

1 **Revision 2**

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6 **Yusupovite, Na<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub>, a new mineral species from the Darai-Pioz alkaline massif and its**  
7 **implications as a new microporous filter for large ions**

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## ABSTRACT

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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

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massif in the upper reaches of the Darai-Pioz river, area of the joint Turkestan, Zeravshan and

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Alaisky ridges, Tajikistan. Yusupovite was found in a pegmatite composed mainly of reedmergnerite,

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aegirine, microcline and polyolithionite. It occurs as prismatic grains about 2 mm in size embedded in

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reedmergnerite; associated minerals are quartz, pectolite, zeravshanite, mendeleevite-(Ce), fluorite,

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leucosphenite, a pyrochlore-group mineral, neptunite, telyushenkoite, moskvinit-(Y) and shibkovite.

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Yusupovite is colorless, transparent with a white streak, has a vitreous luster, and does not fluoresce

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under ultraviolet light. Cleavage is perfect on  $\{110\}$ , parting was not observed. Mohs hardness is 5.

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Yusupovite is brittle with a splintery fracture. The measured and calculated densities are 2.69(2) and

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2.713  $\text{g}/\text{cm}^3$ , respectively. Yusupovite is optically biaxial (+) with refractive indices ( $\lambda = 589 \text{ nm}$ )  $\alpha =$

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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

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monoclinic,  $C2/m$ ,  $a$  14.5975(4),  $b$  14.1100(4),  $c$  14.4394(4) Å,  $\beta$  90.0399(4)°,  $V$  2974.1(3) Å<sup>3</sup>. The six

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strongest reflections in the X-ray powder diffraction data [ $d$  (Å),  $I$ , ( $h k l$ )] are 7.05, 100, (020); 3.24, 96,

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(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

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composition (electron microprobe) is:  $\text{Nb}_2\text{O}_5$  0.39,  $\text{SiO}_2$  58.84,  $\text{ZrO}_2$  16.55,  $\text{HfO}_2$  0.30,  $\text{FeO}$  0.01,  $\text{Y}_2\text{O}_3$

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3.05,  $\text{Cs}_2\text{O}$  2.58,  $\text{K}_2\text{O}$  0.95,  $\text{Na}_2\text{O}$  8.91,  $\text{H}_2\text{O}_{\text{calc.}}$  7.40, total 98.98 wt%, with  $\text{H}_2\text{O}$  calculated from structure

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refinement. The empirical formula (based on 17.5 O apfu) is  $(\text{Na}_{1.76}\text{K}_{0.12}\text{Cs}_{0.11})_{\Sigma 1.99}$

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$(\text{Zr}_{0.82}\text{Y}_{0.17}\text{Nb}_{0.02}\text{Hf}_{0.01})_{\Sigma 1.02}(\text{Si}_{6.01}\text{O}_{14.98})(\text{H}_2\text{O})_{2.52}$ ,  $Z = 8$ . The crystal structure of yusupovite was refined to

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$R_1 = 3.51\%$  based on 4428 observed reflections. In the crystal structure, there are six Si sites occupied by

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Si, two M sites occupied mainly by Zr with minor Y and Hf. Si tetrahedra form an epididymite  $\text{Si}_6\text{O}_{15}$

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ribbon along [010]. Epididymite ribbons and Zr-dominant M octahedra share common vertices to form a

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heteropolyhedral Si-Zr-O framework. There are six interstitial sites partly occupied by alkali cations Na,

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K and Cs. The three [7]-coordinated Na sites are occupied by Na at 95, 84 and 78%. The three A sites are

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occupied by K and Cs at 12, 18 and 16%. There are 10 W sites occupied by  $\text{H}_2\text{O}$  groups at 18-84%. Due

49 to (K,Cs), Na and H<sub>2</sub>O disorder, the symmetry of yusupovite decreases from orthorhombic, space group  
50 *Pbcm* (elpidite), to monoclinic, space group *C2/m*, and the *b* unit-cell parameter of yusupovite is doubled  
51 compared to the corresponding cell parameter in elpidite,  $b_{\text{yus}} = 2a_{\text{elp}}$ . Yusupovite, ideally  
52 Na<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub>, is a dimorph of elpidite, Na<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub>.

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

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## INTRODUCTION

58           Yusupovite is a new mineral found in the moraine of the Darai-Pioz glacier in the upper reaches  
59 of the Darai-Pioz River, the Alaisky mountain ridge, Tien-Shan Mountains, Tajikistan. The new mineral  
60 species and its name were approved by the Commission on New Minerals, Nomenclature and  
61 Classification of the International Mineralogical Association (IMA 2014-022). The mineral is named  
62 *yusupovite* (Cyrillic: *юсуповит*) after Rustam Gumirovich Yusupov (born 1935), a prominent Uzbek  
63 mineralogist and a curator at the Geological Museum, Tashkent, Uzbekistan. The holotype specimen has  
64 been deposited in the mineral collection of the Fersman Mineralogical Museum, Moscow, Russia,  
65 registration # 4543/1. We describe here this new Zr silicate and report its crystal structure.

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## REVIEW OF THE RELEVANT LITERATURE

68           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  
69 1). The crystal structure of elpidite was first solved on a heavily twinned crystal from Lovozero, Kola  
70 Peninsula, Russia, by Neronova and Belov (1963): space group *Pbmm*,  $a = 7.4$ ,  $b = 14.4$ ,  $c = 7.05$  Å.  
71 They described the Zr-Si-O heteropolyhedral framework which consists of epididymite  $\text{Si}_6\text{O}_{15}$  ribbons  
72 [described in epididymite by Pobedinskaya and Belov (1960)] connected by isolated Zr octahedra with  
73 Na atoms and  $\text{H}_2\text{O}$  groups occupying the interstitial space within the Zr-Si-O framework, and gave the  
74 formula of elpidite as  $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15}) \cdot 3\text{H}_2\text{O}$ ,  $Z = 2$ . Dissatisfied with their results, Neronova and Belov  
75 (1965) lowered the symmetry to *P2cm* in order to explain certain features of the electron-density map.  
76 Cannillo et al. (1973) refined the crystal structure of elpidite on perfect single crystals from Mt. St.  
77 Hilaire, Quebec, Canada, in space group *Pbcm*,  $a = 7.14$ ,  $b = 14.68$ ,  $c = 14.65$  Å,  $Z = 4$ , and found an  
78 overall agreement with the topology of the structure of Neronova and Belov (1963). Grigor'eva et al.  
79 (2011) refined the crystal structures of elpidite from Khan Bongo (Mongolia), which is in accord with  
80 Cannillo et al. (1973), and its cation-exchanged forms that were obtained on heating up to 90 and 150°C.  
81 They reported orthorhombic symmetry for all high-temperature Rb- and K-exchanged forms of elpidite:  
82 the same unit-cell parameters and space group *Pbcm* for the Rb-exchanged form (90°C) and doubling of

83 the *a* unit-cell parameter and space group *Cmca* for the Rb-exchanged form (150°C) and two K-  
84 exchanged forms (90 and 150°C). For the cation-exchanged forms of elpidite, they reported depletion of  
85 Na at the Na sites and drastic decrease in the water content due to the occurrence of K and Rb at the W (=   
86 H<sub>2</sub>O) sites of elpidite.

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#### SAMPLE PROVENANCE

89 Yusupovite was found in rock samples from the Upper Darai-Pioz alkaline massif collected in the  
90 moraine of the Darai-Pioz glacier, located in the Rasht (formerly Garm) district, Tajikistan. The massif is  
91 situated near the watershed on the southern slope of the Alaisky mountain range (N 39° 27', E 70° 43'). In  
92 plan, the Darai-Pioz massif is equant and covers an area of ~16 km<sup>2</sup>. The massif has a multiphase  
93 structure; the root is granite and the central part of the massif is composed of aegirine quartz-bearing and  
94 quartz-free syenites. A small stock of cancrinite syenite occurs in the southwestern part of the massif. In  
95 the massif, there is a variety of granitic, alkaline granitic and syenitic pegmatites, various metasomatic  
96 rocks (albitites, fenites) and carbonatites. Abundant and various mineralization of Cs, Li, B, Zr, REE, Ti,  
97 and Ba is related to the rocks of the massif. The most complete description of the geology and mineralogy  
98 of the massif was given by Dusmatov (1968, 1971). Specific details of the mineralogy and geochemistry  
99 of the Darai-Pioz massif have been discussed in numerous publications (Ganzeyev et al. 1969; Semenov  
100 and Dusmatov 1975; Efimov 1983; Belakovskiy 1991; Grew et al. 1993; Reguir et al. 1999).

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

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### PHYSICAL PROPERTIES

110 Yusupovite occurs as colorless prismatic grains about 2 mm in size embedded in reedmergnerite  
111 (Figs. 1, 2). It is transparent with a white streak and vitreous luster, and does not fluoresce under  
112 ultraviolet light. It is brittle with a splintery fracture. It has perfect cleavage on {110}, parting was not  
113 observed. Mohs hardness is 5. The measured (by flotation in  $\text{CHBr}_3 / \text{C}_3\text{H}_7\text{ON}$ ) and calculated densities  
114 are 2.69(2) and 2.713  $\text{g/cm}^3$ , respectively. Yusupovite is optically biaxial (+) with refractive indices ( $\lambda =$   
115 589 nm)  $\alpha = 1.563(2)$ ,  $\beta = 1.565(2)$ ,  $\gamma = 1.577(2)$ ;  $2V_{\text{meas.}} = 42(3)^\circ$ ,  $2V_{\text{calc.}} = 45^\circ$ . Dispersion is strong:  $r >$   
116  $v$ . A Gladstone-Dale calculation gives a compatibility index of 0.017, which is rated as superior.

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### CHEMICAL COMPOSITION

119 Crystals were analyzed with a JEOL Superprobe JXA-733 electron microprobe operating in  
120 energy-dispersive mode with an accelerating voltage of 20 kV, a beam current of 2 nA, and a beam  
121 diameter of 5  $\mu\text{m}$ . The following standards were used: microcline USNM143966 (Si, K), omphacite  
122 USNM110607 (Na),  $\text{LiNbO}_3$  (Nb),  $\text{ZrO}_2$  (Zr),  $\text{HfO}_2$  (Hf), ilmenite USNM96189 (Fe),  $\text{Y}_2\text{O}_3$  (Y) and  
123  $\text{CsHo}(\text{PO}_3)_4$  (Cs). The data were reduced and corrected using the *PAP* method of Pouchou and Pichoir  
124 (1985). Table 2 gives the chemical composition (which is the mean of ten point analyses) and the  
125 empirical formula based on 17.5 O atoms per formula unit (apfu), the content of  $\text{H}_2\text{O}$  was calculated from  
126 structure refinement. The empirical formula is  $(\text{Na}_{1.76}\text{K}_{0.12}\text{Cs}_{0.11})_{\Sigma 1.99}(\text{Zr}_{0.82}\text{Y}_{0.17}\text{Nb}_{0.02}\text{Hf}_{0.01})_{\Sigma 1.02}(\text{Si}_{6.01}\text{O}_{14.98})$   
127  $(\text{H}_2\text{O})_{2.52}$ ,  $Z = 8$ ; the ideal formula is  $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$ .

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### INFRARED SPECTROSCOPY

130 The FTIR spectrum of a randomly oriented single crystal of yusupovite was collected using a  
131 Bruker Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. Data over  
132 the range 4000-650  $\text{cm}^{-1}$  were obtained by averaging 100 scans with a resolution of 4  $\text{cm}^{-1}$ . Base-line  
133 correction was done using OPUS spectroscopic software (Bruker Optic GmbH). In the principal OH-  
134 stretching region (4000-3000  $\text{cm}^{-1}$ ) (Fig. 3a), there is a peak at 3615  $\text{cm}^{-1}$  and a broad peak (with fine

135 structure) centered at  $\sim 3470\text{ cm}^{-1}$ ; both are attributed to O-H stretching vibrations of H<sub>2</sub>O groups in the  
136 structure of yusupovite. The peak at  $1635\text{ cm}^{-1}$ , with shoulders at  $\sim 1660$  and  $1610\text{ cm}^{-1}$ , is due to H<sub>2</sub>O  
137 bending vibrations. The OH-stretching region of the yusupovite spectrum (Fig. 3a) is somewhat similar to  
138 that of partially dehydrated elpidite (Zubkova et al. 2011) and Rb-exchanged elpidite (Grigor'eva et al.  
139 2011). They all show an additional peak at  $\sim 3600\text{ cm}^{-1}$ , not seen in the FTIR spectrum of elpidite which  
140 shows a triplet at  $3551$ ,  $3505$ , and  $3453\text{ cm}^{-1}$  (Grigor'eva et al. 2011). This peak may be assigned to an  
141 H<sub>2</sub>O group with weaker hydrogen bonds than those of the H<sub>2</sub>O groups in elpidite (Zubkova et al. 2011).  
142 Furthermore, the spectra of yusupovite, partially-dehydrated elpidite and Rb-exchanged elpidite generally  
143 show a reduction in OH-stretching peak resolution compared to that of elpidite, and this is ascribed to  
144 dehydration during ion exchange (Grigor'eva et al. 2011). For yusupovite, this decrease in resolution  
145 could be due to disorder and depletion of H<sub>2</sub>O at the W sites as a result of the occurrence of K and Cs  
146 cations at the A sites.

147 The IR spectrum of yusupovite in the range  $1500 - 400\text{ cm}^{-1}$  was collected from the powder in  
148 KBr microtablet using a double-beam Specord 75-IR Carl Zeiss spectrometer (Fig. 3b). The spectrum is  
149 similar to that of elpidite but has lower peak resolution compared to that of elpidite. The strongest  
150 absorbance is observed in the region of the Si-O stretching vibrations: a broad peak at  $1032\text{ cm}^{-1}$  and a  
151 poorly resolved doublet at  $1130$  and  $1150\text{ cm}^{-1}$ . Several peaks about  $790\text{ cm}^{-1}$  can be attributed to Zr-O  
152 stretching vibrations in ZrO<sub>6</sub> octahedra, and poorly resolved peaks at  $652$ ,  $642$  and  $430\text{ cm}^{-1}$  to bending  
153 vibrations of SiO<sub>4</sub> groups.

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### X-RAY POWDER DIFFRACTION

156 X-ray powder-diffraction data were collected with a Rigaku R-AXIS Rapid II single-crystal  
157 diffractometer (CoK $\alpha$ ) equipped with a cylindrical image plate detector and using Debye-Sherrer  
158 geometry ( $D = 127.4\text{ mm}$ ). The X-ray powder-diffraction data for yusupovite are given in Table 3. Unit  
159 cell parameters refined from the powder data are as follows:  $a = 14.5981(5)$ ,  $b = 14.1077(6)$ ,  $c =$   
160  $14.4455(6)\text{ \AA}$ ,  $\beta = 90.169(5)^\circ$ ,  $V = 2975.0(4)\text{ \AA}^3$ .

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## CRYSTAL STRUCTURE

### 163 **Data collection and structure refinement**

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Single-crystal X-ray data for yusupovite were collected with a Bruker APEX II ULTRA

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diffractometer with a rotating-anode generator ( $\text{MoK}\alpha$ ), multilayer optics and an APEX II 4K CCD

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detector. A total of 17349 reflections was measured out to  $60^\circ 2\theta$  using 30 s per  $0.2^\circ$  frame. Unit-cell

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dimensions were determined by least-squares refinement of 9572 reflections with  $I > 10\sigma I$ , and are given

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in Table 4, together with other miscellaneous information on data collection and structure refinement. An

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absorption correction was done using the SADABS program (Sheldrick 2008). All calculations were done

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with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 2008). The diffraction data were

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merged in four different ways to test the symmetry of the data. For orthorhombic symmetry,  $R_{\text{int}}$  (the

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measure of agreement of symmetry-equivalent reflections) is 6.1%. For monoclinic symmetry,  $R_{\text{int}}$  is 6.1,

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0.91 and 6.1% for the three different possible choices of the unique monoclinic axis. The data thus

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indicate monoclinic symmetry with the unique monoclinic axis along [010] (see Table 4), and systematic

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absences in the single-crystal X-ray diffraction data are consistent with the space group  $C2/m$ . The crystal

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structure was refined in space group  $C2/m$  to an  $R_1$  index of 3.51%. Scattering curves for neutral atoms

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were taken from the International Tables for Crystallography (Wilson 1992). The site occupancies for the

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M, Na, A and W sites were refined with the scattering parameters of Zr, Na, Cs and O. Final atom

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coordinates and anisotropic-displacement parameters are listed in Table 5, selected interatomic distances

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and framework angles are given in Table 6, and refined site-scattering and assigned site-population for

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selected cation sites values are given in Table 7. The CIF is on deposit and available as listed below.<sup>1</sup>

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<sup>1</sup> Deposit item AM-XX-XXX, CIF, is stored on the MSA web site and available via the American Mineralogist Table of Contents. Find the article in the table of contents at GSW ([ammin.geoscienceworld.org](http://ammin.geoscienceworld.org)) or MSA ([www.minsocam.org](http://www.minsocam.org)), and then click on the deposit link.



## 184 **Structure description**

185 In the crystal structure of yusupovite, there are six Si sites occupied by Si, tetrahedrally  
186 coordinated by O atoms with  $\langle \text{Si-O} \rangle = 1.613 \text{ \AA}$  (Tables 5, 6). There are two M sites occupied mainly by  
187 Zr with minor Y and Hf; ideally they give 1 Zr apfu (Table 7). The M(1,2) sites are octahedrally  
188 coordinated by O atoms, with  $\langle \text{M-O} \rangle = 2.114$  and  $2.103 \text{ \AA}$ , respectively. Si tetrahedra share vertices to  
189 form an epididymite  $\text{Si}_6\text{O}_{15}$  ribbon along [010]. Epididymite ribbons and Zr-dominant M octahedra share  
190 common vertices to form a heteropolyhedral framework (Figs. 4a, 4b).

191 There are six interstitial sites occupied by the alkali cations Na, K and Cs. There are three [7]-  
192 coordinated Na sites partly occupied by Na. The Na1 site is occupied by Na at 95% and is coordinated by  
193 O atoms, with  $\langle \text{Na1-O} \rangle = 2.567 \text{ \AA}$  (Tables 6, 7). The Na2 and Na3 sites are occupied by Na at 84 and  
194 78%, respectively, and they are coordinated by O atoms and  $\text{H}_2\text{O}$  groups which occur at the W sites, with  
195  $\langle \text{Na2-}\varphi \rangle = 2.555$  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  
196 Na apfu. There are three A sites partly occupied by K and Cs (c.f. analogous sites in Rb-exchanged  
197 elpidite,  $90^\circ\text{C}$ ). The A sites occur at short distances from the Na sites.  $\text{A1-Na2} = 2.648$ ,  $\text{A2-Na3} = 1.617$   
198 and  $\text{A3-Na3} = 2.637 \text{ \AA}$  (Table 6), and hence the A and Na sites cannot be locally occupied. The A1, A2  
199 and A3 sites are occupied by (K + Cs) at 12, 18 and 16%, respectively (Table 7). The A1-A3 sites give  
200  $\text{K}_{0.12}\text{Cs}_{0.11}$  apfu. Ideally, the composition of the A1-A3 sites is  $\square_{1.5}$  pfu. The Na and A sites sum to  $\text{Na}_2 +$   
201  $\square_{1.5} = \text{Na}_2$  apfu. There are 10 W sites occupied by  $\text{H}_2\text{O}$  groups at 18-84% (Table 5); the W1-W10 sites  
202 give  $(\text{H}_2\text{O})_{2.52}$  pfu, ideally  $(\text{H}_2\text{O})_3$  pfu.

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### **COMPARISON OF YUSUPOVITE AND ELPIDITE**

205 The crystal structure of yusupovite, ideally  $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$ , monoclinic, space group  $C2/m$ ,  
206 is a superstructure of elpidite,  $\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$ , orthorhombic, space group  $Pbcm$  (Figs. 4c, 4d; Table  
207 1). In yusupovite, (1) the Na2 site of elpidite (Figs. 4c, 4d) is split into two sites, Na2 and Na3 (Figs. 4a,  
208 4b), and (2) the two W1 and W2 sites (fully occupied by  $\text{H}_2\text{O}$  groups) of elpidite (Cannillo et al. 1973) are  
209 split into ten W1-W10 sites partly occupied by  $\text{H}_2\text{O}$  groups (Table 5). In the crystal structure of

210 yusupovite, the occurrence of the interstitial alkali cations K and Cs at the A sites results in the disorder  
211 and depletion of Na at the Na sites and disorder and depletion of H<sub>2</sub>O at the W sites.

212 Due to the (K,Cs), Na and H<sub>2</sub>O disorder, the symmetry of yusupovite decreases from  
213 orthorhombic, space group *Pbcm* (elpidite) to monoclinic, space group *C2/m* and the *b* cell parameter of  
214 yusupovite is doubled when compared to the corresponding cell parameter in elpidite,  $b_{yus} = 2a_{elp}$ . We  
215 conclude that yusupovite, ideally Na<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub>, is a dimorph of elpidite, Na<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub>.

216 It is tempting to suggest that the (Na,Cs)<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub> structure undergoes a compositionally  
217 induced ferroelastic transition with only minor incorporation of Cs into the elpidite structure.

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### IMPLICATIONS

220 Yusupovite and elpidite are heteropolyhedral-framework structures, materials that have been the  
221 subject of extensive examination over the last fifteen years because of their potential use as industrial  
222 microporous materials; they have great potential use as ion-exchange materials and highly selective  
223 molecular sieves, catalysts and ion conductors (Krivovichev 2012). Of particular interest with regard to  
224 yusupovite are the ion-exchange experiments of Grigor'eva et al. (2011) on elpidite. They showed that  
225 elpidite, Na<sub>2</sub>Zr(Si<sub>6</sub>O<sub>15</sub>)(H<sub>2</sub>O)<sub>3</sub>, easily exchanges Na for K and Rb at relatively low temperature (90 and  
226 150°C) in aqueous solutions enriched in K and Rb. Detailed work by Zubkova et al. (2011) showed that  
227 the structure of elpidite contracts considerably on heating-induced dehydration, accompanied by doubling  
228 of the *a* cell-dimension. The chemical composition of yusupovite is characterised by the presence of a  
229 small amount of Cs<sub>2</sub>O: 2.58 wt%, 0.11 apfu. Obviously the elpidite structure can accommodate large  
230 alkali cations (K, Rb, Cs) at low temperature, making it an attractive potential atomic-scale container for  
231 these elements, particularly for low-temperature waste-water filtration (Popa and Pavela 2012). This  
232 capability seems of obvious significance to the potential encapsulation of <sup>137</sup>Cs from radiogenic waste.  
233 The framework structure of elpidite contracts on dehydration at fairly modest temperature ( $\leq 300^\circ\text{C}$ ;  
234 Zubkova et al. 2011), suggesting that dehydration of Cs-exchanged elpidite may help “seal” the  
235 exchanged Cs in the contracted dehydrated structure.

236

237

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314

## FIGURE CAPTIONS

315 **Figure 1.** BSE image of a (broken) crystal of yusupovite (yus) cemented by quartz (Q), with  
316 zeravshanite (zer), reedmergnerite (reed) and fluorite (flu).

317

318 **Figure 2.** BSE image of an intergrowth of yusupovite (white) and quartz (grey), and X-ray maps  
319 of the distribution of Si, Na, Zr, Cs and K.

320

321 **Figure 3.** The FTIR spectra of a randomly oriented single crystal of yusupovite ( $4000\text{-}1350\text{ cm}^{-1}$ )  
322 (a) and a powder sample of yusupovite ( $1500\text{ - }400\text{ cm}^{-1}$ ) (b).

323

324 **Figure 4.** The crystal structures of yusupovite (a, b) and elpidite (c,d, after Cannillo et al. 1973).

325 Zr and Si polyhedra are green and lilac, Na atoms and H<sub>2</sub>O groups are shown as blue and red spheres,

326 (K,Cs) atoms at the A sites in yusupovite are shown as yellow spheres. Unit cells are shown with thin

327 black lines.

**TABLE 1.** Comparison of yusupovite and elpidite

	Yusupovite	Elpidite*
Formula	$\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$	$\text{Na}_2\text{Zr}(\text{Si}_6\text{O}_{15})(\text{H}_2\text{O})_3$
Symmetry	monoclinic	orthorhombic
Space group	<i>C2/m</i>	<i>Pbcm</i>
<i>a</i> (Å)	14.5975(4) ( <i>b</i> <sub>elp</sub> )	7.14(2)
<i>b</i>	14.1100(4) (2 <i>a</i> <sub>elp</sub> )	14.68(1)
<i>c</i>	14.4394(4) ( <i>c</i> <sub>elp</sub> )	14.65(1)
$\alpha$ (°)	90	90
$\beta$	90.0399(4)	90
$\gamma$	90	90
<i>Z</i>	8	4
Strongest reflections in the powder data, <i>d</i> <sub>obs.</sub> (Å)( <i>I</i> )	7.05(100), 3.24(96), 3.10(69), 5.13(53), 6.51(42), 3.17(34), 2.941(27)	3.271(100), 3.124(90), 7.11(90), 5.18(85), 6.56(85), 2.546(75), 2.965(75)
Colour	colourless	colourless, white
Lustre	vitreous	vitreous
<i>D</i> <sub>meas.</sub> , g/cm <sup>3</sup>	2.69(2)	2.615
<i>D</i> <sub>calc.</sub> , g/cm <sup>3</sup>	2.713	2.573
Hardness (Mohs')	5	5
Optical sign	Biaxial (+)	Biaxial (+)
2 <i>V</i> (°)	42 (3)	84
$\alpha$	1.563(2)	1.563
$\beta$	1.565(2)	1.569
$\gamma$	1.577(2)	1.577

\* crystallographic data (Cannillo et al. 1973); *D*<sub>calc.</sub> (Grigor'eva et al. 2011); powder pattern (PDF-2#50-223); colour, lustre, *D*<sub>meas.</sub>, hardness and optical properties (Tikhonenkov et al. 1957).



**TABLE 2.** Chemical analysis and unit formula for yusupovite

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

\* the formula was calculated on the basis of 17.50 O apfu, Z = 8.

\*\* H<sub>2</sub>O calculated from structure refinement.

**TABLE 3.** X-ray powder diffraction data for yusupovite

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

**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)
$\beta$ (°)	90.0399(4)
<i>V</i> (Å <sup>3</sup> )	2974.1(3)
Space group	<i>C2/m</i>
<i>Z</i>	8
Absorption coefficient (mm <sup>-1</sup> )	2.29
<i>F</i> (000)	2381.6
<i>D</i> <sub>calc.</sub> (g/cm <sup>3</sup> )	2.713
Crystal size (mm)	0.100 x 0.040 x 0.025
Radiation/monochromator	MoK $\alpha$ /graphite
2 $\theta$ -range for data collection (°)	60.14
<i>R</i> (int) (%)	0.91
Reflections collected	17349
Independent reflections	4519
<i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i>	4428
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup> , fixed weights proportional to 1/ $\sigma$ <i>F</i> <sub>o</sub> <sup>2</sup>
No. of refined parameters	267
Final <i>R</i> (obs) (%)	
[ <i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i> ]	3.46
<i>R</i> <sub>1</sub>	3.51
<i>wR</i> <sub>2</sub>	8.94
Highest peak, deepest hole (e Å <sup>-3</sup> )	1.37 -3.44
Goodness of fit on <i>F</i> <sup>2</sup>	1.117

**TABLE 5.** Atom coordinates and displacement parameters ( $\text{\AA}^2$ ) for yusupovite

Atom	Sof (%)*	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}^{**}$
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)

**TABLE 5.** continued

Atom	Sof (%)*	x	y	z	$U_{eq}$ **
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

W = O atom of an H<sub>2</sub>O group.

\* site-occupancy factor.

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

**TABLE 6.** Selected interatomic distances (Å) and angles (°) in yusupovite\*

M1-O5	2.104(2) x2	M2-O4	2.095(2) x2
M1-O17	2.110(2) x2	M2-O16a	2.097(2) x2
M1-O10	<u>2.128(2)</u> x2	M2-O3	<u>2.118(2)</u> x2
<M1-O>	2.114	<M2-O>	2.103
Na1-O1	2.333(3)	Na2-O3c	2.369(3) x2
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) x2
Na1-O16	2.539(3)	Na2-O16	<u>2.767(3)</u> x2
Na1-O4b	2.735(3)	<Na2-φ>	2.555
Na1-O5	<u>2.843(3)</u>		
<Na1-O>	2.567		
Na3-O10	2.374(3) x2	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) X2		
Na3-W9	<u>2.93(2)</u>		
<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	<u>1.635(2)</u>	Si2-O15	<u>1.637(2)</u>
<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	<u>1.629(2)</u>	Si4-O14	<u>1.626(2)</u>
<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	<u>1.627(2)</u>	Si6-O1	<u>1.628(2)</u>
<Si5-O>	1.612	<Si6-O>	1.612
A1-W7	2.736(6)	A2-O10	3.011(5) x2
A1-W4	2.96(1)	A2-O11h	3.053(5)
A1-O4	3.065(3) x2	A2-O17	3.255(3) x2
A1-O3	3.208(5) x2	A2-O12i	3.287(3) x2
A1-O9	3.249(6) x2	A2-O6	3.212(5)
A1-O2	<u>3.244(4)</u>	A2-W10	3.37(4) x2
<A1-O>	3.109	A2-O11	<u>3.565(7)</u>
		<A2-φ>	3.231

**TABLE 6.** continued

A3-W1	2.96(1)	Si5b-O1-Si6	150.5(2)
A3-O5	3.013(2) x2	Si3-O2-Si3j	156.5(2)
A3-W2	3.08(1) x2	Si4-O6-Si4j	156.5(2)
A3-O10	3.202(6) x2	Si1-O7-Si1j	144.8(2)
A3-O13	3.261(6) x2	Si1e-O8-Si5	144.4(2)
A3-O6	<u>3.493(8)</u>	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	<u>143.2(2)</u>
		<Si-O-Si>	146.9

φ = O, H<sub>2</sub>O.

\* 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).

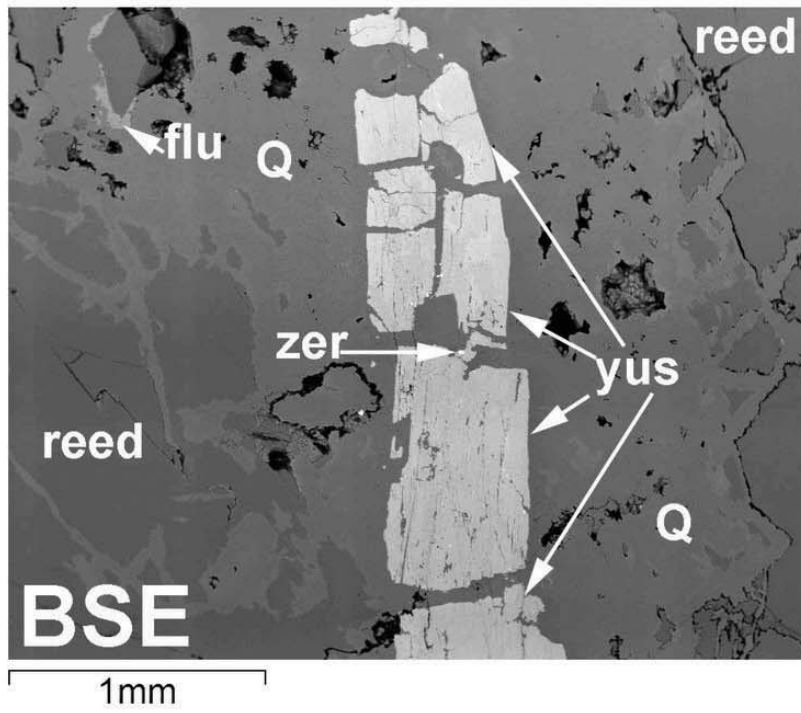
Symmetry operators: a: x, y, z-1; b: -x+1/2, -y+1/2, -z+1; c: x, y, z+1; d: x+1/2, -y+1/2, z; e: x-1/2, -y+1/2, z; f: -x+1, y, -z+1; g: -x, y, -z+1; h: -x, -y, -z+1; i: -x+1/2, y-1/2, -z+1; j: x, -y, z

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

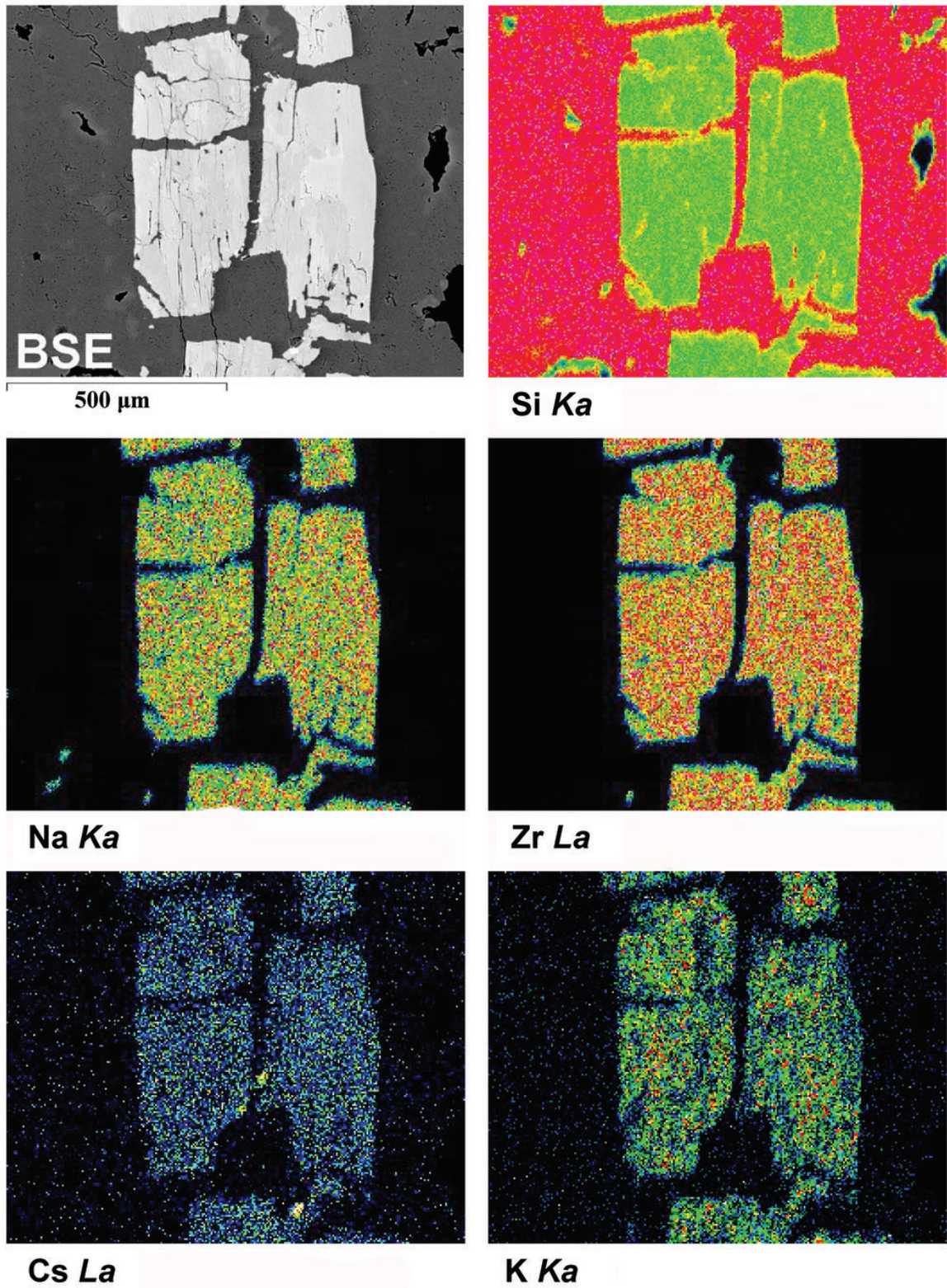
Site	Refined site-scattering (epfu)	Site population (apfu)	Calculated site-scattering (epfu)	$\langle X-\phi \rangle_{\text{obs}}^*$ (Å)
<sup>[6]</sup> M1	20.8(5)	0.41 Zr + 0.08 Y + 0.01 Hf	20.24	2.114
<sup>[6]</sup> M2	20.6(5)	0.41 Zr + 0.09 Y	19.93	2.103
$\Sigma M(1,2)$	41.4	0.82 Zr + 0.17 Y + 0.01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

\*X = cation, φ = anion.

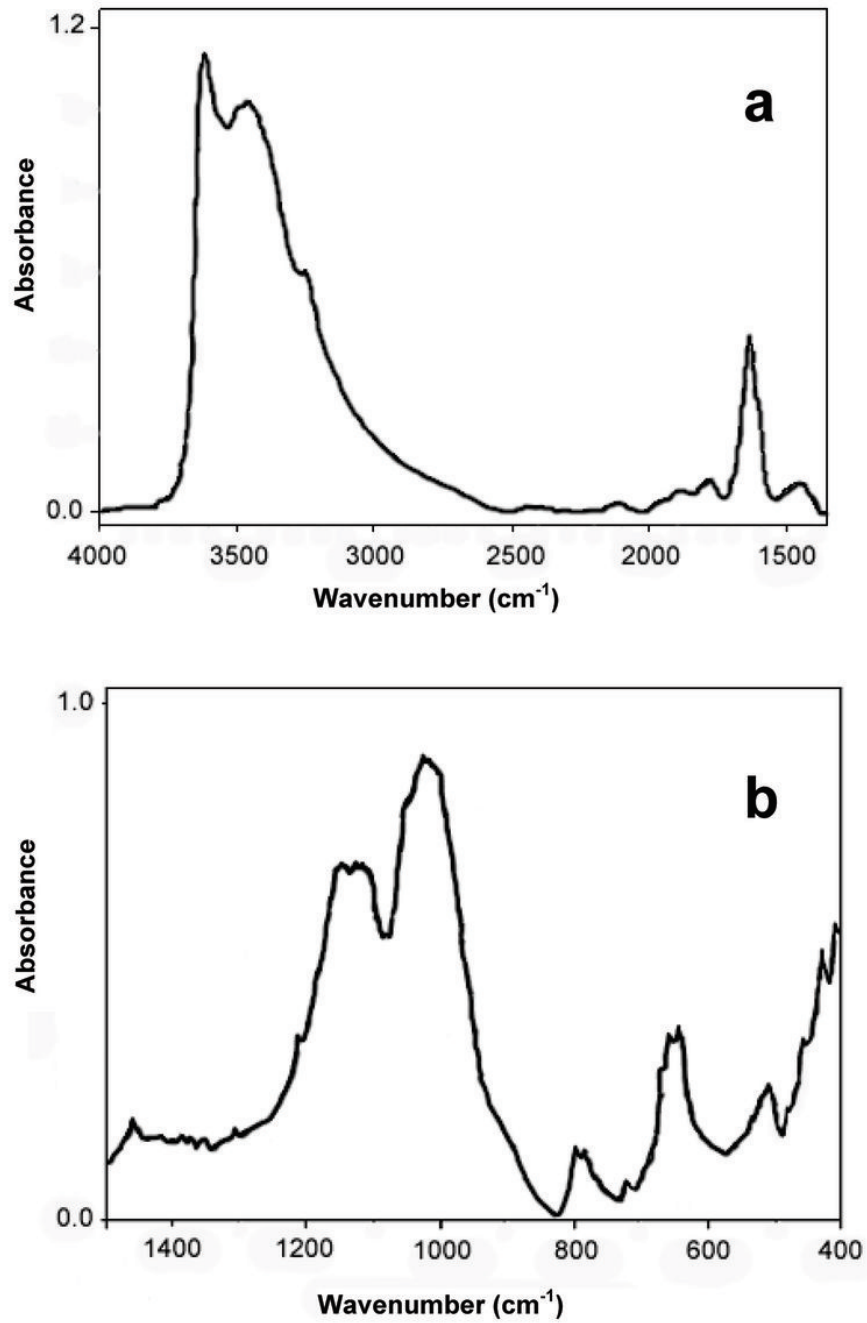




**Fig. 1**

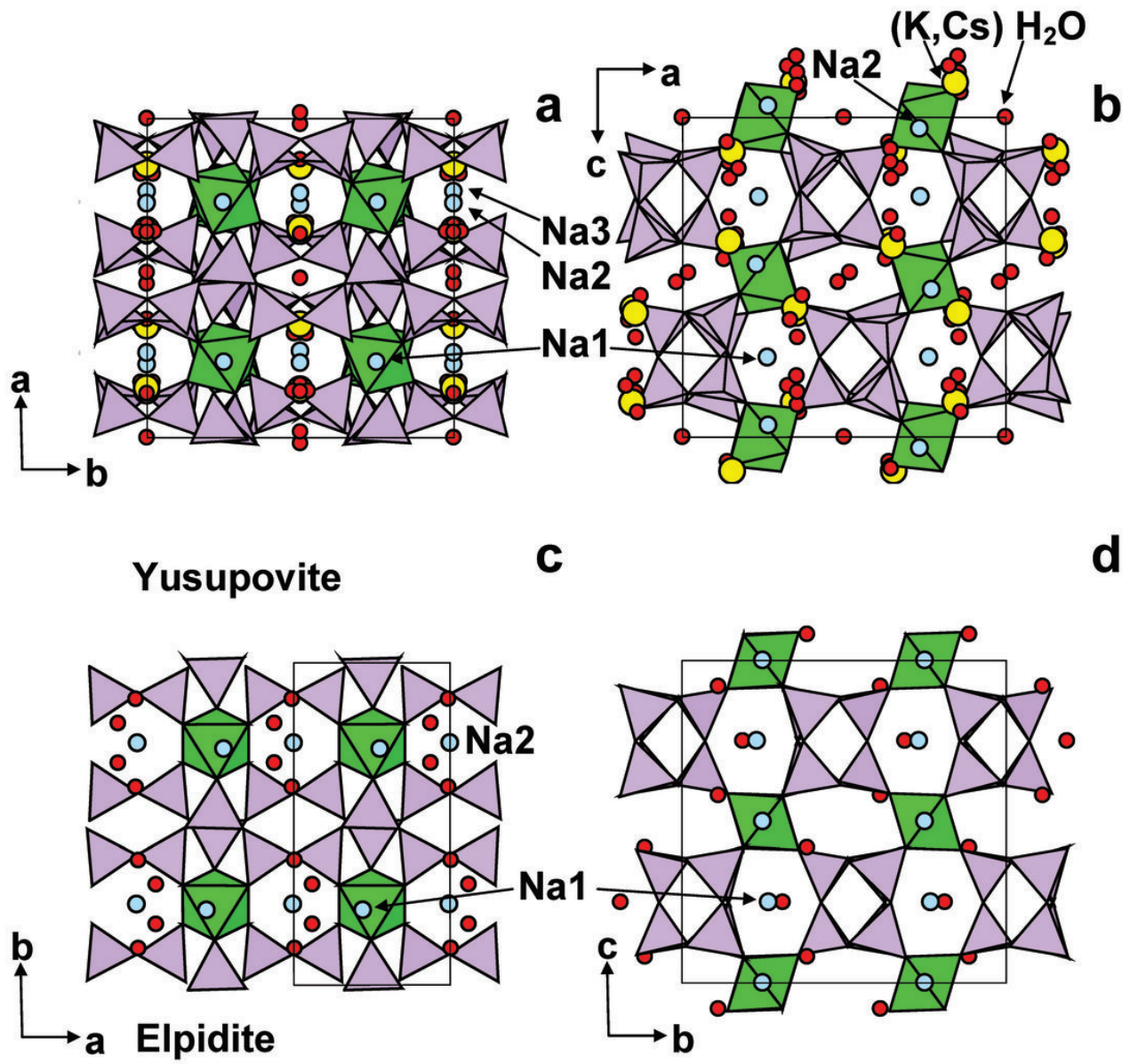


**Fig. 2**



**Fig. 3**





**Fig. 4**