

Yusupovite, $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$, a new mineral species from the Darai-Pioz alkaline massif and its implications as a new microporous filter for large ions

ATALI A. AGAKHANOV^{1,2}, LEONID A. PAUTOV², VLADIMIR Y. KARPENKO², ELENA SOKOLOVA^{3,*}, YASSIR A. ABDU³, FRANK C. HAWTHORNE³, IGOR V. PEKOV⁴ AND OLEG I. SIIDRA¹

¹Department of Crystallography, St. Petersburg State University, University Embankment 7/9, 119034 St. Petersburg, Russia

²Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Pr-kt, 18-2, 119071 Moscow, Russia

³Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

⁴Department of Mineralogy, Moscow State University, Vorob'ovy Gory, 119991 Moscow, Russia

ABSTRACT

Yusupovite, ideally $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$, is a new silicate mineral from the Darai-Pioz alkaline massif in the upper reaches of the Darai-Pioz river, area of the joint Turkestan, Zeravshansky, and Alaisky ridges, Tajikistan. Yusupovite was found in a pegmatite composed mainly of reedmergnerite, aegirine, microcline, and polyolithionite. It occurs as prismatic grains about 2 mm in size embedded in reedmergnerite; associated minerals are quartz, pectolite, zeravshanite, mendeleevite-(Ce), fluorite, leucosphenite, a pyrochlore-group mineral, neptunite, telyushenkoite, moskvinite-(Y), and shibkovite. Yusupovite is colorless, transparent with a white streak, has a vitreous luster, and does not fluoresce under ultraviolet light. Cleavage is perfect on {110}, parting was not observed. Mohs hardness is 5. Yusupovite is brittle with a splintery fracture. The measured and calculated densities are 2.69(2) and 2.713 g/cm³, respectively. Yusupovite is optically biaxial (+) with refractive indices ($\lambda = 589$ nm) $\alpha = 1.563(2)$, $\beta = 1.565(2)$, $\gamma = 1.577(2)$; $2V_{\text{meas}} = 42(3)^\circ$, $2V_{\text{calc}} = 45^\circ$, strong dispersion: $r > v$. Yusupovite is monoclinic, $C2/m$, $a = 14.5975(4)$, $b = 14.1100(4)$, $c = 14.4394(4)$ Å, $\beta = 90.0399(4)^\circ$, $V = 2974.1(3)$ Å³. The six strongest reflections in the X-ray powder diffraction data [d (Å), I , (hkl)] are 7.05, 100, (020); 3.24, 96, (420); 3.10, 69, (241, $\bar{2}41$); 5.13, 53, (202, $\bar{2}02$); 6.51, 42, (201, $\bar{2}01$); 3.17, 34, (042). The chemical composition (electron microprobe) is: Nb₂O₅ 0.39, SiO₂ 58.84, ZrO₂ 16.55, HfO₂ 0.30, FeO 0.01, Y₂O₃ 3.05, Cs₂O 2.58, K₂O 0.95, Na₂O 8.91, H₂O_{calc} 7.40, total 98.98 wt%, with H₂O calculated from structure refinement. The empirical formula (based on 17.5 O apfu) is $(\text{Na}_{1.76}\text{K}_{0.12}\text{Cs}_{0.11})_{\Sigma 1.99}(\text{Zr}_{0.82}\text{Y}_{0.17}\text{Nb}_{0.02}\text{Hf}_{0.01})_{\Sigma 1.02}(\text{Si}_{6.01}\text{O}_{14.98})(\text{H}_2\text{O})_{2.52}$, $Z = 8$. The crystal structure of yusupovite was refined to $R_1 = 3.46\%$ based on 4428 observed reflections. In the crystal structure, there are six Si sites occupied by Si, two M sites occupied mainly by Zr with minor Y and Hf. Si tetrahedra form an epididymite Si_6O_{15} ribbon along [010]. Epididymite ribbons and Zr-dominant M octahedra share common vertices to form a heteropolyhedral Si-Zr-O framework. There are six interstitial sites partly occupied by alkali cations Na, K, and Cs. The three [7]-coordinated Na sites are occupied by Na at 95, 84, and 78%. The three A sites are occupied by K and Cs at 12, 18, and 16%. There are 10 W sites occupied by H₂O groups at 18–84%. Due to (K,Cs), Na and H₂O disorder, the symmetry of yusupovite decreases from orthorhombic, space group $Pbcm$ (elpidite), to monoclinic, space group $C2/m$, and the b unit-cell parameter of yusupovite is doubled compared to the corresponding cell parameter in elpidite, $b_{\text{yus}} = 2a_{\text{elp}}$. Yusupovite, ideally $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$, is a dimorph of elpidite, $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$.

Keywords: Yusupovite, new mineral species, silicate, Darai-Pioz massif, Tajikistan, electron microprobe analysis, X-ray powder diffraction data, elpidite, crystal structure, alkaline pegmatite

INTRODUCTION

Yusupovite is a new mineral found in the moraine of the Darai-Pioz glacier in the upper reaches of the Darai-Pioz River, the Alaisky mountain ridge, Tien-Shan Mountains, Tajikistan. The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2014-022). The mineral is named yusupovite (Cyrillic: *юсуповит*) after

Rustam Gumirovich Yusupov (born 1935), a prominent Uzbek mineralogist and a curator at the Geological Museum, Tashkent, Uzbekistan. The holotype specimen has been deposited in the mineral collection of the Fersman Mineralogical Museum, Moscow, Russia, registration no. 4543/1. We describe here this new Zr silicate and report its crystal structure.

REVIEW OF THE RELEVANT LITERATURE

Yusupovite, ideally $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$, is a dimorph of elpidite, $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$ (Table 1). The crystal structure of elpidite was first solved on a heavily twinned crystal from

* E-mail: elena_sokolova@umanitoba.ca

TABLE 1. Comparison of yusupovite and elpidite

	Yusupovite	Elpidite ^a
Formula	Na ₂ Zr(Si ₆ O ₁₅)(H ₂ O) ₃	Na ₂ Zr(Si ₆ O ₁₅)(H ₂ O) ₃
Symmetry	monoclinic	orthorhombic
Space group	<i>C2/m</i>	<i>Pbcm</i>
<i>a</i> (Å)	14.5975(4) (<i>b</i> _{elp})	7.14(2)
<i>b</i>	14.1100(4) (2 <i>a</i> _{elp})	14.68(1)
<i>c</i>	14.4394(4) (<i>c</i> _{elp})	14.65(1)
α (°)	90	90
β	90.0399(4)	90
γ	90	90
<i>Z</i>	8	4
Strongest reflections in the powder data	7.05(100), 3.24(96) 3.10(69), 5.13(53), 6.51(42), 3.17(34)	3.271(100), 3.124(90), 7.11(90), 5.18(85), 6.56(85), 2.546(75), 2.965(75)
<i>d</i> _{obs} (Å)(<i>l</i>)	2.941(27)	2.965(75)
Color	colorless	colorless, white
Luster	vitreous	vitreous
<i>D</i> _{meas} (g/cm ³)	2.69(2)	2.615
<i>D</i> _{calc} (g/cm ³)	2.713	2.573
Hardness (Mohs)	5	5
Optical sign	Biaxial (+)	Biaxial (+)
2 <i>V</i> (°)	42 (3)	84
α	1.563(2)	1.563
β	1.565(2)	1.569
γ	1.577(2)	1.577

^a Crystallographic data (Cannillo et al. 1973); *D*_{calc} (Grigor'eva et al. 2011); powder pattern (PDF-2# 50-223); color, luster, *D*_{meas} hardness and optical properties (Tikhonenkov et al. 1957).

Lovozero, Kola Peninsula, Russia, by Neronova and Belov (1963): space group *Pbmm*, *a* = 7.4, *b* = 14.4, *c* = 7.05 Å. They described the Zr-Si-O heteropolyhedral framework, which consists of epididymite Si₆O₁₅ ribbons [described in epididymite by Pobedinskaya and Belov (1960)] connected by isolated Zr octahedra with Na atoms and H₂O groups occupying the interstitial space within the Zr-Si-O framework, and gave the formula of elpidite as Na₂Zr(Si₆O₁₅)·3H₂O, *Z* = 2. Dissatisfied with their results, Neronova and Belov (1965) lowered the symmetry to *P2cm* to explain certain features of the electron-density map. Cannillo et al. (1973) refined the crystal structure of elpidite on perfect single crystals from Mt. St. Hilaire, Quebec, Canada, in space group *Pbcm*, *a* = 7.14, *b* = 14.68, *c* = 14.65 Å, *Z* = 4, and found an overall agreement with the topology of the structure of Neronova and Belov (1963). Grigor'eva et al. (2011) refined the crystal structures of elpidite from Khan Bongo (Mongolia), which is in accord with Cannillo et al. (1973), and its cation-exchanged forms that were obtained on heating up to 90 and 150 °C. They reported orthorhombic symmetry for all high-temperature Rb- and K-exchanged forms of elpidite: the same unit-cell parameters and space group *Pbcm* for the Rb-exchanged form (90 °C) and doubling of the *a* unit-cell parameter and space group *Cmca* for the Rb-exchanged form (150 °C) and two K-exchanged forms (90 and 150 °C). For the cation-exchanged forms of elpidite, they reported depletion of Na at the Na sites and drastic decrease in the water content due to the occurrence of K and Rb at the W (= H₂O) sites of elpidite.

SAMPLE PROVENANCE

Yusupovite was found in rock samples from the Upper Darai-Pioz alkaline massif collected in the moraine of the Darai-Pioz glacier, located in the Rasht (formerly Garm) district, Tajikistan. The massif is situated near the watershed on the southern slope of the Alaisky mountain range (N39°27', E70°43'). In plan, the Darai-Pioz massif is equant and covers an area of ~16 km². The

massif has a multiphase structure; the root is granite and the central part of the massif is composed of aegirine quartz-bearing and quartz-free syenites. A small stock of cancrinite syenite occurs in the southwestern part of the massif. In the massif, there is various granitic, alkaline granitic and syenitic pegmatites, various metasomatic rocks (albitites, fenites) and carbonatites. Abundant and various mineralization of Cs, Li, B, Zr, REE, Ti, and Ba is related to the rocks of the massif. The most complete description of the geology and mineralogy of the massif was given by Dusmatov (1968, 1971). Specific details of the mineralogy and geochemistry of the Darai-Pioz massif have been discussed in numerous publications (Ganzeyev et al. 1969; Semenov and Dusmatov 1975; Efimov 1983; Belakovskiy 1991; Grew et al. 1993; Reguir et al. 1999).

In the Darai-Pioz massif, seven Cs minerals have been described to date (excluding Cs-bearing yusupovite): kupletskite-(Cs) (Yefimov et al. 1971), telyushenkoite (Agakhanov et al. 2003), sokolovaitite (Pautov et al. 2006), zeravshanite (Pautov et al. 2004), senkevichite (Agakhanov et al. 2005), kirchhoffite (Agakhanov et al. 2012), and mendeleevite-(Ce) (Pautov et al. 2013). Yusupovite was found in a pegmatite composed mainly of reedmergnerite, aegirine, microcline, and polyolithionite. Other associated minerals are quartz, pectolite, fluorite, zeravshanite, mendeleevite-(Ce), leucosphenite, a pyrochlore-group mineral, neptunite, telyushenkoite, moskvinitite-(Y), and shibkovite.

PHYSICAL PROPERTIES

Yusupovite occurs as colorless prismatic grains about 2 mm in size embedded in reedmergnerite (Figs. 1 and 2). It is transparent with a white streak and vitreous luster, and does not fluoresce under ultraviolet light. It is brittle with a splintery fracture. It has perfect cleavage on {110}, parting was not observed. Mohs hardness is 5. The measured (by flotation in CHBr₃/C₃H₇ON) and calculated densities are 2.69(2) and 2.713 g/cm³, respectively. Yusupovite is optically biaxial (+) with refractive indices (λ = 589 nm) α = 1.563(2), β = 1.565(2), γ = 1.577(2); 2*V*_{meas} = 42(3)°, 2*V*_{calc} = 45°. Dispersion is strong: *r* > *v*. A Gladstone-Dale calculation gives a compatibility index of 0.017, which is rated as superior.

Chemical composition

Crystals were analyzed with a JEOL Superprobe JXA-733 electron microprobe operating in energy-dispersive mode with an accelerating voltage of 20 kV, a beam current of 2 nA, and a beam diameter of 5 μm. The following standards were used: microcline USNM143966 (Si, K), omphacite USNM110607 (Na), LiNbO₃ (Nb), ZrO₂ (Zr), HfO₂ (Hf), ilmenite USNM96189 (Fe), Y₂O₃ (Y), and CsHo(PO₃)₄ (Cs). The data were reduced and corrected using the PAP method of Pouchou and Pichoir (1985). Table 2 gives the chemical composition (which is the mean of 10 point analyses) and the empirical formula based on 17.5 O atoms per formula unit (apfu), the content of H₂O was calculated from structure refinement. The empirical formula is (Na_{1.76}K_{0.12}Cs_{0.11})_{Σ1.99}(Zr_{0.82}Y_{0.17}Nb_{0.02}Hf_{0.01})_{Σ1.02}(Si_{6.01}O_{14.98})(H₂O)_{2.52}, *Z* = 8; the ideal formula is Na₂Zr(Si₆O₁₅)(H₂O)₃.

Infrared spectroscopy

The FTIR spectrum of a randomly oriented single crystal of yusupovite was collected using a Bruker Hyperion 2000

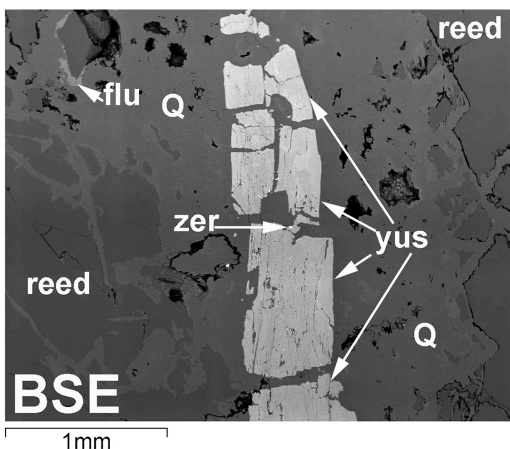


FIGURE 1. BSE image of a (broken) crystal of yusupovite (yus) cemented by quartz (Q), with zeravshanite (zer), reedmergerite (reed), and fluorite (flu).

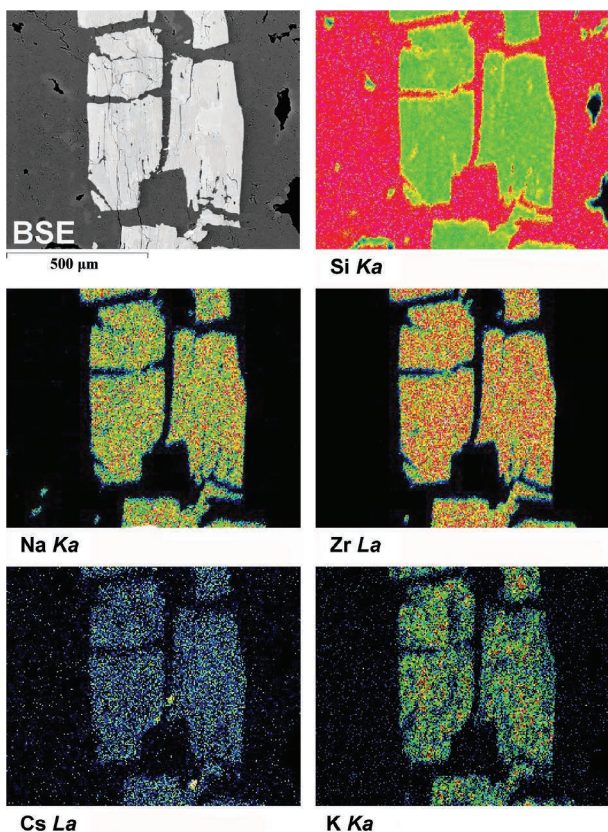


FIGURE 2. BSE image of an intergrowth of yusupovite (white) and quartz (gray), and X-ray maps of the distribution of Si, Na, Zr, Cs, and K.

IR microscope equipped with a liquid-nitrogen-cooled MCT detector. Data over the range 4000–650 cm^{-1} were obtained by averaging 100 scans with a resolution of 4 cm^{-1} . Baseline correction was done using OPUS spectroscopic software (Bruker Optic GmbH). In the principal OH-stretching region (4000–3000 cm^{-1}) (Fig. 3a), there is a peak at 3615 cm^{-1} and a

TABLE 2. Chemical analysis and unit formula for yusupovite

Constituent	Average (wt%)	Range	e.s.d.	Unit formula ^a (apfu)	
Nb ₂ O ₅	0.39	0.22–0.69	0.13	Nb	0.02
SiO ₂	58.84	57.98–59.45	0.39	Si	6.01
ZrO ₂	16.55	15.30–17.35	0.60	Zr	0.82
HfO ₂	0.30	0.07–0.67	0.21	Hf	0.01
FeO	0.01	0.00–0.07	0.03	Fe	0
Y ₂ O ₃	3.05	2.24–3.56	0.38	Y	0.17
Cs ₂ O	2.58	2.15–3.31	0.41	Cs	0.11
K ₂ O	0.95	0.61–1.31	0.24	K	0.12
Na ₂ O	8.91	8.25–9.51	0.41	Na	1.76
H ₂ O ^b	7.40			H ⁺	5.04
Total	98.98	98.47–99.42			

^a The formula was calculated on the basis of 17.50 O apfu, Z = 8.

^b H₂O calculated from structure refinement.

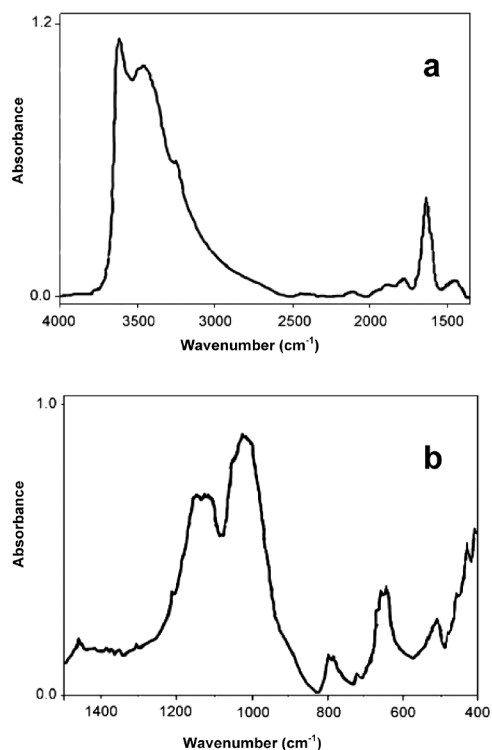


FIGURE 3. The FTIR spectra of a randomly oriented single crystal of yusupovite (4000–1350 cm^{-1}) (a) and a powder sample of yusupovite (1500–400 cm^{-1}) (b).

broad peak (with fine structure) centered at $\sim 3470 \text{ cm}^{-1}$; both are attributed to O-H stretching vibrations of H₂O groups in the structure of yusupovite. The peak at 1635 cm^{-1} , with shoulders at ~ 1660 and 1610 cm^{-1} , is due to H₂O bending vibrations. The OH-stretching region of the yusupovite spectrum (Fig. 3a) is somewhat similar to that of partially dehydrated elpidite (Zubkova et al. 2011) and Rb-exchanged elpidite (Grigor'eva et al. 2011). They all show an additional peak at $\sim 3600 \text{ cm}^{-1}$, not seen in the FTIR spectrum of elpidite that shows a triplet at 3551, 3505, and 3453 cm^{-1} (Grigor'eva et al. 2011). This peak may be assigned to an H₂O group with weaker hydrogen bonds than those of the H₂O groups in elpidite (Zubkova et al. 2011). Furthermore, the spectra of yusupovite, partially dehydrated elpidite, and Rb-exchanged elpidite generally show a reduction in

OH-stretching peak resolution compared to that of elpidite, and this is ascribed to dehydration during ion exchange (Grigor'eva et al. 2011). For yusupovite, this decrease in resolution could be due to disorder and depletion of H₂O at the W sites as a result of the occurrence of K and Cs cations at the A sites.

The IR spectrum of yusupovite in the range 1500–400 cm⁻¹ was collected from the powder in KBr microtablet using a double-beam Specord 75-IR Carl Zeiss spectrometer (Fig. 3b). The spectrum is similar to that of elpidite but has lower peak resolution compared to that of elpidite. The strongest absorbance is observed in the region of the Si-O stretching vibrations: a broad peak at 1032 cm⁻¹ and a poorly resolved doublet at 1130 and 1150 cm⁻¹. Several peaks about 790 cm⁻¹ can be attributed to Zr-O stretching vibrations in ZrO₆ octahedra, and poorly resolved peaks at 652, 642, and 430 cm⁻¹ to bending vibrations of SiO₄ groups.

TABLE 3. X-ray powder diffraction data for yusupovite

<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>h k l</i>	<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>h k l</i>
3	8.31	8.30	1 1 1	3	2.120	2.121	$\bar{1}$ 3 6
15	7.21	7.22	0 0 2	9	2.074	2.075	4 4 4
100	7.05	7.05	0 2 0	4	2.015	2.016	$\bar{6}$ 0 4
42	6.51	6.51	2 0 1	7	2.004	2.003	6 4 0
53	5.13	5.13	$\bar{2}$ 0 1	3	1.968	1.970	0 6 4
19	4.78	4.79	2 0 2	10	1.936	1.938	6 2 4
12	4.15	4.15	2 2 1	8	1.903	1.905	$\bar{6}$ 2 4
6	3.88	3.88	2 2 2	4	1.863	1.864	4 4 5
14	3.61	3.61	2 2 1	3	1.825	1.825	4 4 5
2	3.53	3.53	3 1 2	3	1.803	1.805	0 0 8
4	3.40	3.40	3 1 2	7	1.764	1.764	0 8 0
96	3.24	3.24	0 0 4	9	1.748	1.749	0 2 8
34	3.17	3.17	4 2 0	4	1.734	1.735	4 6 4
69	3.10	3.10	0 4 2	2	1.714	1.714	4 6 4
27	2.941	2.941	$\bar{2}$ 4 1	2	1.704	1.702	2 8 0
9	2.907	2.907	$\bar{2}$ 4 1	7	1.690	1.691	$\bar{2}$ 2 8
6	2.838	2.840	2 2 4	6	1.681	1.681	6 6 0
2	2.719	2.719	2 4 2	3	1.663	1.668	0 6 6
4	2.686	2.686	2 4 2	8	1.580	1.581	8 4 2
3	2.650	2.651	3 1 4	5	1.549	1.549	2 8 4
4	2.567	2.265	3 1 4	3	1.478	1.478	$\bar{2}$ 8 4
15	2.534	2.535	1 5 1	6	1.453	1.453	8 4 4
11	2.522	2.523	2 0 5	3	1.430	1.430	8 4 4
2	2.446	2.446	2 0 5	3	1.420	1.421	6 8 1
7	2.399	2.399	$\bar{2}$ 4 3	2	1.401	1.400	6 8 1
6	2.386	2.386	2 4 3	3	1.388	1.388	5 1 9
5	2.300	2.301	4 0 4	5	1.349	1.349	2 2 10
5	2.240	2.241	4 0 4	4	1.341	1.340	$\bar{2}$ 2 10
4	2.172	2.171	4 0 4	3	1.315	1.314	10 4 0
5	2.136	2.137	6 0 3	4	1.315	1.314	8 6 4
			6 0 3	3			2 4 10
			2 6 2				$\bar{2}$ 4 10
			$\bar{2}$ 6 2				

X-ray powder diffraction

X-ray powder-diffraction data were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer (CoK α) equipped with a cylindrical image plate detector and using Debye-Scherrer geometry ($D = 127.4$ mm). The X-ray powder-diffraction data for yusupovite are given in Table 3. Unit-cell parameters refined from the powder data are as follows: $a = 14.5981(5)$, $b = 14.1077(6)$, $c = 14.4455(6)$ Å, $\beta = 90.169(5)^\circ$, $V = 2975.0(4)$ Å³.

CRYSTAL STRUCTURE

Data collection and structure refinement

Single-crystal X-ray data for yusupovite were collected with a Bruker APEX II ULTRA diffractometer with a rotating-anode generator (MoK α), multilayer optics and an APEX II 4K CCD detector. A total of 17 349 reflections was measured out to 60° 2 θ using 30 s per 0.2° frame. Unit-cell dimensions were determined by least-squares refinement of 9572 reflections with $I > 10\sigma I$, and are given in Table 4, together with other miscellaneous information on data collection and structure refinement. An absorption correction was done using the SADABS program (Sheldrick 2008). All calculations were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 2008). The diffraction data were merged in four different ways to test the symmetry of the data. For orthorhombic symmetry, R_{int} (the measure of agreement of symmetry-equivalent reflections) is 6.1%. For monoclinic symmetry, R_{int} is 6.1, 0.91, and 6.1% for the three different possible choices of the unique monoclinic axis. The data thus indicate monoclinic symmetry with the unique monoclinic axis along [010] (see Table 4), and systematic absences in the single-crystal X-ray diffraction data are consistent with the space group $C2/m$. The crystal structure was refined in space group $C2/m$ to an R_1 index of 3.46%. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992). The site occupancies for the M, Na, A, and W sites were refined

TABLE 4. Miscellaneous refinement data for yusupovite

<i>a</i> (Å)	14.5975(4)
<i>b</i>	14.1100(4)
<i>c</i>	14.4394(4)
β (°)	90.0399(4)
<i>V</i> (Å ³)	2974.1(3)
Space group	$C2/m$
<i>Z</i>	8
Absorption coefficient (mm ⁻¹)	2.29
<i>F</i> (000)	2381.6
<i>D</i> _{calc} (g/cm ³)	2.713
Crystal size (mm)	0.100 × 0.040 × 0.025
Radiation/monochromator	MoK α /graphite
2 θ -range for data collection (°)	60.14
R_{int} (%)	0.91
Reflections collected	17349
Independent reflections	4519
$F_o > 4\sigma F$	4428
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	267
Final R_{obs} (%)	
R_1 [$F_o > 4\sigma F$]	3.46
R_1 (all data)	3.51
wR_2	8.94
Highest peak, deepest hole (e Å ⁻³)	1.37 -3.44
Goodness of fit on F^2	1.117

with the scattering parameters of Zr, Na, Cs, and O. Final atom coordinates and anisotropic-displacement parameters are listed in Table 5, selected interatomic distances and framework angles are given in Table 6, and refined site-scattering and assigned site-population for selected cation sites values are given in Table 7. The CIF is on deposit and available as listed below.¹

Structure description

In the crystal structure of yusupovite, there are six Si sites occupied by Si, tetrahedrally coordinated by O atoms with $\langle\text{Si-O}\rangle = 1.613 \text{ \AA}$ (Tables 5 and 6). There are two M sites occupied mainly by Zr with minor Y and Hf; ideally they give 1 Zr apfu (Table 7). The M(1,2) sites are octahedrally coordinated by O atoms, with $\langle\text{M-O}\rangle = 2.114$ and 2.103 \AA , respectively. Si tetrahedra share vertices to form an epididymite Si_6O_{15} ribbon along [010]. Epididymite ribbons and Zr-dominant M octahedra share common

vertices to form a heteropolyhedral framework (Figs. 4a and 4b).

There are six interstitial sites occupied by the alkali cations Na, K, and Cs. There are three [7]-coordinated Na sites partly occupied by Na. The Na1 site is occupied by Na at 95% and is coordinated by O atoms, with $\langle\text{Na1-O}\rangle = 2.567 \text{ \AA}$ (Tables 6 and 7). The Na2 and Na3 sites are occupied by Na at 84 and 78%, respectively, and they are coordinated by O atoms and H_2O groups that occur at the W sites, with $\langle\text{Na2-}\varphi\rangle = 2.555$ and $\langle\text{Na3-}\varphi\rangle = 2.575 \text{ \AA}$ ($\varphi = \text{O}, \text{H}_2\text{O}$). These three Na sites give $\text{Na}_{1.76}\square_{0.24}$ or ideally 2 Na apfu. There are three A sites partly occupied by K and Cs (cf. analogous sites in Rb-exchanged elpidite, 90°C). The A sites occur at short distances from the Na sites. A1–Na2 = 2.648 , A2–Na3 = 1.617 , and A3–Na3 = 2.637 \AA (Table 6), and hence the A and Na sites cannot be locally occupied. The A1, A2, and A3 sites are occupied by (K + Cs) at 12, 18, and 16%, respectively (Table 7). The A1–A3 sites give $\text{K}_{0.12}\text{Cs}_{0.11}$ apfu. Ideally, the composition of the A1–A3 sites is $\square_{1.5}$ pfu. The Na and A sites sum to $\text{Na}_2 + \square_{1.5} = \text{Na}_2$ apfu. There are 10 W sites occupied by H_2O groups at 18–84% (Table 5); the W1–W10 sites give $(\text{H}_2\text{O})_{2.52}$ pfu, ideally $(\text{H}_2\text{O})_3$ pfu.

¹ Deposit item AM-15-75092, CIF. Deposit items are free to all readers and found on the MA web site, via the specific issue's Table of Contents (go to <http://www.minsocam.org/MSA/AmMin/TOC/>).

TABLE 5. Atom coordinates and displacement parameters (\AA^2) for yusupovite

Atom	Sof (%) ^a	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}^b
M1	100	¼	¼	½	0.00725(14)	0.00838(15)	0.00689(14)	-0.00052(10)	-0.00024(10)	0.00023(10)	0.00751(8)
M2	100	¼	¼	0	0.00717(14)	0.00861(15)	0.00707(14)	-0.00066(10)	-0.00020(10)	-0.00039(10)	0.00762(8)
Na1	95	0.26322(10)	0.24852(14)	0.75107(12)	0.0149(6)	0.0579(12)	0.0316(9)	0.0113(7)	-0.0016(6)	-0.0004(6)	0.0348(4)
Na2	84	0.2658(2)	0	0.9641(2)	0.0508(17)	0.0182(12)	0.0571(19)	0	-0.0361(15)	0	0.0421(8)
Na3	78	0.2289(3)	0	0.4604(3)	0.067(2)	0.0198(14)	0.072(2)	0	0.052(2)	0	0.0532(11)
Si1	100	0.40226(5)	0.10964(5)	0.12184(5)	0.0117(3)	0.0082(3)	0.0109(3)	0.0003(2)	-0.0016(2)	-0.0010(2)	0.01024(13)
Si2	100	0.09773(5)	0.10957(5)	0.62292(5)	0.0118(3)	0.0082(3)	0.0105(3)	0.0003(2)	0.0010(2)	0.0012(2)	0.01015(13)
Si3	100	0.11967(5)	0.11179(5)	0.83638(5)	0.0130(3)	0.0071(3)	0.0119(3)	-0.0005(2)	-0.0035(2)	0.0002(2)	0.01068(14)
Si4	100	0.37685(5)	0.11193(5)	0.33527(5)	0.0138(3)	0.0073(3)	0.0120(3)	-0.0007(2)	0.0036(2)	-0.0002(2)	0.01102(14)
Si5	100	0.04951(5)	0.23600(5)	0.14315(5)	0.0087(3)	0.0125(3)	0.0108(3)	0.0005(3)	0.0012(2)	0.0014(2)	0.01065(14)
Si6	100	0.45223(5)	0.23339(5)	0.64091(5)	0.0088(3)	0.0129(3)	0.0107(3)	-0.0000(3)	-0.0015(2)	-0.0018(2)	0.01080(14)
A1	12	0.1546(4)	0	0.1072(5)	0.035(3)	0.0176(17)	0.067(4)	0	0.004(2)	0	0.0400(13)
A2	18	0.1454(3)	0	0.3871(4)	0.0294(16)	0.0308(16)	0.108(4)	0	0.0073(19)	0	0.0562(12)
A3	16	0.3490(4)	0	0.5975(5)	0.052(3)	0.038(2)	0.081(5)	0	-0.004(3)	0	0.05703
O1	100	0.42304(16)	0.24713(18)	0.74887(15)	0.0177(10)	0.0377(14)	0.0108(9)	-0.0013(8)	-0.0004(7)	-0.0004(9)	0.0221(5)
O2	100	0.1271(2)	0	0.8579(2)	0.0290(16)	0.0059(12)	0.0271(16)	0	-0.0072(13)	0	0.0207(6)
O3	100	0.32442(14)	0.13087(15)	0.04805(14)	0.0172(9)	0.0170(10)	0.0163(9)	0.0007(8)	-0.0057(7)	-0.0005(8)	0.0169(4)
O4	100	0.14180(14)	0.21603(16)	0.08931(15)	0.01459(9)	0.0212(10)	0.0206(10)	0.0006(8)	0.0061(8)	0.0050(8)	0.0187(4)
O5	100	0.36157(15)	0.21273(17)	0.58484(15)	0.0153(9)	0.0245(11)	0.0208(10)	0.0004(9)	-0.0075(8)	-0.0056(8)	0.0202(4)
O6	100	0.3689(2)	0	0.3565(2)	0.0307(17)	0.0065(12)	0.0277(16)	0	0.0054(13)	0	0.0216(6)
O7	100	0.4357(2)	0	0.1189(2)	0.0214(14)	0.0074(12)	0.0312(17)	0	-0.0025(12)	0	0.0200(6)
O8	100	-0.00603(15)	0.32790(16)	0.10747(16)	0.0175(9)	0.0179(10)	0.0232(10)	0.0022(8)	0.0009(8)	0.0072(8)	0.0195(4)
O9	100	0.01651(15)	0.14345(16)	0.86301(17)	0.0160(9)	0.0168(10)	0.0322(12)	0.0006(9)	0.0023(8)	0.0040(8)	0.0216(4)
O10	100	0.17591(14)	0.13037(15)	0.54935(14)	0.0179(9)	0.0177(10)	0.0162(9)	0.0004(8)	0.0041(7)	-0.0002(8)	0.0173(4)
O11	100	0.0636(2)	0	0.6197(2)	0.0213(14)	0.0083(12)	0.0292(16)	0	0.0006(12)	0	0.0196(6)
O12	100	0.50610(15)	0.32775(16)	0.60866(16)	0.0176(10)	0.0176(10)	0.0245(11)	0.0015(8)	-0.0015(8)	-0.0073(8)	0.0199(4)
O13	100	0.52078(15)	0.14284(17)	0.63442(17)	0.0181(10)	0.0186(10)	0.0290(11)	-0.0017(9)	-0.0030(8)	0.0048(8)	0.0219(4)
O14	100	0.36265(16)	0.13228(17)	0.22537(14)	0.0251(11)	0.0252(11)	0.0117(9)	-0.0001(8)	0.0019(8)	0.0033(9)	0.0206(4)
O15	100	0.13732(16)	0.13192(17)	0.72676(14)	0.0266(11)	0.0237(11)	0.0117(9)	-0.0009(8)	-0.0021(8)	-0.0026(9)	0.0207(4)
O16	100	0.19624(15)	0.16703(16)	0.89243(15)	0.0211(10)	0.0163(10)	0.0199(10)	-0.0029(8)	-0.0082(8)	-0.0037(8)	0.0191(4)
O17	100	0.29891(15)	0.16735(16)	0.38874(15)	0.0228(10)	0.0157(10)	0.0222(10)	-0.0022(8)	0.0093(8)	0.0039(8)	0.0202(4)
Atom	Sof (%) ^a	x	y	z	U_{eq}^b						
W1	50	0.5181(7)	0	0.4851(8)	0.05						
W2	42	0.3534(6)	0.0249(6)	0.8096(6)	0.05						
W3	50	0.3552(8)	0	0.8995(8)	0.05						
W4	78	0.1438(5)	0	0.3120(5)	0.05						
W5	48	0.3556(8)	0	0.8599(9)	0.05						
W6	84	0.1386(6)	0	0.0775(6)	0.05						
W7	28	0	0	0	0.05						
W8	40	0.3708(11)	0	0.5575(11)	0.05						
W9	36	0.3338(14)	0	0.6338(13)	0.05						
W10	18	0.173(3)	0.017(3)	0.156(3)	0.05						

Note: W = O atom of an H_2O group.

^a Site-occupancy factor.

^b U_{iso} for W(1–10) where $U_{\text{iso}} = 0.05 \text{ \AA}^2$ (fixed).

TABLE 6. Selected interatomic distances (Å) and angles (°) in yusupovite^a

M1-O5	2.104(2) ×2	M2-O4	2.095(2) ×2
M1-O17	2.110(2) ×2	M2-O16a	2.097(2) ×2
M1-O10	2.128(2) ×2	M2-O3	2.118(2) ×2
<M1-O>	2.114	<M2-O>	2.103
Na1-O1	2.333(3)	Na2-O3c	2.369(3) ×2
Na1-O15	2.491(3)	Na2-W6c	2.48(1)
Na1-O17b	2.511(3)	Na2-O2	2.539(4)
Na1-O14b	2.514(3)	Na2-W2	2.596(9) ×2
Na1-O16	2.539(3)	Na2-O16	2.767(3) ×2
Na1-O4b	2.735(3)	<Na2-φ>	2.555
Na1-O5	2.843(3)		
<Na1-O>	2.567		
Na3-O10	2.374(3) ×2	Short distances	
Na3-W4	2.477(9)	Na2-A1c	2.648(9)
Na3-W8	2.50(2)	Na3-A2	1.617(7)
Na3-O6	2.536(5)	Na3-A3	2.637(9)
Na3-O17	2.773(3) ×2		
Na3-W9	2.93(2)		
<Na3-φ>	2.575		
Si1-O3	1.586(2)	Si2-O10	1.587(2)
Si1-O8d	1.616(2)	Si2-O12e	1.617(2)
Si1-O7	1.623(1)	Si2-O11	1.625(1)
Si1-O14	1.635(2)	Si2-O15	1.637(2)
<Si1-O>	1.615	<Si2-O>	1.617
Si3-O16	1.585(2)	Si4-O17	1.582(2)
Si3-O2	1.611(1)	Si4-O6	1.613(1)
Si3-O9	1.617(2)	Si4-O13f	1.617(3)
Si3-O15	1.629(2)	Si4-O14	1.626(2)
<Si3-O>	1.611	<Si4-O>	1.610
Si5-O4	1.581(2)	Si6-O5	1.578(2)
Si5-O8	1.614(2)	Si6-O12	1.615(2)
Si5-O9g	1.625(3)	Si6-O13	1.626(3)
Si5-O1b	1.627(2)	Si6-O1	1.628(2)
<Si5-O>	1.612	<Si6-O>	1.612
A1-W7	2.736(6)	A2-O10	3.011(5) ×2
A1-W4	2.96(1)	A2-O11h	3.053(5)
A1-O4	3.065(3) ×2	A2-O17	3.255(3) ×2
A1-O3	3.208(5) ×2	A2-O12i	3.287(3) ×2
A1-O9	3.249(6) ×2	A2-O6	3.212(5)
A1-O2	3.244(4)	A2-W10	3.37(4) ×2
<A1-O>	3.109	A2-O11	3.565(7)
		<A2-φ>	3.231
A3-W1	2.96(1)	Si5b-O1-Si6	150.5(2)
A3-O5	3.013(2) ×2	Si3-O2-Si3j	156.5(2)
A3-W2	3.08(1) ×2	Si4-O6-Si4j	156.5(2)
A3-O10	3.202(6) ×2	Si1-O7-Si1j	144.8(2)
A3-O13	3.261(6) ×2	Si1e-O8-Si5	144.4(2)
A3-O6	3.493(8)	Si2-O11-Si2j	144.2(2)
A3-φ	3.165	Si2d-O12-Si6	144.8(2)
		Si4f-O13-Si6	139.9(2)
		Si1-O14-Si4	144.4(2)
		Si2-O15-Si3	143.2(2)
		<Si-O-Si>	146.9

Notes: φ = O, H₂O. Symmetry operators: a: x, y, z-1; b: -x+1/2, -y+1/2, -z+1; c: x, y, z+1; d: x+1/2, -y+1/2, z; e: x-1/2, -y+1/2, z; f: -x+1, y, -z+1; g: -x, y, -z+1; h: -x, -y, -z+1; i: -x+1/2, y-1/2, -z+1; j: x, -y, z.

^a Due to partial occupancy of Na2, A2, A3, W2, and W10 sites and short-range order (SRO) arrangements between them, [Na2-W2], [A2-W10], and [A3-W2] bond-lengths are taken into account at 50% (see text).

COMPARISON OF YUSUPOVITE AND ELPIDITE

The crystal structure of yusupovite, ideally Na₂Zr(Si₆O₁₅)(H₂O)₃, monoclinic, space group *C2/m*, is a superstructure of elpidite, Na₂Zr(Si₆O₁₅)(H₂O)₃, orthorhombic, space group *Pbcm* (Figs. 4c and 4d; Table 1). In yusupovite, (1) the Na2 site of elpidite (Figs. 4c and 4d) is split into two sites, Na2 and Na3 (Figs. 4a and 4b), and (2) the two W1 and W2 sites (fully occupied by H₂O groups) of elpidite (Cannillo et al. 1973) are split into 10 W1–W10 sites partly occupied by H₂O groups (Table 5). In the crystal structure of yusupovite, the occurrence of the interstitial alkali cations K and Cs at the A sites results in the disorder and depletion of Na at the Na sites and disorder and

TABLE 7. Refined site-scattering and assigned site-population for yusupovite

Site	Refined site-scattering (epfu)	Site population (apfu)	Calculated site-scattering (epfu)	<X-φ> _{obs} ^a (Å)
^[6] M1	20.8(5)	0.41 Zr + 0.08 Y + 0.01 Hf	20.24	2.114
^[6] M2	20.6(5)	0.41 Zr + 0.09 Y	19.93	2.103
ΣM(1,2)	41.4	0.82 Zr + 0.17 Y + 0.01 Hf	40.17	
^[7] Na1	10.45(8)	0.95 Na + 0.05 □	10.45	2.567
^[7] Na2	4.62(6)	0.42 Na + 0.08 □	4.62	2.555
^[7] Na3	4.29(6)	0.39 Na + 0.11 □	4.29	2.575
ΣNa(1–3)	19.39	1.76 Na + 0.24 □	19.36	
^[9] A1	2.26(9)	0.03 Cs + 0.03 K + 0.44 □	2.22	3.109
^[10] A2	3.19(7)	0.05 K + 0.04 Cs + 0.41 □	3.15	3.231
^[9] A3	2.7(1)	0.04 Cs + 0.04 K + 0.42 □	2.96	3.165
ΣA(1–3)	8.15	0.12 K + 0.11 Cs + 1.27 □	8.33	

^a X = cation, φ = anion.

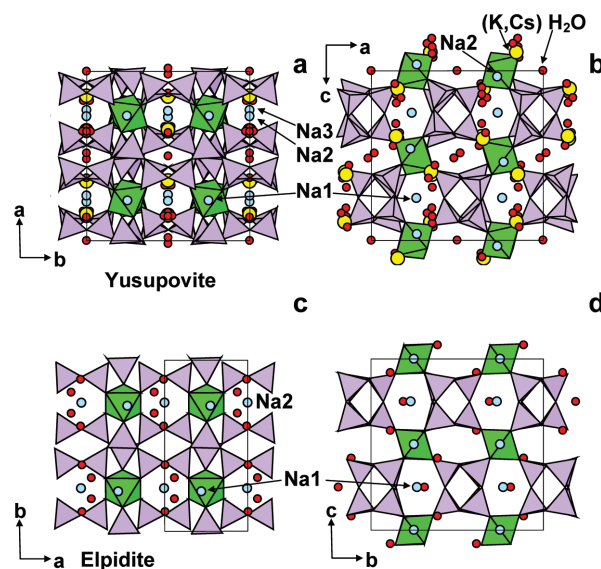


FIGURE 4. The crystal structures of yusupovite (a and b) and elpidite (c and d, after Cannillo et al. 1973). Zr and Si polyhedra are green and lilac, Na atoms and H₂O groups are shown as blue and red spheres, (K,Cs) atoms at the A sites in yusupovite are shown as yellow spheres. Unit cells are shown with thin black lines.

depletion of H₂O at the W sites.

Due to the (K,Cs), Na, and H₂O disorder, the symmetry of yusupovite decreases from orthorhombic, space group *Pbcm* (elpidite) to monoclinic, space group *C2/m* and the *b* cell parameter of yusupovite is doubled when compared to the corresponding cell parameter in elpidite, $b_{\text{yus}} = 2a_{\text{elp}}$. We conclude that yusupovite, ideally Na₂Zr(Si₆O₁₅)(H₂O)₃, is a dimorph of elpidite, Na₂Zr(Si₆O₁₅)(H₂O)₃.

It is tempting to suggest that the (Na,Cs)₂Zr(Si₆O₁₅)(H₂O)₃ structure undergoes a compositionally induced ferroelastic transition with only minor incorporation of Cs into the elpidite structure.

IMPLICATIONS

Yusupovite and elpidite are heteropolyhedral-framework structures, materials that have been the subject of extensive examination over the last 15 years because of their potential use as industrial microporous materials; they have great potential use

as ion-exchange materials and highly selective molecular sieves, catalysts, and ion conductors (Krivovichev 2012). Of particular interest with regard to yusupovite are the ion-exchange experiments of Grigor'eva et al. (2011) on elpidite. They showed that elpidite, $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$, easily exchanges Na for K and Rb at relatively low temperature (90 and 150 °C) in aqueous solutions enriched in K and Rb. Detailed work by Zubkova et al. (2011) showed that the structure of elpidite contracts considerably on heating-induced dehydration, accompanied by doubling of the *a* cell dimension. The chemical composition of yusupovite is characterized by the presence of a small amount of Cs_2O : 2.58 wt%, 0.11 apfu. Obviously the elpidite structure can accommodate large alkali cations (K, Rb, Cs) at low temperature, making it an attractive potential atomic-scale container for these elements, particularly for low-temperature waste-water filtration (Popa and Pavela 2012). This capability seems of obvious significance to the potential encapsulation of ^{137}Cs from radiogenic waste. The framework structure of elpidite contracts on dehydration at fairly modest temperature (≤ 300 °C; Zubkova et al. 2011), suggesting that dehydration of Cs-exchanged elpidite may help “seal” the exchanged Cs in the contracted dehydrated structure.

ACKNOWLEDGMENTS

We are grateful to P. Bayliss for useful comments, an anonymous reviewer for comments on CIF, and Associate Editor B. Hofmann for handling the manuscript. We thank M.A. Cooper for collection of the single-crystal X-ray data for yusupovite. A.A.A. and O.I.S. acknowledge financial support by the St. Petersburg State University internal grant 3.50.2099.2013. A.A.A., L.A.P., and V.Y.K. acknowledge financial support by the grant 12-05-00911-a from the Russian Foundation for Basic Research, and I.V.P. acknowledges financial support by the grant 13-05-12021_ofi_m from the Russian Foundation for Basic Research. This work was also supported by a Canada Research Chair in Crystallography and Mineralogy and by a Discovery grant from the Natural Sciences and Engineering Research Council of Canada and by Innovation Grants from the Canada Foundation for Innovation to F.C.H.

REFERENCES CITED

- Agakhanov, A.A., Pautov, L.A., Belakovskii, D.I., Sokolova, E., and Hawthorne, F.C. (2003) Telyushenkoite, $\text{CsNa}_6[\text{Be}_2(\text{Si}, \text{Al}, \text{Zn})_{18}\text{O}_{39}\text{F}_2]$, a new cesium mineral of the leifite group. *New Data on Minerals*, 38, 5–8.
- Agakhanov, A.A., Pautov, L.A., Uvarova, Yu.A., Sokolova E.V., Hawthorne, F.C., and Karpenko, V. Yu. (2005) Senkevichite, $\text{CsKNaCa}_2\text{TiO}[\text{Si}_7\text{O}_{18}(\text{OH})]$, a new mineral. *New Data on Minerals*, 40, 17–22.
- Agakhanov, A.A., Pautov, L.A., Karpenko, V. Yu., Sokolova, E., and Hawthorne, F.C. (2012) Kirchhoffite, CsBSi_2O_6 , a new mineral from the Darai-Pioz alkaline massif, Tajikistan: description and crystal structure. *Canadian Mineralogist*, 50, 523–529.
- Belakovskiy, D.I. (1991) Die seltenen Mineralien von Dara-i-Pioz im Hochgebirge Tadshikistans. *Lapis*, 16, 42–48.
- Cannillo, E., Rossi, G., and Ungaretti, L. (1973) The crystal structure of elpidite. *American Mineralogist*, 58, 106–109.
- Dusmatov, V.D. (1968) On geochemistry and mineralogy in alkaline rocks (Southern Tien-Shan). 2nd Republican Scientific Conference of Tajikskoi SSR, Dushanbe, Abstracts, 147–148 (in Russian).
- (1971) Mineralogy of the Darai-Pioz alkaline massif (southern Tien-Shan), 18 p. Extended abstract of Ph.D. dissertation. Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Moscow (in Russian).
- Efimov, A.F. (1983) Typomorphism of Rock-Forming Melanocratic Minerals of Alkaline Rocks, 256 p. Nauka, Moscow (in Russian).
- Ganzev, A.A., Efimov, A.F., and Semenova, N.G. (1969) Isomorphism of alkali elements in the astrophyllite-group minerals. *Geokhimiya*, 1969(4), 235–240 (in Russian).
- Grew, E.S., Belakovskiy, D.I., Fleet, M.E., Yates, M.G., McGee, J.J., and Marquez, N. (1993) Reedmergnerite and associated minerals from peralkaline pegmatite, Dara-i-Pioz, southern Tien-Shan, Tajikistan. *European Journal of Mineralogy*, 5, 971–984.
- Grigor'eva, A.A., Zubkova, N.V., Pekov, I.V., Kolitsch, U., Pushcharovsky, D.Y., Vigasina, M.F., Giesler, G., Dordevic, T., Tillmanns, E., and Chukanov, N.V. (2011) Crystal chemistry of elpidite from Khan Bogdo (Mongolia) and its K- and Rb-exchanged forms. *Crystallography Reports*, 56, 832–841.
- Krivovichev, S.V., Ed. (2012) *Minerals as Advanced Materials II*, 427 p. Springer Verlag.
- Neronova, N.N., and Belov, N.V. (1963) The crystal structure of elpidite. Dimorphism of dimetasilicate radicals. *Doklady Akademii Nauk SSSR*, 150, 642–645 (in Russian).
- (1965) Crystal structure of elpidite, $\text{Na}_2\text{Zr}[\text{Si}_6\text{O}_{15}] \cdot 3\text{H}_2\text{O}$. *Soviet Physics—Crystallography*, 9, 700–705.
- Pautov, L.A., Agakhanov, A.A., Uvarova, Y.A., Sokolova, E.V., and Hawthorne, F.C. (2004) Zeravshanite, $\text{Cs}_4\text{Na}_2\text{Zr}_3(\text{Si}_{18}\text{O}_{45})(\text{H}_2\text{O})_2$, new cesium mineral from Dara-i-Pioz massif (Tajikistan). *New Data on Minerals*, 39, 20–25.
- Pautov, L.A., Agakhanov, A.A., and Bekenova, G.K. (2006) Sokolovaite $\text{CSLi}_2\text{AlSi}_4\text{O}_{10}\text{F}_2$ —a new mineral species of the mica group. *New Data on Minerals*, 41, 5–13.
- Pautov, L.A., Agakhanov, A.A., Karpenko, V. Yu., Sokolova, E., and Hawthorne, F.C. (2013) Mendeleevite-(Ce), $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6(\text{REE}, \text{Ca}, \square)_{30}(\text{Si}_{70}\text{O}_{175})(\text{H}_2\text{O}, \text{OH}, \text{F}, \square)_{35}$: a new mineral from the Darai-Pioz massif, Tajikistan. *Doklady Earth Sciences*, 452, 1023–1026.
- Pobedimskaya, E.A., and Belov, N.V. (1960) The crystal structure of epididymite $\text{NaBeSi}_3\text{O}_7(\text{OH})$: a new type of $(\text{Si}_6\text{O}_{15})$ chain. *Zhurnal Strukturnoi Khimii*, 1, 51–63 (in Russian).
- Popa, K., and Pavela, C.C. (2012) Radioactive wastewaters purification using titanosilicates materials: State of the art and perspectives. *Desalination*, 293, 78–86.
- Pouchou, J.L., and Pichoir, F. (1985) “PAP” (ppZ) procedure for improved quantitative microanalysis. In J.T. Armstrong, Ed., *Microbeam Analysis*, 104–106. San Francisco Press, California.
- Requir, E.P., Chakhmouradian, A.R., and Evdokimov, M.D. (1999) The mineralogy of a unique baratovite- and miserite-bearing quartz–albite–aegirine rock from the Darai-Pioz complex, northern Tajikistan. *Canadian Mineralogist*, 37, 1369–1384.
- Semenov, E.I., and Dusmatov, V.D. (1975) On mineralogy of the Darai-Pioz alkaline massif (Central Tajikistan). *Doklady Akademii Nauk Tajikskoi SSR*, 18, 39–41 (in Russian).
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, A64, 112–122.
- Tikhonenkov, I.P., Semenov, E.I., and Kazakova, M.E. (1957) The first finding of elpidite in the Soviet Union. *Doklady Akademii Nauk SSSR*, 114, 1101–1103 (in Russian).
- Wilson, A.J.C., Ed. (1992) *International Tables for Crystallography*. Volume C: Mathematical, physical and chemical tables. Kluwer, Dordrecht, The Netherlands.
- Yefimov, A.F., Dusmatov, V.D., Ganzev, A.A., and Katayeva, Z.T. (1971) Cesium kupletskite, a new mineral. *Doklady of the Academy of Sciences U.S.S.R. Earth Sciences*, 197, 140–143.
- Zubkova, N.V., Ksenofontov, D.A., Kabalov, Yu.K., Chukanov, N.V., Nedel'ko, V.V., Pekov, I.V., and Pushcharovsky, D. Yu. (2011) Dehydration-induced structural transformations of the microporous zirconosilicate elpidite. *Inorganic Materials*, 47, 506–512.

MANUSCRIPT RECEIVED JUNE 10, 2014
 MANUSCRIPT ACCEPTED JANUARY 20, 2015
 MANUSCRIPT HANDLED BY BEDA HOFMANN