Cámaraite, Ba₃NaTi₄(Fe²⁺,Mn)₈(Si₂O₇)₄O₄(OH,F)₇. I. A new Ti-silicate mineral from the Verkhnee Espe Deposit, Akjailyautas Mountains, Kazakhstan

E. SOKOLOVA^{1,2,*}, Y. ABDU¹, F. C. HAWTHORNE¹, A. V. STEPANOV³, G. K. BEKENOVA³ AND P. E. KOTEL'NIKOV³

³ Satpaev Institute of Geological Sciences, ul. Kabanbai batyr, 69, Almaty 050010, Kazakhstan

[Received 5 June 2009; Accepted 5 August 2009]

ABSTRACT

Cámaraite, ideally Ba₃NaTi₄(Fe²⁺,Mn)₈(Si₂O₇)₄O₄(OH,F)₇, is a new mineral from the Verkhnee Espe deposit, Akjailyautas Mountains, Kazakhstan. It occurs as intergrowths with bafertisite and jinshajiangite in separate platy crystals up to 8 mm × 15 mm × 2 mm in size, or as star-shaped aggregates of crystals with different orientations. Individual crystals are orange-red to brownish-red, and are platy on {001}. Cámaraite is translucent and has a pale-yellow streak, a vitreous lustre, and does not fluoresce under cathode or ultraviolet light. Cleavage is {001} perfect, no parting was observed, and Mohs hardness is <5; the mineral is brittle. The calculated density is 4.018 g cm⁻³. In transmitted light, cámaraite is strongly pleochroic, X = light brown, Y = reddish-brown, Z = yellowbrown, with Z < X < Y. Cámaraite is biaxial +ve and $2V_{\text{meas.}} = 93(1)^{\circ}$. All refractive indices are greater than 1.80. Cámaraite is triclinic, space group $C\overline{1}$, a = 10.678(4) Å, b = 13.744(8) Å, c = 10.678(4)21.40(2) Å, $\alpha = 99.28(8)^{\circ}$, $\beta = 92.38(5)^{\circ}$, $\gamma = 90.00(6)^{\circ}$, V = 3096(3) Å³, Z = 4, $a:b:c = 20.00(6)^{\circ}$ 0.7761:1:1.5565. The seven strongest lines in the X-ray powder-diffraction pattern are as follows: [d(A), (I), (hkl)]: 2.63, (100), (401); 2.79, (90), ($\overline{2}\overline{4}3$, $\overline{2}41$, 2 $\overline{2}6$, 225); 1.721, (70), ($\overline{2}\overline{4}11$, $\overline{2}49$, 0 $\overline{8}2$); 3.39, (50), ($2\overline{2}4$, 223); 3.18, (50), ($\overline{2}\overline{2}5$, $\overline{2}24$); 2.101, (50), ($\overline{4}42$, $\overline{4}40$); 1.578, (50), ($\overline{6}41$, $\overline{6}42$, $\overline{6}41$, $\overline{6}40$). Chemical analysis by electron microprobe gave: Nb₂O₅ 1.57, SiO₂ 25.25, TiO₂ 15.69, ZrO₂ 0.33, Al₂O₃ 0.13, Fe₂O₃ 2.77, FeO 16.54, MnO 9.46, ZnO 0.12, MgO 0.21, CaO 0.56, BaO 21.11, Na₂O 1.41, K_2O 0.84, H_2O 1.84, F 3.11, less $O \equiv F$ 1.31, total 99.63 wt.%, where the valence state of Fe was determined by Mössbauer spectroscopy [Fe³⁺/(Fe²⁺ + Fe³⁺) = 0.13(8)] and the H₂O content was derived by crystal-structure determination. The resulting empirical formula on the basis of 39 anions is $(Ba_{2.61}K_{0.34})_{\Sigma 2.95}(Na_{0.86}Ca_{0.14})_{\Sigma 1}(Ti_{3.72}Nb_{0.22}Al_{0.05})_{\Sigma 3.99}(Fe_{4.36}^{2+}Fe_{0.66}^{3+}Mn_{2.53}Mg_{0.10}Zr_{0.05}Zn_{0.03}$ Ca_{0.05})_{Σ7.78}Si_{7.97}O_{35.89}H_{3.88}F_{3.11}. Cámaraite is a Group-II TS-block mineral in the structure hierarchy of Sokolova (2006). The mineral is named cámaraite after Fernando Cámara (born 1967) of Melilla, Spain, in recognition of his contribution to the fields of mineralogy and crystallography. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2009-11).

KEYWORDS: cámaraite, new mineral species, titanium silicate, Verkhnee Espe deposit, Akjailyautas Mountains, Kazakhstan, TS block.

Introduction

CÁMARAITE was originally discovered at the Verkhnee Espe deposit in Kazakhstan by A.V. Stepanov in the 1980s. The mineral was separated from a concentrate of bafertisite and its chemical

* E-mail: elena_sokolova@umanitoba.ca DOI: 10.1180/minmag,2009.073.5.847

¹ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

² Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Moscow 119017, Russia

composition was determined with a JCXA 733 electron microprobe operated in energy-dispersive mode. Fernando Cámara and Elena Sokolova obtained a sample of bafertisite from this locality (originally collected by A.V. Stepanov) from the Fersman Mineralogical Museum in order to work on bafertisite, as this locality has the best crystals of the mineral (Yakovlevskaya and Mineev, 1965). During this work, they re-discovered cámaraite. Leonid Pautov (of the Fersman Mineralogical Museum) was aware of the unpublished work of Stepanov and his colleagues and informed ES that A.V. Stepanov had found this mineral twenty-five years earlier. The current paper is a collaboration of these two groups.

The mineral is named cámaraite after Fernando Cámara (born 1967) of Melilla, Spain (who discovered the mineral and solved its crystal structure), in recognition of his contribution to the fields of mineralogy and crystallography, particularly with respect to Ti-silicate minerals, amphiboles, arrojadite-group minerals and cancrinite-group minerals. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2009-11). The holotype specimen of cámaraite has been deposited at the Fersman Mineralogical Museum, Moscow, Russia, registration number 3828/1 and 3828/2.

Occurrence

The mineral occurs in the Verkhnee Espe deposit (48°03′–48°10′N, 81°26′–81°29′E), which is related spatially to two small oval outcrops of alkaline granite at the northern exo-contact of the large Akjailyautas granite massif in the northern part of the Tarbagatai mountain range, eastern Kazakhstan (Stepanov and Bekenova, 2009). Both these small intrusions are part of a belt of alkaline-granite dykes which extend 5 km NNE and more than 20 km SSW from these outcrops, and almost coincide with the western exo- and endo-contacts of the Akjailyautas granite massif. The Verkhnee Espe rare-element (Zr, Nb, REEs, Th, etc.) deposit formed probably during the later stages of the intrusion of the Akjailyautas massif.

Cámaraite was found at one locality in the deposit where fenites are most enriched in alkalies and have been extensively recrystallized. The accumulation of post-magmatic fluids and their contamination by host-rock fluids resulted in intense reworking of the granites and the host

rocks. The granites were intensely recrystallized with significant enrichment in F, Li and rare elements, with loss of the typical hypidiomorphic texture and development of granoblastic texture. Primary quartz and microcline inclusions partially survived, but primary platy albite and tartantwinned microcline recrystallized extensively. Primary biotite and sodic-calcic amphiboles were replaced by Li-bearing riebeckite, aggirine and astrophyllite. Secondary feldspars differ from primary feldspars in that they lack perthite or antiperthite textures, do not contain micro-flakes of hematite, and show no sign of alteration or replacement. Due to the freshness of these secondary feldspars, the resulting fenitized granite has a white or bluish-white colour.

Crystals of riebeckite, aggirine and albite are oriented NW-SE irrespective of the orientation of the contact, suggesting recrystallization was accompanied by strong NE-SW stress. The associated pegmatites were extensively albitized or microclinized, with sporadic introduction of Zr, Th, Nb and REEs. Subsequent greisenization was very heterogeneous and weak, and was accompanied by partial to complete breakdown of riebeckite, aegirine, elpidite, astrophyllite and formation of polylithionite, quartz, rutile and fluorite. Cámaraite is of hydrothermal origin and occurs with bafertisite (Peng, 1959) and jinshajiangite (Hong and Fu, 1982) in a zone of fenites. The source of Ba for these minerals (also for other Ba minerals: capellenite, barylite and bazirite) may have been the adjacent tuffaceous aleurolites and dykes of basic and intermediate rocks. Cámaraite is associated with various rare-metal minerals: bafertisite, jinshajiangite, zircon, pyrochlore-group minerals, thorite, monazite, xenotime etc., and formed at the exo-contact zone of the fenitized and granitized host rocks.

Physical properties

Cámaraite occurs on fracture surfaces (Fig. 1) as intergrowths with jinshajiangite (Fig. 2a) and bafertisite (Fig. 2b). Both these intergrowths resemble separate platy crystals up to 8 mm \times 15 mm \times 2 mm in size. Cámaraite also occurs as star-shaped aggregates of crystals with different orientations. Individual crystals are orange-red to brownish-red (paler than bafertisite), platy on $\{001\}$ and show no twinning. Cámaraite is translucent and has a pale-yellow streak, a vitreous lustre, and does not fluoresce under cathode or ultraviolet light. Cleavage is $\{001\}$

CáMARAITE, A NEW TI-SILICATE

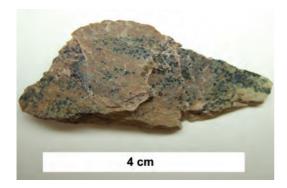


Fig. 1. Fenitized rock consisting of K-feldspar and albite with disseminated alkali amphiboles, astrophyllite, aegirine, cámaraite, bafertisite, jinshajiangite etc.

perfect, no parting is observed, and Mohs hardness is <5 (less than bafertisite); the mineral is brittle. The measured density (obtained by weighing 10 grains of cámaraite in air and in alcohol) is 3.871(1) and the calculated density is 4.018 g cm⁻³ (from the empirical formula and unit-cell parameters of the single crystal used for the crystal-structure determination). The measured density is less than the calculated density because the grains of cámaraite are intergrown with bafertisite and jinshajiangite (Fig. 2).

In transmitted light, cámaraite is strongly pleochroic, X = light brown, Y = reddish-brown, Z = yellow-brown, with Z < X < Y. The relation

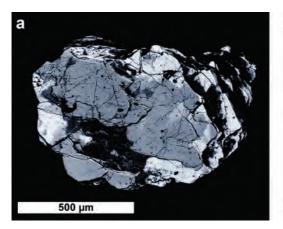
between the optic axes (X, Y, Z) and crystallographic axes (a, b, c) is as follows:

	а	b	C
X	90.4°	3.2°	96.2°
Y	73.6°	86.9°	164.7°
\mathbf{Z}	163.6°	89.5°	103.9°

where the entries in the matrix denote the angles between the corresponding directions. Cámaraite is biaxial +ve and $2V_{\rm meas.}=93(1)^{\rm o}$. All refractive indices are greater than 1.80 but we were unable to measure their exact values due to safety restrictions. The calculated mean refractive index is 1.866, and measurement of the birefringence confirmed that all refractive indices are above 1.80. We were unable to measure the dispersion due to the combination of optic orientation and crystal shape.

Chemical composition

Crystals were analysed with a Cameca SX100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a probe current of 20 nA, and a final beam diameter of 10 μ m. The following standards were used in the analysis: fluor-riebeckite (F- $K\alpha$); albite (Na- $K\alpha$); forsterite (Mg- $K\alpha$); andalusite (Al- $K\alpha$); diopside (Si- $K\alpha$, Ca- $K\alpha$); orthoclase (K- $K\alpha$); titanite (Ti- $K\alpha$); spessartine (Mn- $K\alpha$); fayalite (Fe- $K\alpha$); gahnite (Zn- $K\alpha$); zircon (Zr- $L\alpha$); synthetic Ba₂NaNb₅O₁₅ (Nb- $L\alpha$); and baryte (Ba- $L\alpha$). The elements Rb, Sr, Cs, Ta and Pb were sought but not detected. The data were



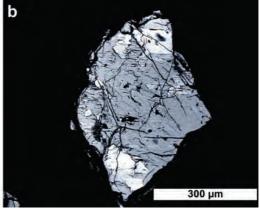


Fig. 2. Backscattered electron images of cámaraite intergrown with other Ti-silicate minerals; (a) cámaraite (white) and jinshajiangite (grey); (b) cámaraite (grey) and bafertisite (white); note the parallel intergrowth of all minerals.

TABLE 1. Chemical composition (wt.%) and formula (a.p.f.u.) for cámaraite¹.

	1		2 ——		1	2
		Average	Range			
Nb_2O_5	1.51	1.57	1.36-1.82	Si	8.14	7.97
SiO ₂	26.04	25.25	25.09-25.40			
TiO ₂	15.86	15.69	15.41 - 15.88	Ti	3.73	3.72
ZrO_2	n.a.	0.33	0.22 - 0.52	Nb	0.21	0.22
Al_2O_3 $Fe_2O_3^2$	n.a.	0.13	0.09 - 0.22	Al	_	0.05
$Fe_2O_3^2$	n.a.	2.77		Σ	3.94	3.99
FeO	22.29	16.54	$18.76 - 19.37^3$			
MnO	7.12	9.46	9.34 - 9.60	Fe ²⁺	5.82	4.36
ZnO	n.a.	0.12	0.09 - 0.17	Mn	1.88	2.53
MgO	n.a.	0.21	0.20 - 0.22	Fe ³⁺	_	0.66
CaO	0.57	0.56	0.48 - 0.70	Mg	_	0.1
BaO	22.51	21.11	20.60 - 21.66	Zr	_	0.05
Na ₂ O	1.41	1.41	1.32 - 1.48	Ca	0.04	0.05
K ₂ O	0.8	0.84	0.80 - 0.89	Zn	_	0.03
H_2O^4	3.36	1.84		Σ	7.74	7.78
F	n.a.	3.11	2.93 - 3.33			
sub total		100.94		Na	0.85	0.86
less O≡F	_	1.31		Ca	0.15	0.14
Total	101.47	99.63		Σ	1	1
				Ba	2.76	2.61
				K	0.32	0.34
				Σ	3.08	2.95
				O	35	35.89
				H	7	3.88
				F	_	3.11

¹ 1: Original EMP analysis (A.V. Stepanov); 2: EMPA for single crystal used for structure solution and optics.

reduced and corrected by the 'PAP' method of Pouchou and Pichoir (1985). The presence and quantity of (OH) groups were established by crystal-structure solution and refinement. The H₂O content was calculated by stoichiometry on the basis that (OH + F) = 7 a.p.f.u. Table 1 gives the chemical composition (mean of 13 determinations). Milli-Mössbauer spectroscopy on the same crystal used for the X-ray data collection (Fig. 3) gave $Fe^{3+}/Fe_{total} = 0.13(8)$. The unit-formula (analysis 2, Table 1) calculation was based on 39 anions per formula unit (p.f.u.)]. The general formula may be written as Ba₃NaTi₄(Fe²⁺,Mn)₈ (Si₂O₇)₄O₄(OH,F)₇. There is very close correspondence between the original analysis of cámaraite (analysis 1, Table 1) and the

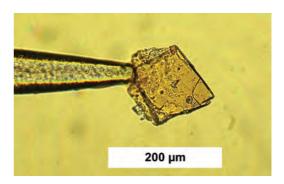


Fig. 3. A single crystal of cámaraite on a glass fibre, note the platy nature of the mineral.

² determined by Mössbauer spectroscopy. ³ for Fe total measured as Fe²⁺.

⁴ calculated from structure solution and refinement.

n.a. = not analysed.

composition of the crystal used for the structural analysis (analysis 2, Table 1). Comparison between analyses 1 and 2 indicates that cámaraite shows some variation in the amounts of Fe²⁺ and Mn but that all other constituents are in very close correspondence. Cámaraite is a Group-II TS-block mineral in the structure hierarchy of Sokolova (2006).

Mössbauer spectroscopy

The Mössbauer spectrum was collected at room temperature (RT) on a single crystal $(140 \text{ mm} \times 140 \text{ mm} \times 30 \text{ } \mu\text{m}, \text{ Fig. 3}) \text{ using a}$ ⁵⁷Co(Rh) point source. Due to the small size of the sample and the low signal-to-noise ratio, the collection time was about five weeks. Of course, these conditions are not optimal, but one must work with whatever amount of sample is available for new minerals. The off-resonance background of the folded spectrum is ~3.3 megacounts. The spectrometer was calibrated using the spectrum of α -Fe at room T. The cámaraite spectrum (Fig. 4) is fitted with two sites (each with one Gaussian component) due to Fe²⁺ (solid line) and Fe³⁺ (dashed line), using a Voigt-based quadrupolesplitting-distribution (QSD) analysis. Assuming equal recoil-free fractions for Fe²⁺ and Fe³⁺, the Fe^{3+}/Fe_{tot} ratio is 0.13(8). The ratio of the spectral areas of the low-velocity peak to the high-velocity peak (A-/A+) was allowed to vary for the Fe^{2+}

site, whereas it was constrained to be equal to unity for the minor Fe^{3+} . The Lorentzian linewidth of the elemental doublet of the QSD was fixed at $0.1~{\rm mm~s}^{-1}$, and the Gaussian width was fixed at $0.3~{\rm mm~s}^{-1}$ for both Fe^{2+} and Fe^{3+} components. Furthermore, the centre shift (CS) and the quadrupole splitting (QS) for Fe^{3+} were constrained to $0.4~{\rm mm~s}^{-1}$ and $0.7~{\rm mm~s}^{-1}$ respectively. The refined parameters for Fe^{2+} are: $CS = 1.13(2)~{\rm mm~s}^{-1}$; $QS = 1.94(5)~{\rm mm~s}^{-1}$ characteristic of high-spin Fe^{2+} in octahedral coordination.

X-ray powder diffraction

The powder-diffraction pattern was recorded with monochromated Co- $K\alpha$ X-radiation (λ = 1.79021 Å) and a 57.3 mm diameter Debye-Scherrer camera. Table 2 shows the X-ray powder-diffraction data for cámaraite. The unitcell parameters were refined, giving the following values: a = 10.678(4) Å, b = 13.744(8) Å, c =21.40(2) Å, $\alpha = 99.28(8)^{\circ}$, $\beta = 92.38(5)^{\circ}$, $\gamma =$ $90.00(6)^{\circ}$, $V = 3096(3) \text{ Å}^3$. Cámaraite is triclinic, space group $C\overline{1}$, Z = 4. Unit-cell dimensions were also determined on a Bruker diffractometer using graphite-monochromated Mo- $K\alpha$ X-radiation (a =10.6965(7) Å, b = 13.7861(9) Å, c = 21.478(2) Å, $\alpha = 99.345(1)^{\circ}$, $\beta = 92.315(2)^{\circ}$, $\gamma = 89.993(2)^{\circ}$, V =3122.6(4) Å³) and are close to the values determined by powder diffraction.

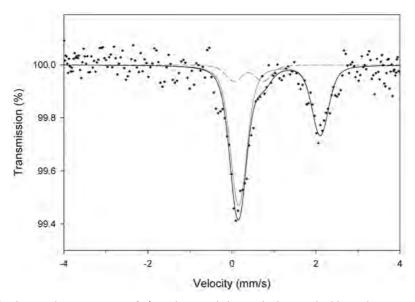


Fig. 4. The Mössbauer spectrum of cámaraite recorded on a single crystal with a point γ-ray source.

TABLE 2. Powder-diffraction pattern for cámaraite.

I	$d_{ m meas.} \ (m \AA)$	$d_{ m calc.} \ (m A)$	h	k	l
<10	4.231				
<10	4.00	4.001	2	2	2
		4.000		2	1
30	3.83	3.831	2 2 2 2 2	0	4
		3.821	2	2	3
		3.820	2	2	2
10	3.53	3.516	0	0	6
50	3.39	3.402	2	2	4
		3.400	2	2	3
20	3.26	3.268	0	4	3
		3.267	0	4	1
		3.244	2	0	5
50	3.18	3.187	2 2 2	2 2	5
		3.186			4
40	2.87	2.878	0	4	3
		2.871	2	4	2
0.0	2.50	2.871	0 2 2 2 2 2 2 2 2 4 2 4	4	0
90	2.79	2.803	2	4	3
		2.802	2	4	1
		2.791	2	2	6
10	2.69	2.790	2	2 2 4	5 4 ²
10 100	2.68	2.701 2.632	4	0	
100	2.63 2.259	2.258	4+ 5	4	1 7
10	2.239	2.257	2 2	4	5
20	2.212	2.213	1	0	5
<10	2.161	2.162	4	2	5
\10	2.101	2.161		2	4
50	2.101	2.101	4 4	2 4	2
30	2.101	2.103			0
30	2.012	2.012	4 4	4 2 2 4	7
50	2.012	2.012	4	2	6
70	1.721	1.723	4 2 2	$\frac{2}{4}$	11
		1.722	$\bar{\bar{2}}$	4	9
		1.718			2
$50d^3$	1.578	1.579	$\frac{0}{6}$	8 4	1
		1.579	<u>-</u>	4	2
		1.579	6	4	1
		1.579	5	4	0
30d	1.440	1.439		8	3
		1.439	4 4	8	1
20d	1.331	1.330	8	0	2

¹ This reflection is due to admixture of bafertisite, of which it is the (210) reflection; other strong lines of bafertisite overlap, e.g., (120), I = 100, d = 3.25 Å. ² not included in cell-parameter refinement.

The space group CI

Cámaraite is triclinic, space group $C\overline{1}$, Z = 4. The non-conventional space group $C\overline{1}$ was used rather than the conventional choice of $P\overline{1}$. Cámaraite, $Ba_3NaTi_4(Fe^{2+},Mn)_8(Si_2O_7)_4O_4(OH,F)_7$, is a Ti-di-orthosilicate mineral with a TS (Titanium Silicate) block. It is closely related to jinshajiangite, ideally $Ba_2Na_2Ti_4Fe_8^{2+}(Si_2O_7)_4O_4(OH)_4F_2$, and bafertisite, ideally Ba₂Ti₂Fe₄² (Si₂O₇)₂O₂(OH)₄. Cámaraite, jinshajiangite (Sokolova et al., 2009) and bafertisite (Guan et al., 1963) have a TS block of the same topology [Fe²⁺-dominant Group-II minerals in the terminology of Sokolova (2006)]. The TS block consists of a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5]and [6]-coordinated polyhedra and (Si₂O₇) groups. The TS block is characterized by a planar cell based on translation vectors, t₁ and $\mathbf{t_2}$, with $t_1 \sim 5.5$ and $t_2 \sim 7$ Å and $\mathbf{t_1} \wedge \mathbf{t_2}$ close to 90°. For cámaraite, we chose the unconventional space group $C\bar{1}$ and corresponding unit-cell parameters a = 10.6965 (2 t_1) and $b = 13.7861(2 t_2)$ for better comparison with the related Group-II structures of bafertisite, jinshajiangite, hejtmanite, perraultite and surkhobite (Table 3) and 22 other minerals with the TS block, detailed structural descriptions of which can be found in Sokolova (2006), Cámara and Sokolova (2007), Sokolova and Hawthorne (2008) and Sokolova et al. (2009). Here, we also report the (Niggli) reduced unit cell: a = 8.724(2) Å, b = 8.725(1) Å, c = $21.478(4) \text{ Å}, \ \alpha = 81.20(3)^{\circ}, \ \beta = 84.06(3)^{\circ}, \ \gamma =$ 75.62(3)°, $V = 1561.3(6) \text{ Å}^3$, space group $P\bar{1}$, Z =2. The $P\bar{1}$ cell can be derived from the $C\bar{1}$ cell via the transformation matrix $[-\frac{1}{2}\frac{1}{2}0/\frac{1}{2}0/\frac{1}{2}0/00-1]$. The crystal structure of cámaraite will be discussed in a separate paper with regard to the crystal chemistry of 27 minerals possessing the TS block.

Acknowledgements

We thank Dmitriy Belakovskii, Fersman Mineralogical Museum (RAS, Moscow, Russia), for lending us the sample used for this work. We acknowledge the comments of two anonymous reviewers, Giovanni Ferraris, Associate Editor Sergey Krivovichev and Principal Editor Mark Welch. This work was supported by the Program of Fundamental Research of the Ministry of Education and Science of the Republic of Kazakhstan 2006-2008 (Geology) to AVS, GKB

 $^{^{3}}$ d = diffuse reflection.

TABLE 3. Comparison of cámaraite, bafertisite, jinshajiangite, hejtmanite, perraultite and surkhobite.

t minerals ————————————————————————————————————	$(Si_2O_7)_4O_4(OH,Pe^{2^+})_8 \\ (Si_2O_7)_4O_4(OH,P)_6 \\ (Si_2O_7)_4O_4(F,OH,O)_6 \\ (Si_2O_7)_4O_4(F,OH,O)_6 \\ (5)_2O_7)_4O_4(F,OH,O)_6 \\ (5)_2O_7O_4(F,OH,O)_6 \\ (5)_2O_7O_4(F,OH,O)_6 \\ (5)_2O_7O_7(F,OH,O)_6 \\ (7)_2O_7(F,OH,O)_6 \\ (8)_2O_7(F,OH,O)_6 \\ (9)_2O_7(F,OH,O)_6 \\ (1)_2O_7(F,OH,O)_6 \\ (2)_2O_7(F,OH,O)_6 \\ (3)_2O_7(F,OH,O)_6 \\ (4)_2O_7(F,OH,O)_6 \\ (4)_2O_7(F,OH,O)_6 \\ (5)_2O_7(F,OH,O)_6 \\ (5)_2O_7(F,OH,O)_6 \\ (6)_2O_7(F,OH,O)_6 \\ (6)_2O_$	C2 10.723 13.826 20.791 95.00	(8, 9) (5)	3.98 3.84	3.454 (100) 2.592 (70) 2.592 (70) 2.074 (40) 10.39 (20) 3.186 (15) 2.862 (15) 2.862 (15) 1.728 (15) 1.728 (15) 1.79 (calc. from 2V) 1.810 1.86 1.825 1.89 80-85 65(5)
Mn ²⁺ -dominan	, .	Cm C2 10.7232 10.82 13.812 13.843 12.563 20.93 119.9 95.09	4 (7	3.808	3.474 (100) 10.43 (42) 2.606 (40) 3.186 (15) 2.867 (15) 2.867 (15) 3.573 (11) biaxial (-) 1.785 1.81 1.82 66(1) 64
Hejtmanite -		P2//m 5.361 6.906 12.556	(7)	4.29 4.02	2.726 (100) 5.472 (32) 3.241 (21) 3.241 (21) 3.455 (17) 1.2180 (16) 2.535 (14) biaxial (-) 1.814 1.867 76.4
als ———— Jinshajiangite	$\begin{array}{c} Ba_2Na_2Ti_4\\ (Fe^{2+},Mn)_8\\ (Si_2O_7)_4O_4(OH,F)_6\\ (2) \end{array}$	C2/m 10.6785 13.786 20.700 94.937	(2)	3.767 3.61	Å) (f) 3.44 (100) 3.15 (80) 2.630 (80) 2.630 (80) 1.02 (70) 1.715 (50 broad) 2.202 (40) biaxial (+) 1.792 1.801 1.852 - 7.2
Fe ²⁺ -dominant minerals Bafertisite	$Ba_2Ti_2(Fe^{2+},Mn)_4 (Si_2O_7)_2O_2 (OH,F)_4 (1)$	Cm 10.60 13.64 12.47 119.5	(9)	3.8 3.96–4.25	action pattern, d'n (2.65 (100) 2.11 (40) 1.72 (40) 2.52 (30) 2.23 (30) 2.07 (30) 1.75 (30) biaxial (-) 1.805 1.805 1.805 1.805 86
Cámaraite	$\begin{array}{c} Ba_3NaTi_4\\ (Fe^{2+}Mn)_8(Si_2O_7)_4\\ O_4(OH,F)_7\\ This\ work \end{array}$	CĪ 10.6965(7) 13.7861(9) 21.4778(15) 99.345(1) 92.315(2) 89.993(2)	This work	4.018	Strongest lines in the X-ray powder-diffraction pattern, dn (Å) (I) 2.63 (100) 2.65 (100) 3.4 (102.79 (90) 2.11 (40) 3.7 (100) 1.72 (40) 2.13 (100) 2.18 (100) 2.18 (100) 2.18 (100) 2.18 (100) 2.18 (100) 2.18 (100) 2.19 (100) 2.1
Mineral	Simplified formula ¹ Reference ²	Space group a (A) b c c c α(**) β β γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ	Z Reference	$D_{ m calc.}~({ m g}~{ m cm}^{-3}) \ D_{ m meas.}~({ m g}~{ m cm}^{-3})$	Strongest lines in the Optical class (sign) α (589.3 mm) β γ

¹ except for surkhobite
² each reference applies to the information given above in the column: (1) Anthony et al. (1995); (2) Sokolova et al. (2009); (3) Vrána et al. (1992); (4) Sokolova (2006); (5) Rastsvetaeva et al. (2008); (6) Guan et al. (1963); (7) Rastsvetaeva et al. (1991); (8) Chao (1991); (9) Yamnova et al. (1998); (10) Yakovlevskaya and Mineev (1965); (11) Hong and Fu (1982); (12) Pekov et al. (1999).

and PEK and a Canada Research Chair in Crystallography and Mineralogy and by Natural Sciences and Engineering Research Council of Canada Discovery, Equipment and Major Installation grants of the Natural Sciences and Engineering Research Council of Canada, and by Innovation grants from the Canada Foundation for Innovation to FCH.

References

- Anthony, J.W., Bideaux, R.A., Bladh, K.W. and Nichols, M.C. (1995) *Handbook of Mineralogy*. Vol. II. Silica, Silicates. Mineral Data Publishing, Tucson, Arizona.
- Cámara, F. and Sokolova, E. (2007) From structure topology to chemical composition. VI. Titanium silicates: the crystal structure and crystal chemistry of bornemanite, a group-III Ti-disilicate mineral. *Mineralogical Magazine*, 71, 593–610.
- Chao, G.Y. (1991) Perraultite, a new hydrous Na-K-Ba-Mn-Ti-Nb silicate species from Mont Saint-Hilaire, Quebec. *The Canadian Mineralogist*, 29, 355–358.
- Guan, Ya.S., Simonov, V.I. and Belov, N.V. (1963) Crystal structure of bafertisite, BaFe₂TiO [Si₂O₇](OH)₂. Doklady Akademii Nauk SSSR, **149**, 123–126.
- Hong, W. and Fu, P. (1982) Jinshajiangite, a new Ba-Mn-Fe-Ti-bearing silicate mineral. *Geochemistry* (*China*), **1**, 458–464.
- Pekov, I.V., Belovitskaya, Yu.V., Kartashov, P.M., Chukanov, N.V., Yamnova, N.A. and Egorov-Tismenko, Yu.K. (1999) The new data on perraultite (The Azov sea region). *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, **128**(3), 112–120. (in Russian).
- Peng, C. (1959) The discovery of several new minerals of rare elements. *Ti-chih K-o-hsueh*, **10**, 289. (in Chinese).
- Pouchou, J.L. and Pichoir, F. (1985) "PAP" φ(ρZ) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, San

- Francisco, California, USA.
- Rastvetaeva, R.K., Tamazyan, R.A., Sokolova, E.V. and Belakovskii, D.I. (1991) Crystal structures of two modifications of natural Ba,Mn-titanosilicate. *Soviet Physics Crystallography*, 36, 186–189.
- Rastvetaeva, R.K., Eskova, E.M., Dusmatov, V.D., Chukanov, N.V. and Schneider, F. (2008) Surkhobite: revalidation and redefinition with the new formula, (Ba,K)₂CaNa(Mn,Fe²⁺,Fe³⁺)₈Ti₄ (Si₂O₇)₄O₄(F,OH,O)₆. European Journal of Mineralogy, **20**, 289–295.
- Sokolova, E. (2006) From structure topology to chemical composition. I. Structural hierarchy and stereochemistry in titanium disilicate minerals. *The Canadian Mineralogist*, 44, 1273–1330.
- Sokolova, E. and Hawthorne, F.C. (2008) From structure topology to chemical composition. V. Titanium silicates: the crystal chemistry of nacareniobsite-(Ce). *The Canadian Mineralogist*, **46**, 1493–1502.
- Sokolova, E., Cámara, F., Hawthorne, F.C. and Abdu, Y. (2009) From structure topology to chemical composition. VII. Titanium silicates: the crystal structure and crystal chemistry of jinshajiangite. *European Journal of Mineralogy*, 21, 871–883.
- Stepanov, A.V. and Bekenova, G.K. (2009) Brief description of the Verkhnee Espe rare-element deposit. International Conference Satpaev's Lecturing: Geology, minerageny and future trends of mineral resources development. Proceedings, Almaty, 248–258.
- Vrána, S., Rieder, M. and Gunter, M.E. (1992) Hejtmanite, a manganese-dominant analogue of bafertisite, a new mineral. European Journal of Mineralogy, 4, 35–43.
- Yakovlevskaya, T.A. and Mineev, D.A. (1965) On the crystals and optic orientation of bafertisite. Proceedings of the Fersman Mineralogical Museum, 16, 293-294. (in Russian).
- Yamnova, N.A., Egorov-Tismenko, Yu.K. and Pekov, I.V. (1998) Crystal structure of perraultite from the coastal region of the Sea of Azov. *Crystallography Reports*, 43, 401–410.