

Chivruaiite, $\text{Ca}_4(\text{Ti,Nb})_5[(\text{Si}_6\text{O}_{17})_2(\text{OH},\text{O})_5]\cdot 13\text{--}14\text{H}_2\text{O}$, a new mineral from hydrothermal veins of Khibiny and Lovozero alkaline massifs

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ABSTRACT

Chivruaiite is a new Ca titanosilicate [orthorhombic, *Cmmm*, $a = 7.17(2)$, $b = 22.98(9)$, $c = 6.94(2)$ Å, $V = 1144.4$ Å³, $Z = 1$], chemically and structurally related to zorite. The mineral is found in three different hydrothermal veins within the Khibiny and Lovozero alkaline massifs, Kola Peninsula, Russia. It is associated with microcline, eudialyte, natrolite, astrophyllite, aegirine, etc. Chivruaiite occurs as elongate-prismatic crystals (up to 3 mm long) with {100}, {010}, {001}, {101}, and {011} as dominant faces, as well as radiating aggregates. The mineral is transparent, pale-pink to colorless, with vitreous luster and white streak. Cleavage is distinct on {100} and {010}; fracture is step-like. Mohs hardness is about 3. In transmitted light, the mineral is pale-pink, with a faint pleochroism: $Z = \text{pale-pink}$, on X and $Y = \text{colorless}$; dispersion $r < v$. Chivruaiite is biaxial (+): $\alpha = 1.705(5)$, $\beta = 1.627(2)$, $\gamma = 1.612(2)$ (for $\lambda = 589$ nm), $2V_{\text{meas}} = 40 \pm 5^\circ$, $2V_{\text{calc}} = 31.7^\circ$. Optical orientation: $X = b$, $Y = a$, $Z = c$, $D_{\text{calc}} = 2.42$ g/cm³, $D_{\text{meas}} = 2.40\text{--}2.42$ g/cm³. The mean chemical composition determined by electron microprobe is (wt%): SiO₂ 45.14; TiO₂ 20.63; Al₂O₃ 0.07; Fe₂O₃ 0.18; MnO 0.02; MgO 0.01; CaO 10.53; Na₂O 0.10; K₂O 1.30; SrO 0.28; Nb₂O₅ 3.63; H₂O 17.30; sum. 99.19. Empirical formula calculated on the basis of Si = 12 is $(\text{Ca}_{3.00}\text{K}_{0.44}\text{Na}_{0.05}\text{Sr}_{0.04}\text{Mn}_{0.01})_{\Sigma=3.54}(\text{Ti}_{4.13}\text{Nb}_{0.44}\text{Fe}_{0.04}^{3+}\text{Al}_{0.02})_{\Sigma=4.63}[\text{Si}_{12}\text{O}_{34}(\text{OH})_{4.51}\text{O}_{0.49}]\cdot 13.08\text{H}_2\text{O}$. Simplified formula is $\text{Ca}_4(\text{Ti,Nb})_5[(\text{Si}_6\text{O}_{17})_2(\text{OH},\text{O})_5]\cdot 13\text{--}14\text{H}_2\text{O}$. The strongest X-ray powder-diffraction lines [d in Å, (hkl)] are 11.6 (100) (020), 6.91 (90) (110, 001), 5.23 (50) (130), 3.41 (50) (220), 3.35 (50) (061, 151), 3.04 (80) (221, 240). The structure of chivruaiite was refined to $R_1 = 0.038$ on the basis of 687 unique observed reflections. It is based upon an open framework of SiO₄ tetrahedra, TiO₆ octahedra, and TiO₅ pyramids. Framework cavities are occupied by Ca²⁺ and K⁺ cations, and H₂O molecules. The mineral is named after its type locality in the Chivruai River valley (the Lovozero massif, Kola Peninsula, Russia). Chivruaiite is a Ca-analog of zorite and ETS-4 and is closely related to haïneaultite.

Keywords: Chivruaiite, zorite, titanosilicate, new mineral, crystal structure, Kola Peninsula

INTRODUCTION

Microporous titano- and niobosilicates 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). The most famous representatives of the titanosilicate family are Engelhard Titanosilicates, ETS-4 and ETS-10. ETS-4 is a synthetic analog of zorite, $\text{Na}_6[\text{Ti}(\text{Ti,Nb})_4(\text{Si}_6\text{O}_{17})_2(\text{OH})_5](\text{H}_2\text{O})_{10.5}$, a rare mineral discovered by Mer'kov et al. (1973) in the aegirine-microcline-natrolite vein "Yubileinaya" within lujavrite at Mt. Karnasurt (the Lovozero alkaline massif, Kola Peninsula, Russia). In this paper, we report occurrence and structure of chivruaiite, a Ca analog of zorite.

Chivruaiite was first found by the first author in 1978 in an astrophyllite-aegirine-microcline vein in foyaite at the Eves-

logchorr Mountain, the Khibiny massif, Kola peninsula, Russia. On the basis of its X-ray powder-diffraction pattern, it had initially been identified as zorite. However, subsequent finds of this mineral in 1999 (Mt. Eveslogchorr, the Khibiny massif) and 2004 (the Chivruai River valley, the Lovozero massif) and chemical studies of the samples showed chivruaiite to be a Ca analog of zorite and therefore to be a new mineral species. The mineral has been named after its type locality in the Chivruai River valley, the Lovozero massif, Kola Peninsula. Both the mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (proposal 2004-052). The holotype specimen of chivruaiite has been deposited at the Mineralogical Museum of St. Petersburg State University. The cotype is deposited at Geological and Mineralogical Museum of the Geological Institute of the Kola Science Centre of Russian Academy of Sciences, Apatity, Russia (no. 6281/1.07.2005).

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OCCURRENCE

Chivruaiite has been found in three hydrothermal veins within nepheline syenite of the Khibiny and Lovozero alkaline massifs: (1) microcline vein in eudialyte-bearing lujavrite of the Chivruai River valley (the Lovozero massif), (2) astrophyllite-aegirine-microcline vein in foyaite at the Eveslogchorr Mt. (the Khibiny massif), and (3) natrolite-microcline vein in foyaite at the Eveslogchorr Mt. (the Khibiny massif).

The concordant microcline vein no. 1 in eudialyte-bearing lujavrite of the Chivruai River valley is the up to 20 cm wide. The central zone of the vein consists of microcline, murmanite, lorenzenite, eudialyte, aegirine, pectolite, lamprophyllite, and loparite-(Ce). Interstices within microcline aggregates are filled by crystals of sodalite, analcime, natrolite, steenstrupine-(Ce), barytolamprophyllite, galena, sphalerite, hemimorphite, hydroxylapatite, and whewellite. Colorless prismatic crystals (up to 1.5 mm long; Fig. 1a) and spherulites of chivruaiite were found in voids within leached murmanite in association with labuntsovite-group minerals and rhabdophane-(Ce).

The lens-like astrophyllite-aegirine-microcline vein no. 2 in foyaite at Mt. Eveslogchorr has a symmetrically zoned structure. The (up to 30 cm wide) peripheral zone consists of coarse-grained aegirine-microcline aggregates, whereas the central zone (up to 50 cm wide) consists of white tabular microcline and radiating aggregates of astrophyllite. Chivruaiite occurs as pale-pink long-prismatic crystals (up to 3 mm long) within the astrophyllite aggregates in intimate association with natrolite, catapleiite and fluorapatite.

The irregularly shaped natrolite-microcline vein no. 3 in foyaite at Mt. Eveslogchorr is up to 1 m wide and has a concentric zoned structure (Yakovenchuk et al. 1999). The selvages of the vein (10–15 cm) are composed of aggregates of microcline and aegirine with scarce rounded clusters of golden-brown lamprophyllite (up to 2 cm diameter). The microcline zone (up to 50 cm) contains radiating aggregates of murmanite, black sword-shaped crystals of altered pectolite, greenish-yellow belovite-(La), eudialyte, and safflorite. In interstices of the thickest part of the zone, there are irregularly shaped crimson grains of tugtupite (up to 2 cm diameter), partially replaced by white aggregates of epididymite. The interstices also include aggregates (up to 1.5 cm diameter) of yellow bladed crystals of sphalerite and lamprophyllite. The microcline-natrolite parts of the vein are made of

cavernous fine-grained natrolite with microcline, pectolite, and murmanite. Chivruaiite was found here as spherulites of colorless long-prismatic crystals (up to 1.5 mm long; Fig. 1b) grown on microcline and natrolite crystals in intimate association with kuzmenkoite-Mn.

Both chivruaiite and zorite are low-temperature hydrothermal minerals, which crystallized after most of above mentioned minerals, with the exception of the oxalate. These minerals are products of alteration of primary titanosilicates, mainly murmanite (veins nos. 1 and 2), astrophyllite (vein no. 3) and lomonosovite (the “Yubileynaya” vein, the Lovozero massif). Due to their ion-exchange capacities, hydrothermal titanosilicates of Na, K, and Ca, including zorite, easily change their composition dependent upon their chemical environment. When compared to the Khibiny massif, the Lovozero massif is strongly depleted in Ca, which explains the abundance of zorite relative to chivruaiite in the Lovozero massif. Occurrence of chivruaiite in the Chivruai River valley (Lovozero) can be explained by the partial assimilation of numerous xenoliths of Devonian basalt by lujavrite melts.

PHYSICAL AND OPTICAL PROPERTIES

Chivruaiite forms well-shaped crystals with dominant forms {100}, {010}, {001}, {101}, and {011}, sometimes arranged in radiating aggregates. No twinning was observed. Macroscopically, chivruaiite is pale-pink to colorless with a vitreous luster. The mineral is transparent with white streak. Cleavage is distinct on {100} and {010}. Chivruaiite is brittle and has stepped fracture. Mohs hardness is about 3. The density determined by the float and sink method in Clerici solution ranges from 2.40 to 2.42 g/cm³. This value is in a good agreement with the calculated density of 2.42 g/cm³.

Chivruaiite is biaxial (+): $\alpha = 1.705(5)$, $\beta = 1.627(2)$, $\gamma = 1.612(2)$ (for $\lambda = 589$ nm), $2V_{\text{meas}} = 40 \pm 5^\circ$, $2V_{\text{calc}} = 31.7^\circ$. Optical orientation: $X = b$, $Y = a$, $Z = c$. In transmitted light, the mineral is pale-pink, with a faint pleochroism: $Z = \text{pale-pink}$, $X, Y = \text{colorless}$, dispersion $r < v$. Gladstone–Dale calculation provides a compatibility index of 0.054 (good; Mandarino 1981).

CHEMICAL COMPOSITION

The chemical composition of chivruaiite has been studied by wave-length dispersive spectrometry using a Cameca MS-46 electron microprobe (Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Apatity) operating at 20 kV and 20–30 nA. Examination of chivruaiite and zorite crystals revealed their homogeneity, which was also tested using scanning electron microscope Leo-1450. Analyses were performed by defocusing the electron beam up to 30 μm and continuously moving under the sample to minimize mineral damage and water loss during 10-s counting time. The following standards were used: lorenzenite (Na, Ti), pyrope (Mg, Al), diopside (Si, Ca), wadeite (K), metallic vanadium (V), synthetic MnCO₃ (Mn), hematite (Fe), sphalerite (Zn), celestine (Sr), synthetic ZrSiO₄ (Zr), metallic niobium (Nb), barite (Ba), synthetic CeS (Ce), metallic tantalum (Ta), and thorite (Th). Water content was determined by the Penfield method for purified material from the microcline vein no. 1. Table 1 provides analytical results for 7 chivruaiite crystals from the above mentioned veins, as well as for two zorite rosettes from the aegirine-microcline-natrolite vein

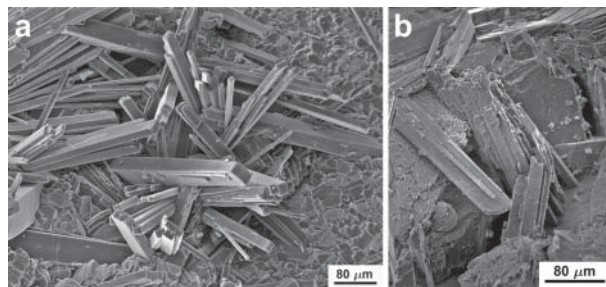


FIGURE 1. Radiating aggregate of chivruaiite from a microcline vein in eudialyte-bearing lujavrite of the Chivruai River valley (a) and elongate-tabular chivruaiite crystal (1) on microcline, with kuzmenkoite-Mn, from natrolite-microcline vein no. 2 in foyaite at the Eveslogchorr Mt (b).

“Yubileinaya” at Mt. Karnasurt (the Lovozero massif). Analyses are an average of 6–10 points for each crystal. The empirical formulae were calculated on the basis of Si = 12.

The composition of chivruaiite corresponds to the empirical formulae $(\text{Ca}_{3.00}\text{K}_{0.44}\text{Na}_{0.05}\text{Sr}_{0.04}\text{Mn}_{0.01})_{\Sigma=3.54}(\text{Ti}_{4.13}\text{Nb}_{0.44}\text{Fe}_{0.04}\text{Al}_{0.02})_{\Sigma=4.63}[\text{Si}_{12}\text{O}_{34}|\text{O}_{0.49}(\text{OH})_{4.51}]\cdot 13\text{--}14\text{H}_2\text{O}$ (vein no. 1), $(\text{Ca}_{2.79}\text{Mn}_{0.35}\text{K}_{0.10}\text{Sr}_{0.06}\text{Mg}_{0.05}\text{Ba}_{0.05}\text{Na}_{0.04}\text{Ce}_{0.02}\text{Th}_{0.01})_{\Sigma=3.47}(\text{Ti}_{3.89}\text{Nb}_{0.58}\text{Fe}_{0.13}\text{Al}_{0.07})_{\Sigma=4.67}[\text{Si}_{12}\text{O}_{34}|\text{O}_{4.10}(\text{OH})_{0.90}]\cdot 13\text{--}14\text{H}_2\text{O}$ (vein no. 2), and $(\text{Ca}_{3.68}\text{Sr}_{0.17}\text{Mn}_{0.03}\text{K}_{0.01})_{\Sigma=3.89}(\text{Ti}_{3.98}\text{Nb}_{0.65}\text{Fe}_{0.04}\text{Al}_{0.02})_{\Sigma=4.69}[\text{Si}_{12}\text{O}_{34}|\text{O}_{2.88}\text{O}_{2.12}]\cdot 13\text{--}14\text{H}_2\text{O}$ (vein no. 3). The simplified formula is $\text{Ca}_4(\text{Ti,Nb})_5[(\text{Si}_6\text{O}_{17})_2]_2(\text{OH},\text{O})_5\cdot 13\text{--}14\text{H}_2\text{O}$. The composition of zorite corresponds to empirical formula $(\text{Na}_{6.71}\text{Ca}_{0.07}\text{Mn}_{0.03}\text{Mg}_{0.01}\text{Sr}_{0.05}\text{Ce}_{0.02}\text{K}_{0.28})_{7.17}(\text{Ti}_{4.05}\text{Nb}_{0.45}\text{Al}_{0.02}\text{Fe}_{0.11})_{4.63}[\text{Si}_{12}\text{O}_{34}|\text{O}_{3.79}\text{O}_{1.21}]\cdot 13\text{--}14\text{H}_2\text{O}$. Based on these results, the formula of the chivruaiite-zorite series can be written as $(\text{Na,Ca,Mn,Sr,K})_8(\text{Ti,Nb})_5[\text{Si}_{12}\text{O}_{34}|\text{O}(\text{OH},\text{O})_5]\cdot 13\text{--}14\text{H}_2\text{O}$. Calculated oxygen contents range from 36.37 to 37.72 apfu that corresponds to the additional O and OH contents ranging from $(\text{OH})_{4.74}$ to $\text{O}_{2.44}(\text{OH})_{2.56}$.

CRYSTAL STRUCTURE

Experimental methods

A crystal of chivruaiite from vein no. 2 was selected for data collection and mounted on a glass fiber. Data were collected by a SMART 1K CCD diffractometer using monochromated $\text{MoK}\alpha$ radiation and frame widths of 0.3° in ω up to $27.5^\circ\theta$. The unit-cell dimensions (Table 2) were refined by least-squares techniques. The

data were corrected for Lorentz, polarization, absorption, and background effects. The intensity statistics indicated the centrosymmetric space group $Cmmm$. The structure was solved and refined by means of the program SHELX-97. Refinement of all atomic-position parameters, allowing for the anisotropic displacement of all atoms, and the inclusion of a refinable weighting scheme of the structure factors, resulted in a final agreement index (R_i) of 0.038, calculated for the 687 unique observed reflections ($|F_o| > 4\sigma F$). The final atomic parameters are listed in Table 3, and selected interatomic distances are given in Table 4.

Results

The structure of chivruaiite is based upon mixed heteropolyhedral framework topologically identical to those found in the structures of zorite (Sandomirskii and Belov 1979), haïneaultite (McDonald and Chao 2004), and ETS-4 (Philippou and Anderson 1996; Braunbarth et al. 2000; Nair et al. 2001; Kuznicki et al. 2001). There are two Ti positions in the structure. The Ti1 site has almost regular octahedral coordination (Ti1-O = 1.92–1.97 Å), whereas the Ti2 site has a square pyramidal coordination and is disordered over two sites that are symmetrically equivalent relative to the (001) mirror plane. The TiO_6 octahedra share *trans*-corners to form chains running parallel to the *a* axis. The SiO_4 tetrahedra form double *dreier* chains parallel to the *c* axis. The tetrahedral chains are further linked by additional half-occupied Ti_2O_5 square pyramids (Fig. 2a). Thus, the structure of chivruaiite has the same defect character (i.e., faulted) as previously reported for zorite, haïneaultite, and ETS-4. Topology of the heteropolyhedral framework in chivruaiite and related structures can be investigated using nodal representation (Krivovichev

TABLE 1. Chemical composition of chivruaiite (wt%)

Mineral Vein	Chivruaiite									Zorite “Yubileinaya”	
	1				2		3			8	9
	1	2	3	Mean	4	5	6	7			
SiO_2	44.10	44.90	46.43	45.14 ± 1.18	43.09	42.86	43.50	43.58	43.90	43.16	
TiO_2	20.11	21.45	20.33	20.63 ± 0.72	18.33	18.75	19.41	18.95	18.82	20.16	
Al_2O_3	0.06	0.06	0.09	0.07 ± 0.02	0.10	0.31	0.07	0.05	0.04	0.05	
Fe_2O_3	0.08	0.15	0.30	0.18 ± 0.11	0.47	0.70	0.18	0.17	0.62	0.42	
MnO	–	–	0.05	0.02 ± 0.03	1.45	1.46	0.13	0.13	0.08	0.12	
MgO	–	–	0.03	0.01 ± 0.02	0.15	0.07	–	–	0.06	–	
CaO	10.52	10.57	10.49	10.53 ± 0.04	9.42	9.21	12.52	12.36	0.36	0.05	
Na_2O	–	0.12	0.18	0.10 ± 0.09	0.14	–	–	–	10.85	14.23	
K_2O	1.28	1.82	0.79	1.30 ± 0.52	0.28	0.24	0.04	0.05	0.63	0.97	
BaO	–	–	–	–	0.52	0.23	–	–	–	–	
SrO	0.37	–	0.48	0.28 ± 0.25	0.77	–	1.00	1.12	0.56	–	
Nb_2O_5	4.62	2.94	3.32	3.63 ± 0.88	4.67	4.47	4.21	6.13	3.82	3.42	
Ce_2O_3	–	–	–	–	0.41	–	–	–	0.31	–	
Ta_2O_5	–	–	–	–	0.13	–	–	–	0.19	–	
ThO_2	–	–	–	–	0.23	–	–	–	–	–	
H_2O				17.30							
Total	81.13	82.01	82.67	99.19	80.16	81.94	81.10	82.53	80.24	82.58	
	Structural formulae calculated on the basis of Si = 12										
Ca^{2+}	3.07	3.03	2.91	3.00	2.81	2.76	3.70	3.65	0.11	0.02	
Mn^{2+}	–	–	0.01	0.01	0.34	0.35	0.03	0.03	0.02	0.03	
Mg^{2+}	–	–	0.01	0.00	0.06	0.03	–	–	0.02	–	
Sr^{2+}	0.06	–	0.07	0.04	0.13	–	0.16	0.18	0.09	–	
Ce^{3+}	–	–	–	–	0.04	–	–	–	0.03	–	
Th^{4+}	–	–	–	–	0.02	–	–	–	–	–	
Ba^{2+}	–	–	–	–	0.06	0.03	–	–	–	–	
K^+	0.45	0.62	0.26	0.44	0.10	0.09	0.01	0.02	0.22	0.34	
Na^+	–	0.06	0.09	0.05	0.08	–	–	–	5.75	7.67	
Ca1+Ca2	3.58	3.71	3.35	3.54	3.64	3.26	3.90	3.88	6.24	8.06	
Ti^{4+}	4.12	4.31	3.95	4.13	3.84	3.95	4.03	3.93	3.87	4.22	
Nb^{5+}	0.57	0.36	0.39	0.44	0.59	0.57	0.53	0.76	0.47	0.43	
Ta^{5+}	–	–	–	–	0.01	–	–	–	0.01	–	
Al^{3+}	0.02	0.02	0.03	0.02	0.03	0.10	0.02	0.02	0.01	0.02	
Fe^{3+}	0.02	0.03	0.06	0.04	0.10	0.15	0.04	0.04	0.13	0.09	
Ti1+Ti2	4.73	4.72	4.43	4.63	4.57	4.77	4.62	4.75	4.49	4.76	
Si^{4+}	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	
H ⁺				30.68							
O^{2-}	37.08	36.97	36.37	52.06	36.97	36.92	37.37	37.72	36.44	37.74	

2004, 2005). Replacement of the Ti and Si centers by black and white vertices, respectively, and linking those vertices that correspond to the corner-sharing polyhedra results in a 3D black-and-white graph shown in Figure 2b. The 3D network contains large polyhedral voids in the form of octangular prisms arranged together to form large channels parallel to [100].

The positions of extra-framework cations within the heteropolyhedral framework is of interest. Large K^+ cations are located within the channels of octangular prisms (Fig. 2b) and is approximately at the center of 8-membered rings of tetrahedra (MRs) formed as a result of condensation of two single tetra-

hedral chains (Fig. 3c). The K^+ -O interatomic distances are in the range of 2.6–3.3 Å. The Ca^{2+} cations are in the walls of the titanosilicate framework: the Ca1 site blocks the 7 MR formed by four silicate tetrahedra and three Ti polyhedra (Fig. 3a), whereas the Ca2 site is approximately at the center of the 6 MR formed by four silicate tetrahedra and two Ti octahedra (Fig. 3b).

The structural formula for chivruaiite from vein no. 2 calculated on the basis of single-crystal structural study can be written as $(Ca_{3.10}Mn_{0.40}Sr_{0.20})(K_{0.20}Ba_{0.10})[Ti_{4.12}Nb_{0.88}](Si_6O_{17})_2[O_{3.48}(OH)_{1.52}(H_2O)_{12.96}]$, which is in good agreement with the results of our chemical analyses.

TABLE 2. Crystallographic data and refinement parameters for chivruaiite

<i>a</i> (Å)	7.1918(9)
<i>b</i> (Å)	23.166(3)
<i>c</i> (Å)	6.9472(8)
<i>V</i> (Å ³)	1157.4(2)
Space group	<i>Cmmm</i>
<i>Z</i>	1
<i>D</i> _{calc} (g/cm ³)	2.42
Crystal size (mm)	0.08 × 0.04 × 0.008
Radiation	MoK α
Total Ref.	3260
Unique Ref.	768
Unique $ F_o \geq 4\sigma_f$	687
<i>R</i> ₁	0.038
<i>wR</i> ₂	0.107
<i>S</i>	1.078

Notes: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$; $w = 1 / (\sum^2(F_o^2) + (aP)^2 + bP)$, where $P = (F_o^2 + 2F_c^2) / 3$; $s = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters.

X-ray powder diffraction pattern

The powder X-ray diffraction pattern of chivruaiite was obtained by means of the URS-1 instrument operated at 40 kV and 30 mA using a 114.7 mm camera and FeK α -radiation. Table 5 provides a comparison of the powder patterns of chivruaiite from veins 1 and 3 with those reported for zorite by Mer'kov et al. (1973). The unit-cell parameters refined from the powder data are (for chivruaiite from veins 1 and 2, respectively): *a* = 7.17(2) and 7.16(2) Å, *b* = 22.98(9) and 23.00(1) Å, *c* = 6.94(2) and 6.92(2) Å, *V* = 1144.4 and 1140.1 Å³.

Discussion

Table 6 shows comparison of mineralogical data for chivruaiite and zorite. Both minerals have the same general structural formula, $A_8(\square, K)(Ti, Nb, \square)_5(Si_6O_{17})_2(OH, O)_5 \cdot 13-14H_2O$, where *A* = Na, Ca, Mn. The structures are related by the fol-

TABLE 3. Atomic coordinates and displacement parameters (Å²) for chivruaiite

Atom	Occupation	x	y	z	<i>U</i> _{eq}
Ti1	Ti _{0.78} Nb _{0.22} *	¼	¼	0	0.0172(4)
Ti2	Ti _{0.25} *	-½	½	0.0319(15)	0.020(3)
Si1	Si	0	0.33852(5)	0.27054(15)	0.0143(3)
Si2	Si _{0.50} *	0.0962(3)	0.43567(9)	0.0000	0.0155(5)
Ca1	Ca _{0.35} Sr _{0.025} *	0	0.13883(12)	0.2145(5)	0.0320(11)
Ca2	Mn _{0.10} Ca _{0.075} *	¼	¼	½	0.024(3)
O1	O	0	½	0	0.0235(14)
O2	O	0	0.3454(2)	½	0.0351(13)
(O,OH)3	O	0	0.21976(18)	0	0.0192(9)
O4	O	0.1851(3)	0.30653(11)	0.2009(4)	0.0341(7)
O5	O	0	0.40438(14)	0.1893(5)	0.0350(9)
H ₂ O6	O	0	0.1986(3)	½	0.072(2)
O7	O _{0.25} *	0.3179(12)	0.4387(3)	0.0420(14)	0.024(3)
H ₂ O8	O _{0.30(2)}	-½	½	0.414(4)	0.064(9)
(O,OH)9	O _{0.25} *	-½	½	0.267(4)	0.042(5)
H ₂ O10	O _{0.34(6)}	0	½	½	0.13(3)
H ₂ O11	O _{0.29(2)}	-½	0.5783(13)	½	0.080*
H ₂ O12	O _{0.12(1)}	0.413(7)	0.411(2)	0	0.080*
H ₂ O13	O _{0.19(1)}	-0.340(3)	0.5686(9)	0.425(3)	0.080*
H ₂ O14	O _{0.11(1)}	0	0.099(3)	0.166(9)	0.080*
K	K _{0.05} Ba _{0.025} *	-0.856(6)	½	½	0.120*

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	0.0224(6)	0.0156(5)	0.0137(5)	0	0	0.0067(3)
Ti2	0.0171(17)	0.0106(15)	0.033(8)	0	0	0
Si1	0.0173(6)	0.0161(6)	0.0096(6)	-0.0002(4)	0	0
Si2	0.0152(12)	0.0101(10)	0.0211(11)	0	0	-0.0007(8)
Ca1	0.0165(14)	0.0247(16)	0.055(2)	0.014(1)	0	0
Ca2	0.023(4)	0.037(5)	0.012(4)	0	0	0.008(3)
O1	0.024(3)	0.011(3)	0.035(4)	0	0	0
O2	0.068(4)	0.028(2)	0.010(2)	0	0	0
(O,OH)3	0.014(2)	0.016(2)	0.028(2)	0	0	0
O4	0.0191(12)	0.0407(14)	0.043(1)	-0.027(1)	-0.004(1)	0.0071(10)
O5	0.067(3)	0.0182(16)	0.020(2)	0.003(1)	0	0
H ₂ O6	0.090(6)	0.071(5)	0.056(4)	0	0	0
O7	0.013(3)	0.020(3)	0.040(10)	0.000(4)	0.000(4)	-0.001(3)

* Fixed during refinement.

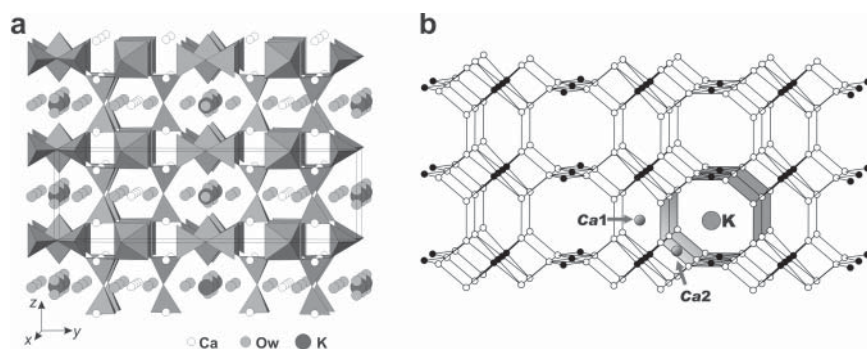


FIGURE 2. Crystal structure of chivruaiite (a) (some H₂O molecules are omitted for clarity) and nodal representation of its titanate framework (Ti and Si centers are symbolized by black and white vertices respectively) (b). In b, positions of K⁺ and Ca²⁺ cations are indicated.

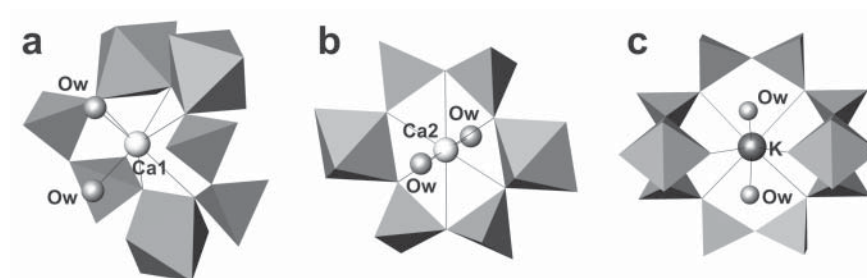


FIGURE 3. Local structural environment of K⁺ and Ca²⁺ cations in the structure of chivruaiite.

TABLE 4. Selected bond lengths (Å) in the structure of chivruaiite

Ti1-O3	1.930(2) 2×	Ca1-O3	2.395(4)
Ti1-O4	1.970(2) 4×	Ca1-H ₂ O6	2.419(6)
<Ti1-O>	1.96	Ca1-H ₂ O11	2.43(2)
		Ca1-H ₂ O13	2.47(2)
Ti2-O9	1.63(3)	Ca1-O7	2.525(9)
Ti2-O7	1.933(8) 4×	Ca1-O4	2.596(3) 2×
<Ti2-O>	1.87	<Ca1-O>	2.49
Si1-O4	1.599(2) 2×	Ca2-H ₂ O6	2.157(4) 2×
Si1-O2	1.602(1)	Ca2-O4	2.500(3) 4×
Si1-O5	1.627(3)	Ca2-O2	2.849(4) 2×
<Si1-O>	1.61	<Ca2-O>	2.50
Si2-O7	1.622(9)	K-H ₂ O8	2.63(4) 2×
Si2-O1	1.643(2)	K-H ₂ O9	3.03(4) 2×
Si2-O5	1.653(3) 2×	K-H ₂ O11	3.14(4) 2×
<Si2-O>	1.63	K-O5	3.26(2) 4×
		<K-O>	3.06

lowing substitution mechanisms: (1) substitutions within the Ca(Na) positions: 2Na ↔ (Ca, Sr, Mn), 3Na ↔ REE etc.; (2) introduction of large cations (K⁺, Ba²⁺, Cs⁺ into the channel position); (3) O²⁻ ↔ OH⁻ substitutions for the anion positions bridging between two Ti1 sites.

McDonald and Chao (2004) reported occurrence and structure of haïneaultite, (Na,Ca)₅Ca(Ti,Nb)₅(Si,S)₁₂O₃₄(OH,F)₈·5H₂O, which can be considered as an intermediate species between zorite and chivruaiite, the pure Na and Ca end-members, respectively. It is noteworthy that haïneaultite crystallizes in space group *C222* vs. *Cmmm* in zorite and chivruaiite. Based on the terminology developed in this study, Ca and Na in haïneaultite occupy two separate sites corresponding to the Ca1 and Ca2 sites, respectively. However, in contrast to chivruaiite, the Ca1 site is dominated by vacancies, whereas the Ca2 site is 63% occupied by Na. The structural formula of haïneaultite can be derived

from Table 3 of McDonald and Chao (2004) as Na_{5.04}Ca_{1.00}Ti_{4.20}Nb_{0.80}Si₁₂O₃₄(OH)₈(H₂O)_{4.96}, which is in stark contrast with the empirical formula given as (Na_{2.41}Ca_{1.83}K_{0.71})_{Σ4.95}Ca(Ti_{3.76}Nb_{0.67}Fe_{0.11}Mn_{0.06}Zr_{0.04}Mg_{0.03})_{Σ4.67}(Si_{11.30}S_{0.52})_{Σ11.82}O₃₄(OH_{7.86}F_{0.14})_{Σ8}·5H₂O. It is interesting that, similarly to chivruaiite and zorite (see above), the total occupancy of the Ti sites is less than 5 (calculated on the basis of structural data).

Our structural data (in particular, the Ca2-O bond lengths) indicate that the Ca2 site is most likely the host site for Mn; however, this site is still dominated by vacancies (see Table 3). Thus, we suggest that zorite, chivruaiite, and haïneaultite can be distinguished as different mineral species on the basis of space group and the dominating cation determined from the sum of the occupancies of the Ca1 and Ca2 sites. Thus, zorite is a Na-dominant species that crystallizes in the *Cmmm* space group, whereas both chivruaiite and haïneaultite are Ca-dominant species crystallizing in the *Cmmm* and *C222* space groups, respectively (if one uses the empirical formula for the identification of haïneaultite).

It has been known that the ETS-4 molecular sieve (synthetic analog of zorite) has a strong ion-exchange capacity for Sr²⁺ (Braunbarth et al. 2000). Analysis of the structural data reported by Braunbarth et al. (2000) shows that Sr²⁺ cations in Sr-exchanged ETS-4 occupy the Ca1 site. Taking into account structural similarities between zorite and chivruaiite, we suggest that chivruaiite can also have similar ion-exchange properties. Moreover, we conclude that chivruaiite can accumulate up to 1 apfu of large cations such as K⁺ and (more importantly) Cs⁺ if the latter are incorporated into the K position within the channels. The possibility of using zorite as a material for the removal of both ¹³⁷Cs and ⁸⁹Sr from radioactive waste solutions was first suggested by Dyer and Pillinger (1999). Very recently, Zubkova

TABLE 5. X-ray powder diffraction data for chivruaiite, zorite, and haineaultite

hkl	Chivruaiite				Zorite		Haineaultite)		
	Vein no.1		Vein no. 3		(Mer'kov et al. 1973)		(McDonald and Chao 2004)		
	<i>I</i>	<i>D</i> _{obs}	<i>D</i> _{calc}	<i>I</i>	<i>D</i>	<i>I</i>	<i>D</i>		
020	100	11.6	11.5	90	11.58	80	11.6	100	11
110	90	6.91	6.94	100	6.89	100	6.9	90	6.932, 6.879
001			6.84						5.949
021								20	5.763
040	20	5.85	5.75	10	5.72	30	5.8	10	5.258
130	50	5.23	5.23	40	5.21	40	5.2	40	
111	20	4.88	4.87	20	4.86	20	4.92		
						10	4.64		
041	30	4.39	4.43	50	4.40	50	4.45	40	4.446
131	10	4.12	4.18	10	4.15			5	4.184
						10	4.01		
200	30	3.58	3.58	20	3.56	20	3.59	35	3.593
220	50	3.41	3.42	60	3.39	50	3.43	35	3.433
151	50	3.35	3.38	90	3.33	80	3.38	10	3.367
061			3.35						
201	10	3.18	3.18	20	3.17	10	3.20	30	3.172
112	30	3.10	3.10	60	3.08				
221	80	3.04	3.07	80	3.04	80	3.07	75	3.052
240			3.04						
042	40	2.97	2.97	90	2.96	80	2.98	70	2.977
132	20	2.88	2.89	30	2.89	30	2.90	25	2.896
171	40	2.76	2.74	40	2.74	30	2.76	20	2.755
260	20	2.62	2.62	10	2.62	20	2.67	35	2.630
062	50	2.58	2.57	100	2.57	80	2.59	40	2.582
									2.583
202	20	2.49	2.49	20	2.49	20	2.505	15	2.499
222	10	2.42	2.44	10	2.43	30	2.44	10	2.435
190				40	2.40			5	2.420
242				10	2.26	10	2.28	5	2.289
172								3	2.272
						10	2.23		
082				20	2.21			1	2.222
						10	2.192		
043	20	2.125	2.146	20	2.14	20	2.158	8	2.147
350				20	2.12			10	2.125
						10	2.101		
262								5	2.096
						10	2.062		
1110	10	2.018	2.006	20	2.012	10	2.031		
351								1	2.020
063								3	1.984
153				20	1.974	10	1.992		
312								10	1.965
0102	30	1.923	1.916	20	1.926	30	1.934	10	1.926
0120			1.916						
282	10	1.881	1.883	30	1.884	30	1.896	5	1.890
2101	20	1.863	1.864	30	1.865			10	1.872
						10	1.840		
352								3	1.826
400	30	1.792	1.792	30	1.794	30	1.802	15	1.793
420			1.770	10	1.768	10	1.781	10	1.774
004	30	1.735	1.735	100	1.732	80	1.742	25	1.736
						10	1.720		
2102	30	1.692	1.690	90	1.692	60	1.701	20	1.697
						10	1.673		
193								5	1.667
						10	1.659		
						10	1.648		
0103								3	1.635
						5	1.616		
422								10	1.583
						5	1.568		
442	20	1.531	1.534	40	1.536	40	1.543	15	1.538
480	20	1.521	1.520	60	1.522	40	1.528		
2122								10	1.525
1150,				30	1.505	20	1.513	3	1.507
2140								3	1.503
2103,				10	1.485	5	1.494		
481								5	1.4890
373				10	1.468	5	1.478		
462								3	1.4722
264	10	1.446	1.446	50	1.445	40	1.453	10	1.4491
						5	1.431		
530				40	1.411	30	1.419		
								10	1.4122

TABLE 6. Comparison of chivruaiite, zorite, and haineaultite

	Chivruaiite	Zorite	Haineaultite
Formula	Ca ₄ (Ti,Nb) ₅ [Si ₁₂ O ₃₄](OH,O) ₃ ·14H ₂ O	Na ₅ (Ti,Nb) ₅ [Si ₁₂ O ₃₄](OH,O) ₃ ·14H ₂ O	(Na,Ca) ₅ Ca(Ti,Nb) ₅ [(Si ₅) ₁₂ O ₃₄](OH,F) ₃ ·5H ₂ O
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Cmmm</i>	<i>Cmmm</i>	C222
<i>a</i> (Å)	7.17	7.24	7.20
<i>b</i> (Å)	22.98	23.24	23.16
<i>c</i> (Å)	6.94	6.96	6.95
<i>V</i> (Å ³)	1144.4	1171.1	1159.8
The strongest lines <i>d</i> _{obs} (l)	11.6 (100), 6.91 (90), 5.23 (50), 3.41 (50), 3.35 (50), 3.04 (80)	11.6 (80), 6.9 (100), 3.38 (80), 3.07 (80), 2.98 (80), 2.59 (80)	11.564(100), 6.932(90), 5.258 (40), 4.446(40), 3.052(75), 2.977(70),
Density (g/cm ³)	2.40–2.42	2.36–2.40	2.28
Mohs hardness	3	3–4	3–4
	biaxial (+)	biaxial (+)	biaxial (+)
α	1.612	1.575	1.599
β	1.627	1.588	1.610
γ	1.705	1.683	1.696
2 <i>V</i> , °	40	43	38

et al. (2005) demonstrated that, in natural zorite, Na⁺ cations can be exchanged for both K⁺ and Cs⁺.

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