12	—	—	—
H ₂ O	19.00	19.15	25.00	21.50
Total	98.99	99.71	99.86	98.97

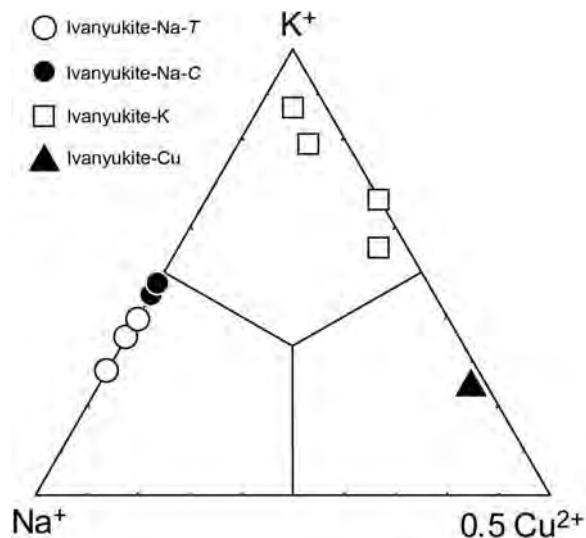
Structural formulae calculated on the basis of Si+Al = 3 apfu

Na	1.82	1.17	0.07	0.04
K	0.95	0.94	1.16	0.43
Cu	—	—	0.21	0.62
Ca	0.03	0.03	0.13	0.03
Sr	—	—	0.01	—
Ba	0.01	—	—	—
A+B	2.81	2.14	1.58	1.12
Ti	3.68	3.32	3.49	3.48
Nb	0.17	0.15	0.21	0.16
Fe	0.06	0.21	0.04	0.07
Mn	0.01	0.03	0.07	0.03
C	3.92	3.71	3.81	3.74
Si	2.99	2.97	2.97	2.99
Al	0.01	0.03	0.03	0.01
T	3.00	3.003.00	3.00	—
H	15.95	14.89	21.39	17.3
S	—	—	—	0.02
O	23.25	21.77	25.26	23.05

patterns within the rim around a sitinakite crystal from swelling no. 2 (see Fig. 2). However, it was clear that the crystal was composed of several blocks with misorientation of 3–5° relative to one another.

The selected crystal was mounted on a STOE IPDS II diffractometer operated at 50 kV and 40 mA. The data were collected using monochromatic MoK α X-radiation, with frame widths of 1° in ω , and with 7 min counting times for each frame. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the STOE program X-RED. An analytical absorption-correction was made on the basis of measured and optimized crystal shape. The structure was solved and refined using the SHELX system of programs. The final model included all atomic positional parameters, anisotropic displacement parameters for all atoms except two extraframework H₂O molecules, and a weighting scheme applied to the structure factors (Table 3). In final refinement, it appeared that one of the Si-O bonds (Si-O3) was too long for a silicate bond (1.73 Å), and a soft restraint was applied to keep the Si-O3 bond length within the limits of 1.59–1.65 Å. The final coordinates and anisotropic displacement parameters are given in Table 4, and selected interatomic distances are in Table 5. Calculated and observed structure factors are available from the authors upon request.

The structure of ivanyukite-Na-T is based upon a 3-dimensional framework of the pharmacosiderite type (Krivovichev 2005). It consists of fundamental building blocks (FBB) of four

**FIGURE 4.** Relation between extraframework cations in the ivanyukite group minerals.

edge-sharing Ti-octahedra interlinked by SiO₄ tetrahedra (Fig. 5a). The resulting framework (Fig. 5b) has a 3-dimensional system of channels defined by 8-membered rings (8-MRs) with a crystallographic free diameter of 3.5 Å. The channels are occupied by Na⁺ and K⁺ cations and H₂O molecules. Coordinations of Na⁺ and K⁺ cations in the framework channels deserve special attention since they are drastically different from those observed in synthetic materials. In ivanyukite-Na-T, K⁺ cations are located within the framework cavities and coordinated by seven anions each with K⁺-O distances of 2.69–3.15 Å (Fig. 6a). In contrast, in synthetic K titanosilicates with the pharmacosiderite structure, HK₃[(TiO)₄(SiO₄)₃](H₂O)₄ (Behrens et al. 1996; Tripathi et al. 2004; Xu et al. 2004), K⁺ cations are in the centers of the 8-MRs and usually have 12-fold coordination with the K⁺-O distances ranging from 3.17 to 3.27 Å. We note that the synthetic K-rich material is cubic and crystallizes in the space group *P* $\bar{3}m$. A similar situation is observed for Na⁺ cations. In ivanyukite-Na-T, these cations are attached to the side of the 8-MR (Fig. 6b) and have fivefold coordination (Na⁺-O = 2.27–2.46 Å). In synthetic Na₄[(TiO)₄(SiO₄)₃](H₂O)₆ that has a rhombohedral *R*3*m* structure (Dadachov and Harrison 1997), Na⁺ cations are located in the corners of the 8-MR and have either fourfold or sixfold coordination with the Na⁺-O distances in the range from 2.67 to 3.04 Å, i.e., substantially longer than in natural specimens. Perhaps the differences between the structures of natural and synthetic materials may be explained on the basis of kinetics of diffusion of cations in the framework channels. In mineral samples, due to the larger time scale, extraframework cations reside in the sites with more characteristic coordinations (with shorter bond lengths than in synthetic materials). In contrast, synthetic samples may have a higher degree of mobility of extraframework cations due to the relatively short time intervals between synthesis and structural investigations. The structural formula of ivanyukite-Na-T determined on the basis of the structure refinement can be written as Na_{1.44}K_{0.52}[Ti₄(OH)_{2.04}O_{1.96}(SiO₄)₃](H₂O)₆. It has lower amounts of Na and K than the average empirical formula, which

TABLE 3. Crystallographic data and refinement parameters for ivanyukite-Na-T

<i>a</i> (Å)	10.921(3)
<i>c</i> (Å)	13.885(4)
<i>V</i> (Å ³)	1434.2(7)
Space group	<i>R</i> 3 <i>m</i>
<i>Z</i>	3
<i>D</i> _{calc} (g/cm ³)	2.384
Crystal size (mm)	0.08 × 0.04 × 0.04
Radiation	MoKα
Total ref.	4503
Unique Ref.	994
Unique <i>F</i> _o ≥ 4σ _{<i>F</i>}	723
Flack parameter <i>x</i>	0.0002(2474)
<i>R</i> ₁	0.147
<i>wR</i> ₂	0.384
<i>S</i>	1.330

TABLE 4. Atomic coordinates, displacement parameters (Å²), and site-occupation factors (SOF) for ivanyukite-Na-T

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}	SOF*
Ti1	0.4793(4)	0.2397(2)	0.3529(2)	0.026(1)	Ti
Ti2	2/3	1/3	0.1747(6)	0.033(2)	Ti
Si	0.3323(7)	0.1661(3)	0.1461(6)	0.031(2)	Si
K	2/3	1/3	0.6181(16)	0.038(7)	K _{0.52}
Na	0.1974(10)	0.3949(19)	0.2062(13)	0.029(7)	Na _{0.48}
O1	0.3317(18)	0.1658(9)	0.2665(13)	0.037(5)	O
O2	0.2616(15)	0.0061(13)	0.1036(8)	0.033(3)	O
O3	0.4934(11)	0.2467(6)	0.1031(12)	0.030(4)	O
O4	2/3	1/3	0.426(2)	0.030(7)	O
O5	0.5900(11)	0.4100(11)	0.2750(15)	0.038(5)	O
H ₂ O6	0.140(2)	0.280(4)	0.352(3)	0.092(10)	O
H ₂ O7	0.098(3)	0.5491(17)	0.238(2)	0.072(7)	O

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ti1	0.025(2)	0.0233(14)	0.029(19)	0.0011(8)	0.0023(16)	0.0126(9)
Ti2	0.027(2)	0.027(2)	0.045(4)	0.000	0.000	0.0134(11)
Si	0.027(3)	0.026(2)	0.041(3)	-0.0068(14)	-0.014(3)	0.0134(16)
O1	0.012(7)	0.044(9)	0.045(11)	-0.006(4)	-0.012(7)	0.006(4)
O2	0.034(7)	0.026(6)	0.035(7)	-0.004(5)	-0.007(5)	0.013(5)
O3	0.027(8)	0.020(5)	0.045(10)	-0.012(4)	-0.024(7)	0.013(4)
O4	0.027(10)	0.027(10)	0.036(16)	0.000	0.000	0.013(5)
O5	0.039(8)	0.039(8)	0.041(11)	0.002(5)	-0.002(5)	0.023(10)

* Site-occupation factor.

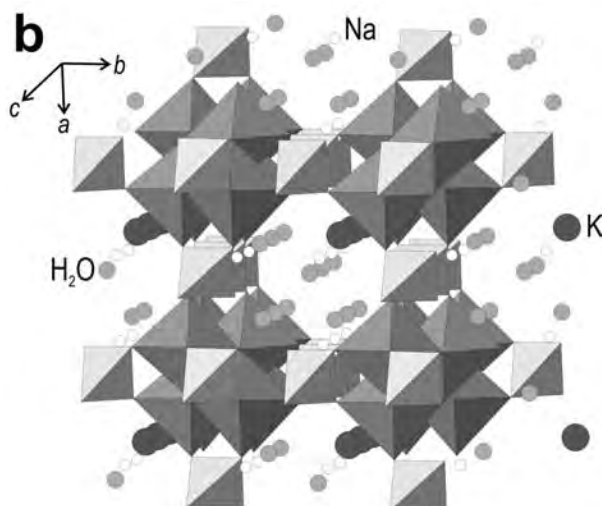
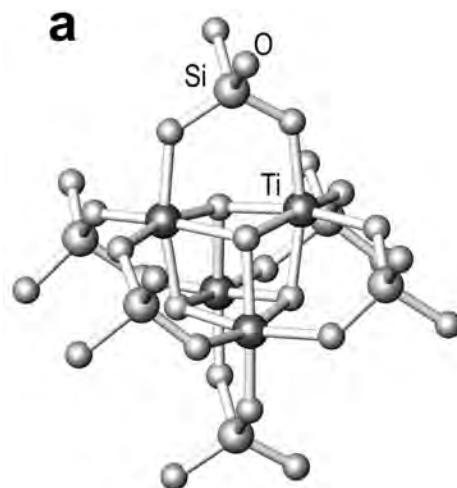
TABLE 5. Selected bond lengths (Å) in the structure of ivanyukite-Na-T

Ti1-O1	1.841(17)	Na-H ₂ O6	2.30(4)
Ti1-O5	1.961(13) 2×	Na-O2	2.43(2) 2×
Ti1-O2	1.978(13) 2×	Na-H ₂ O7	2.457(18) 2×
Ti1-O4	2.039(17)	<Na-O>	2.42
<Ti1-O>	1.97		
		K-O4	2.67(4)
Ti2-O3	1.916(15) 3×	K-H ₂ O6	2.81(4) 3×
Ti2-O5	2.01(2) 3×	K-O1	3.147(18) 3×
<Ti2-O>	1.94	<K-O>	2.93
Si-O2	1.627(13) 2×		
Si-O1	1.636(9)		
Si-O3	1.67(2)		
<Si-O>	1.64		

probably reflects variations in chemical compositions observed for the ivanyukite-group minerals.

X-RAY POWDER DIFFRACTION PATTERN

The powder X-ray diffraction patterns of ivanyukite group minerals were obtained by means of the URS-1 instrument operated at 40 kV and 30 mA with X-ray 114.7 mm camera and FeKα-radiation. Tables 6 and 7 provide a comparison of the powder patterns of these minerals with those of trigonal Na₄(TiO)₄(SiO₄)₃·6H₂O and cubic K₃H(TiO)₄(SiO₄)₃·4H₂O.

**FIGURE 5.** Fundamental building block in the structure of ivanyukite-Na-T (a) and projection of its crystal structure (b).

Space groups for cubic phases have been determined by analogy with known synthetic materials. The unit-cell parameters refined from the powder data consecutively decrease with decationization level from ivanyukiye-Na to ivanyukite-K (see Table 1).

INFRARED SPECTROSCOPY

The infrared-absorption spectra of purified material of both polymorph modifications of ivanyukite-Na were obtained using a Specord M-85 spectrometer. The spectra (Fig. 7) are similar to spectra of synthetic titanosilicates and titanogermanates with pharmacosiderite-type structures (Behrens et al. 1996; Puziy and García 1999). The Si-O stretching vibration is seen at 850 cm⁻¹ (*T*-modification) and 870 cm⁻¹ (*C*-modification). The strong triplet at 370–530 cm⁻¹ is probably due to Ti-O vibration. Weak bands at 1450 cm⁻¹ (*T*- and *C*-modifications) and 3530 cm⁻¹ (*T*-modification only) correspond to the Si-OH vibrations. The O-H stretching vibration in water and (OH)⁻ groups causes an intense doublet at 3170 and 3440 cm⁻¹ in ivanyukite-Na-*T* and

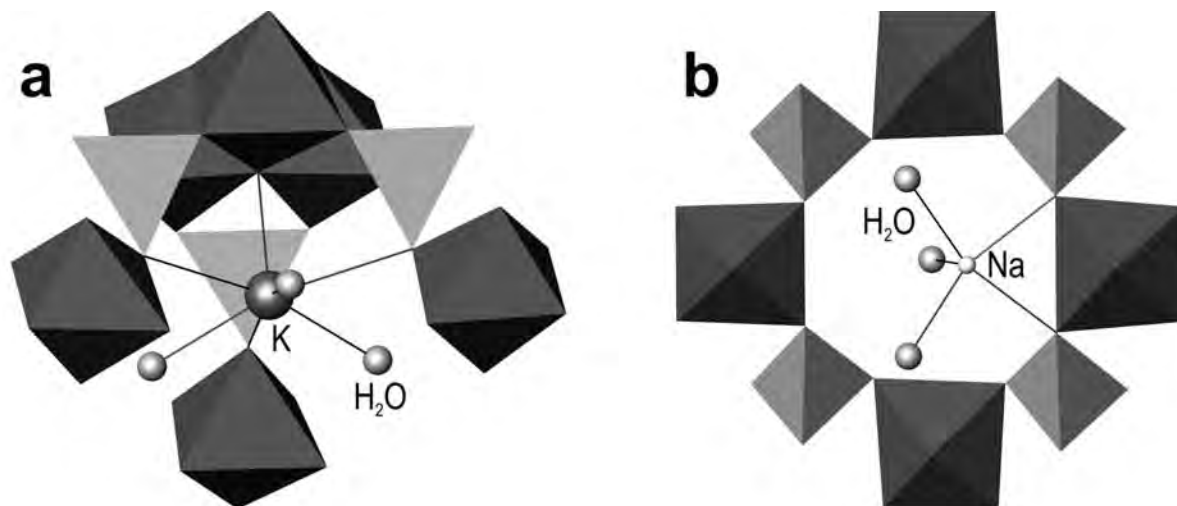


FIGURE 6. Coordination of K^+ (a) and Na^+ (b) cations in the framework channels of ivanyukite-*Na-T*.

a very broad intense band at 3300 cm^{-1} in ivanyukite-*Na-C*. By analogy, a medium strong sharp band of H_2O -bending vibration in ivanyukite-*Na-T* (1610 cm^{-1}) becomes broader in ivanyukite-*Na-C* (1640 cm^{-1}). In the spectrum of ivanyukite-*Na-T*, water-related bands are stronger and sharper than in the spectrum of ivanyukite-*Na-C* due to the higher content and ordering of water within the framework channels of the trigonal modification.

CHEMICAL TESTS AND ION-EXCHANGED PROPERTIES

It has been found (Yakovenchuk et al. 2008) that, in aqueous solutions of NH_4Cl , $CsCl$, $RbCl$, $CuSO_4$, and Clerici liquid, ivanyukite-*Na-T* rapidly (1–5 h) loses excessive Na and transforms into ivanyukite-*Na-C*, whereas in a solution of $SrCl_2$ such transformation occurs within 5–7 days. With regard to the solutions of $CsCl$, $RbCl$, $CuSO_4$, and Clerici liquid, both modifications of ivanyukite-*Na* have extremely strong ion-exchange properties that allow them to obtain up to 57 wt% Ti_2O_3 , 37 wt% Cs_2O , 29 wt% Rb_2O , and 1.6 wt% CuO during 12 h:

Original ivanyukite-*Na-T*: $(Na_{1.76}K_{0.97}Ca_{0.01}Ba_{0.01})_{\Sigma=2.76}$

$[(Ti_{3.79}Nb_{0.15}Fe_{0.05}^{3+})_{\Sigma=3.99}Si_3O_{14.81}(OH)_{1.19}] \cdot 8.2H_2O$,

Tl-exchanged phase: $(Ti_{3.32}Ca_{0.06}Na_{0.05})_{\Sigma=3.44}[(Ti_{3.79}Nb_{0.20}Fe_{0.06}^{3+}Mn_{0.01})_{\Sigma=4.06}Si_3O_{15.85}(OH)_{0.16}] \cdot 1.6H_2O$,

Cs-exchanged phase: $(Cs_{2.15}K_{0.28}Na_{0.10}Ca_{0.03})_{\Sigma=2.56}[(Ti_{3.24}Nb_{0.23}Fe_{0.05}^{3+})_{\Sigma=3.52}Si_3O_{12.84}(OH)_{3.16}]$,

Rb-exchanged phase: $(Rb_{2.48}Na_{0.21}K_{0.03}Ca_{0.02})_{\Sigma=2.73}(Ti_{3.41}Nb_{0.23}Fe_{0.04}^{3+})_{\Sigma=3.68}[Si_3O_{13.67}(OH)_{2.33}] \cdot 2.7H_2O$,

Cu-exchanged phase: $(K_{0.51}Cu_{0.14}Na_{0.02})_{\Sigma=0.67}(Ti_{3.72}Nb_{0.22}Fe_{0.06}^{3+})_{\Sigma=4.00}[Si_3O_{12.98}(OH)_{3.02}] \cdot 7.8H_2O$.

Ion-exchanged forms have exclusively well-defined powder X-ray diffraction patterns, which show improvement in their crystallinity in comparison to the original material. The Cu-exchanged phase is an analogue of ivanyukite-*Cu*. The crystal structure of the Rb-substituted phase is “intermediate” between structures of ivanyukite-*Na-C* and anhydrous $Cs_3H(TiO)_4(SiO_4)_3$ (Harrison et al. 1995). The Tl- and Cs-substituted phases are anhydrous and are structural analogues of synthetic $Cs_3H(TiO)_4(SiO_4)_3$.

TABLE 6. X-ray powder diffraction data for the ivanyukite-*Na-T* and synthetic $Na_4(TiO)_4(SiO_4)_3 \cdot 6H_2O$ (Dadachov and Harrison 1997)

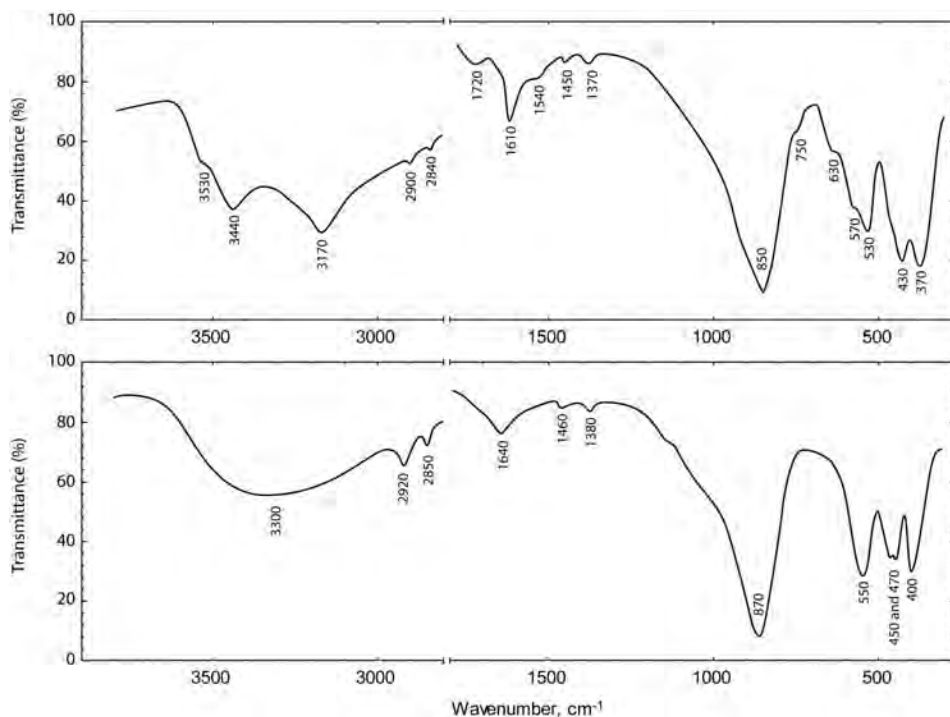
Ivanyukite- <i>Na-T</i>				$Na_4(TiO)_4(SiO_4)_3 \cdot 6H_2O$			<i>hkl</i>
<i>l</i> _{obs}	<i>d</i> _{obs} (Å)	<i>l</i> _{calc}	<i>d</i> _{calc} (Å)	<i>l</i> _{obs}	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	
100	7.88	100	7.841	100	7.807	7.809	011
10	5.60	3	5.622	10	5.577	5.579	102
				9	5.472	5.466	110
				8	4.599	4.604	003
30	4.49	6	4.486	13	4.475	4.478	201
30	3.92	3	3.921	11	3.897	3.904	022
20	3.49	1	3.469	5	3.463	3.464	121
60	3.277	7	3.277	18	3.242	3.244	014
80	3.175	15	3.187	29	3.173	3.177	212
		8	3.158	17	3.153	3.156	300
				8	2.789	2.790	204
50	2.730	6	2.735	11	2.728	2.733	220
				7	2.648	2.652	105
70	2.607	9	2.614	20	2.600	2.603	303
50	2.471	4	2.500	14	2.482	2.485	124
		6	2.459	14	2.452	2.454	132
40	2.417	7	2.407	14	2.384	2.386	025
30	2.351	4	2.358				223
				7	2.331	2.333	041
				5	2.236	2.239	402
				5	2.189	2.187	215
				4	2.088	2.090	314
				5	2.063	2.072	140
60	1.960	6	1.960	18	1.951	1.952	044
				4	1.921	1.932	017
50	1.916	4	1.914	10	1.902	1.903	135
				7	1.883	1.885	143
40	1.848	4	1.845	6	1.836	1.838	234
40	1.825	2	1.829	5	1.824	1.826	052
			1.823	6	1.821	1.822	330
				4	1.772	1.774	421
				4	1.758	1.761	226
				6	1.730	1.732	242
10	1.656	1	1.653				512
40	1.589	1	1.589				317
20	1.549	3	1.548	7	1.545	1.546	341
				4	1.394		
				6	1.379		
10	1.363		1.361	5	1.365		
				4	1.326		
				4	1.309		
				4	1.232		

Note: Eight diagnostic lines are shown as bold for each mineral.

TABLE 7. X-ray powder diffraction data for the cubic member of the ivanyukite group and synthetic $K_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$ (JCPDS 47-43)

Ivanyukite-Na-C			Ivanyukite-K			Ivanyukite-Cu			JCPDS 47-43		<i>hkl</i>
<i>I</i> _{obs}	<i>D</i> _{obs} (Å)	<i>D</i> _{calc} (Å)	<i>I</i> _{obs}	<i>D</i> _{obs} (Å)	<i>D</i> _{calc} (Å)	<i>I</i> _{obs}	<i>D</i> _{obs} (Å)	<i>D</i> _{calc} (Å)	<i>I</i> _{calc}	<i>D</i> _{calc} (Å)	
100	7.88	7.86	100	7.85	7.826	100	7.87	7.85	100	7.7644	100
									1	5.5902	110
30	4.53	4.54	10	4.49	4.518	10	4.53	4.53	11	4.4827	111
20	3.96	3.93	20	3.91	3.913	20	3.94	3.93	10	3.8822	200
			10	3.53	3.492				<1	3.4723	210
80	3.205	3.207	80	3.201	3.188	80	3.205	3.205	40	3.1698	211
30	2.774	2.777	20	2.765	2.761	20	2.774	2.775	16	2.7451	220
40	2.622	2.619	30	2.602	2.603	30	2.616	2.617	8	2.5881	221, 300
40	2.478	2.484	40	2.471	2.469	30	2.481	2.482	18	2.4553	310
20b	2.367	2.369	10	2.356	2.354	10	2.365	2.367	5	2.3410	311
10	2.26	2.267							4	2.2413	222
									<1	2.1534	320
10	2.093	2.099				10	2.096	2.098	3	2.0751	321
30	1.96	1.964	30	1.951	1.952	30	1.960	1.963	5	1.9411	400
20	1.905	1.905	20	1.895	1.894	20	1.903	1.904	6	1.8831	322, 410
30	1.843	1.852	30	1.839	1.840	30	1.843	1.850	5	1.8300	330, 411
									1	1.7812	331
10	1.752	1.757				10	1.752	1.755	4	1.7361	420
									1	1.6943	421
									1	1.6553	332
20	1.598b	1.604	20	1.592	1.594	10	1.599	1.602	3	1.5849	422
20	1.561b	1.571	20	1.561	1.562	20	1.561	1.570	5	1.5528	430, 500
									1	1.5227	431
									2	1.4942	511
			10	1.423	1.425	10	1.430	1.433	<1	1.4418	431
20	1.377		10	1.380	1.380				3	1.4175	521
									5	1.3725	440

Note: Eight diagnostic lines are shown as bold for each mineral.



◀ **FIGURE 7.** Infrared spectra for of ivanyukite-Na-T (upper part) and ivanyukite-Na-C (lower part).

NOMENCLATURE

Nomenclature of the ivanyukite group is based on the dominant extraframework cation (Na, K, Cu, etc., suffixes) and symmetry of the crystal structure (*T* = trigonal, *C* = cubic, etc.). Ordering of the extraframework cations over two or more sites is not taken into account.

DISCUSSION

Ivanyukite-Na-*T* is a low-temperature hydrothermal mineral crystallized from supersaturated Na-rich aqueous solutions together with natrolite, villiumite, sazykinaite-(Y), lucasite-(Ce), and solid organic compounds during the late stage of the hydrothermal activity. According to our experiments (Yakovenchuk

et al. 2008), this polymorph is unstable in dilute water solutions and transforms into the partially decationized cubic phase. Both ivanyukite-Na-*T* and ivanyukite-Na-*C* have strong ion-exchange properties that makes two pathways of the ivanyukite-K and ivanyukite-Cu formation possible: (1) cation-exchange according to the $2\text{Na} \leftrightarrow \text{Cu}$ scheme with ivanyukite-K as an intermediate product of this process (by analogy with our cation-exchange experiments with CuSO_4), and (2) decationization of ivanyukite-Na initially enriched in Cu with ivanyukite-Cu as an intermediate product and ivanyukite-K as the final one.

The first schema seems to be more reliable, since ivanyukite-Na enriched in Cu has not been found, even near the leached djerfisherite grains. Orange crystals of ivanyukite-Na-*C* are closely associated with solid organic material, which can be related to the ability of decationized ivanyukite species to absorb organic molecules.

It has been known that synthetic analogues of the ivanyukite-group minerals can be used as effective cation-exchangers and molecular sieves. According to our experiments, the natural material easily exchanges Na cations with NH_4^+ , Cs^+ , Rb^+ , Tl^+ , Ag^+ , Cu^{2+} , Co^{2+} , Ni^{2+} , and Sr^{2+} from aqueous solutions at ambient conditions and absorbs molecules of thiourea, methylene iodide, hydrazine, etc. It is interesting that we were unable to decationize Cs-exchanged ivanyukite under ambient conditions (Yakovenchuk et al. 2008), which means that the minerals are selective cation-exchangers for Cs and can be used for the removal of ^{137}Cs from radioactive waste solutions.

ACKNOWLEDGMENTS

We are grateful to Giovanni Ferraris and an anonymous referee for their remarks on the manuscript. We thank Swiss National Foundation (SNF) for financial support in the framework of the SCOPES program. S.V.K. and D.V.S. thank the Russian Ministry of Science and Education for the financial support (grant RNP 2.1.1.3077). The equipment used for the structural studies was acquired through the program "Molecular Geochemistry and Biogeochemistry" (national project "Education").

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MANUSCRIPT RECEIVED AUGUST 3, 2008

MANUSCRIPT ACCEPTED JUNE 10, 2009

MANUSCRIPT HANDLED BY G. DIEGO GATTA