



## Article – Gregory Yu. Ivanyuk memorial issue

# A highly hydrated variety of elpidite from the Khibiny alkaline complex, Kola Peninsula, Russia

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### Abstract

An unusual highly hydrated and Na-depleted variety of elpidite was identified in a hydrothermally altered peralkaline pegmatite at Mt. Yukspor in the Khibiny alkaline complex, Kola Peninsula, Russia. It differs from 'ordinary' elpidite, ideally  $\text{Na}_2\text{ZrSi}_6\text{O}_{15}\cdot 3\text{H}_2\text{O}$ , in its crystal chemical features, infrared spectrum and optical characteristics. The chemical composition (wt.%, electron microprobe,  $\text{H}_2\text{O}$  by TGA) is:  $\text{Na}_2\text{O}$  5.45,  $\text{K}_2\text{O}$  0.67,  $\text{CaO}$  0.05,  $\text{SiO}_2$  60.32,  $\text{TiO}_2$  1.34,  $\text{ZrO}_2$  18.43,  $\text{Nb}_2\text{O}_5$  0.65,  $\text{H}_2\text{O}$  12.80, total 99.71. The empirical formula calculated on the basis of 6 Si and 15 O atoms is  $[(\text{Na}_{1.05}\text{K}_{0.08}\text{Ca}_{0.01})_{\Sigma 1.14}(\text{H}_3\text{O})_{0.74}]_{\Sigma 1.88}(\text{Zr}_{0.89}\text{Ti}_{0.10}\text{Nb}_{0.03})_{\Sigma 1.02}\text{Si}_6\text{O}_{15}\cdot 3.47\text{H}_2\text{O}$ ; the  $\text{H}_2\text{O}:\text{H}_3\text{O}$  ratio was calculated from the charge balance requirement, taking into account the results of crystal structure refinement. The highly hydrated variety of elpidite is orthorhombic, *Pma2*,  $a = 14.5916(6)$ ,  $b = 7.3294(3)$ ,  $c = 7.1387(2)$  Å,  $V = 763.47(5)$  Å<sup>3</sup> and  $Z = 2$ . The crystal structure was solved from single-crystal X-ray diffraction data,  $R_1 = 3.43\%$ . The structure is based upon an elpidite-type heteropolyhedral Zr–Si–O framework with  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  cations and  $\text{H}_2\text{O}$  molecules in the zeolitic channels. Hydronium cations substitute for water molecules in one of the extra-framework sites. This variety of elpidite could be considered as an intermediate product of natural ion-exchange reaction between 'ordinary' elpidite and a low-temperature hydrothermal fluid.

**Keywords:** elpidite, microporous zirconosilicate, crystal structure, heteropolyhedral framework, natural ion exchange, peralkaline pegmatite, Khibiny alkaline complex, Kola peninsula

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### Introduction

Elpidite, ideally  $\text{Na}_2\text{ZrSi}_6\text{O}_{15}\cdot 3\text{H}_2\text{O}$ , is known only in alkaline, mainly agpaitic igneous rocks. It is a relatively rare mineral, however, in some peralkaline complexes it occurs in significant concentrations and serves locally as the major Zr host phase. Among natural hydrous zirconosilicates, elpidite is the species richest in Si and, thus, silica-rich peralkaline systems are the most favourable for the formation of this mineral (Kynicky *et al.*, 2011 and references therein), which is in agreement with Na zirconosilicates in the  $\text{NaOH}\text{--}\text{ZrO}_2\text{--}\text{SiO}_2\text{--}\text{H}_2\text{O}$  system (Ilyushin *et al.*, 1983). The largest elpidite deposits occur in peralkaline granites and their pegmatites where this zirconosilicate can be an important accessory or even a major mineral and a potentially useful component of complex rare-element (Zr–Nb–Ta–REE) ores. The most notable examples are deposits associated with the Khan Bogdo (= Khan Bogd) (Vladykin *et al.*, 1981; Kynicky *et al.*, 2011) and Khaldzan Buregte (= Khaldzan

Buregtey or Khaldzan Buragtag) (Kovalenko *et al.*, 1995; Kempe *et al.*, 2015) alkaline granite intrusions in Mongolia and the Strange Lake complex in Canada (Birkett *et al.*, 1992; Salvi and Williams-Jones, 2001). In nepheline-syenite complexes no significant elpidite deposits are known; however, it can be abundant locally. In the Lovozero alkaline complex in the Kola Peninsula, Russia such accumulations of elpidite were described in quartz-bearing fenites (Ivanyuk *et al.*, 2006) and in large hydrothermally altered peralkaline, highly agpaitic pegmatite bodies. For example, in the Elpiditovoe pegmatite this zirconosilicate was found as almost monomineralic aggregates up to 100 kg (Pekov, 2000).

From the crystal chemical viewpoint, elpidite is a typical microporous, zeolite-like zirconosilicate. Its crystal structure is based on a heteropolyhedral Zr–Si–O framework which consists of tetrahedral  $\text{Si}_6\text{O}_{15}$  ribbons (double chains) and isolated  $\text{ZrO}_6$  octahedra. Wide channels inside the heteropolyhedral framework contain  $\text{Na}^+$  cations and  $\text{H}_2\text{O}$  molecules (Neronova and Belov, 1964; Cannillo *et al.*, 1973). The presence of the three-dimensional system of these channels causes distinct zeolitic properties of elpidite: this mineral readily exchanges  $\text{Na}^+$  in aqueous solutions for other large cations ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ ) and demonstrates reversible dehydration in thermal experiments (Turchkova *et al.*, 2006; Grigor'eva *et al.*, 2011; Zubkova *et al.*, 2011, 2019; Cametti *et al.*, 2016). Elpidite is an orthorhombic

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**Table 1.** Some chemical features and physical properties of 'ordinary' elpidite and its highly hydrated variety: comparative data.

Mineral	Highly hydrated variety of elpidite from Khibiny	'Ordinary' elpidite
Chemical composition	empirical formula: $[(\text{Na}_{1.05}\text{K}_{0.08}\text{Ca}_{0.01})_{\Sigma 1.14}(\text{H}_3\text{O})_{0.74}]_{\Sigma 1.88}$ $(\text{Zr}_{0.89}\text{Ti}_{0.10}\text{Nb}_{0.03})_{\Sigma 1.02}\text{Si}_6\text{O}_{15} \cdot 3.47\text{H}_2\text{O}$	$\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$ typically with insignificant variations
H <sub>2</sub> O content (wt.%)	12.8	8–10
Optical data (for $\lambda = 589$ nm)	biaxial(+)	biaxial(+)
$\alpha$	1.5615(10)	1.556–1.563
$\beta$	1.5625(10)	1.565–1.569
$\gamma$	1.572(2)	1.574–1.577
2V	45(5) <sup>o</sup> (meas.) / 36 <sup>o</sup> (calc.)	76–89 <sup>o</sup>
$D_{\text{meas}}$ (g/cm <sup>3</sup> )	2.42	2.52–2.63
Fluorescence in shortwave UV light: colour/intensity	greenish-yellow/very strong	no fluorescence or, rarely, yellowish-white / weak
Fluorescence in longwave UV light: colour/intensity	greenish-yellow/medium	no fluorescence
Source	This work	Anthony <i>et al.</i> (1995); Zubkova <i>et al.</i> (2019) and references therein; our data

mineral. In the literature, its 'basic' unit cell has been described in two settings: (1) in the unconventional space group *Pbm2* (mainly used in early studies) with the following unit-cell parameters:  $a = 7.1\text{--}7.4$ ,  $b = 14.4\text{--}14.7$  and  $c = 7.05\text{--}7.15$  Å (so-called 7–14–7 Å elpidite); and (2) in the standard setting, space group *Pma2* with inverted unit-cell parameters  $a$  and  $b$  (used in this work). Distortions of the Zr–Si–O framework and variations in the location of extra-framework cations and H<sub>2</sub>O molecules cause the structural variations reported for this mineral. For different samples of elpidite and its laboratory-modified (cation-substituted or dehydrated) forms, a variety of space groups (*Pbmm*, *Pbm2*, *Pbcm*, *Bba2*, *Cmce*) was reported and doubling of the  $a$  and/or  $c$  unit-cell parameters was found in some cases. Crystal chemical data on all structurally studied samples of elpidite, its monoclinic (*C2/m*) dimorph yusupovite and modified forms of elpidite were recently summarised and reviewed by Zubkova *et al.* (2019).

In the present paper we describe a new variety of elpidite found in the Khibiny alkaline complex in the Kola Peninsula. Unlike the neighbouring Lovozero complex, where elpidite is locally abundant (Pekov, 2000; Ivanyuk *et al.*, 2006), in Khibiny it is a rare mineral known only in very minor amounts in hydrothermal assemblages related to several peralkaline pegmatite and pegmatoid bodies (Yakovenchuk *et al.*, 2005). The new elpidite variety characterised here is significantly depleted in Na and additionally hydrated in comparison to examples of this mineral from all earlier known localities. Such chemical deviations from the ideal composition are reflected in the unusual crystal chemical features and physical properties of this elpidite variety.

### Occurrence and sample description

The new variety of elpidite was collected in the upper part of the Loparskaya River valley (north-eastern spur of Mt. Yukspor) in the south-western part of the Khibiny alkaline complex. The mineral was found in a cavernous hydrothermally altered axial zone of a relatively small (about two meters across) peralkaline pegmatite body of lenticular shape. It is situated in foyaite and has a mineral composition common for the Khibiny foyaite pegmatites: microcline, nepheline and black coarse-prismatic alkali clinopyroxene are the major minerals, whereas eudialyte, titanite, astrophyllite, biotite, pale greenish fluorapatite and sphalerite are accessory constituents. The hydrothermal mineral assemblage formed in cavities includes green acicular aegirine, yellow–green fluorapatite, zeolites (natrolite, chabazite-K, heulandite-Ca and heulandite-K), ancylite-(Ce) and elpidite. The latter occurs as aqua-transparent

colourless prismatic, lath-like crystals up to 0.1 mm × 0.4 mm × 3 mm, typically assembled in bunches or spherulites up to 6 mm in diameter. They are encrusted by chabazite and heulandite crystals. Under ultraviolet (UV) irradiation, this variety of elpidite fluoresces greenish-yellow, is very bright in shortwave ( $\lambda = 245$  nm) and medium-intense in longwave ( $\lambda = 330$  nm) ultraviolet light. The optical characteristics of this variety of elpidite are given in Table 1. Its density measured by flotation in heavy liquids (bromoform + ethanol) is 2.42(2) g cm<sup>-3</sup>.

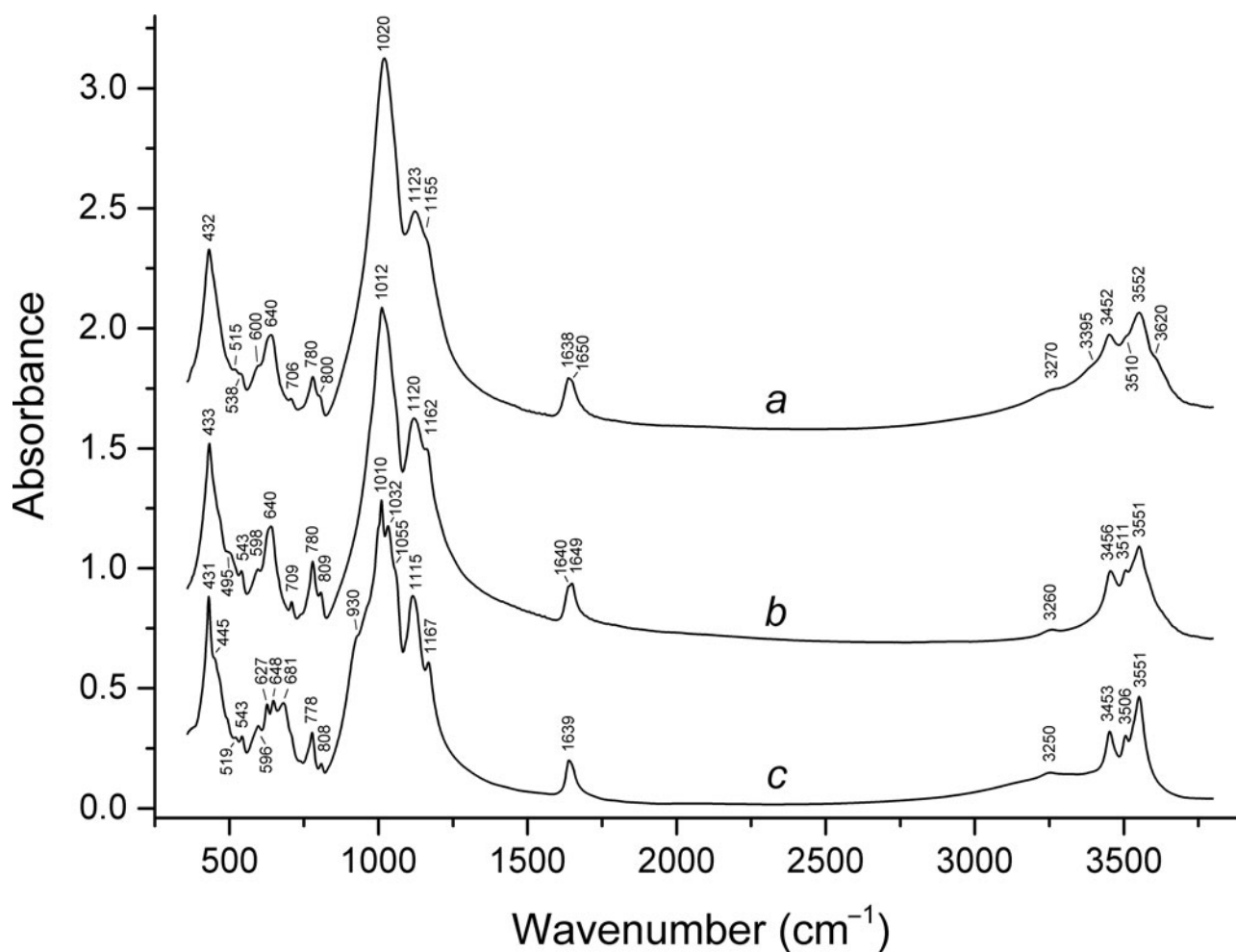
### Infrared spectroscopy

In order to obtain infrared (IR) absorption spectra, powdered samples were mixed with dried KBr, pelletised, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) in the range 360–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. A total of 16 scans were collected for each spectrum. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of the highly hydrated elpidite (Fig. 1a) is close to the spectrum of 7–14–7 Å elpidite (space group *Pbm2*) from Khan Bogdo studied by Sapozhnikov and Kashaev (1978) (Fig. 1b) but differs from the latter by the high-frequency shift of the strongest band of Si–O stretching vibrations (1012 → 1020 cm<sup>-1</sup>), the presence of additional shoulders (at 3395 and 3620 cm<sup>-1</sup>) corresponding to O–H stretching vibrations and ca. 1.7 times higher integrated intensity in the range 2800–3800 cm<sup>-1</sup> (with the bands at 640 and 780 cm<sup>-1</sup> used as internal standards).

It is noteworthy that typically the H<sub>2</sub>O molecule and H<sub>3</sub>O<sup>+</sup> cation cannot be reliably distinguished by means of IR spectroscopy: the band at ~1740 cm<sup>-1</sup> is indicative of the monohydrated H<sub>3</sub>O<sup>+</sup> cation (i.e. Zundel cation, H<sub>5</sub>O<sub>2</sub><sup>+</sup>) with a strong symmetric hydrogen bond, but not of the H<sub>3</sub>O<sup>+</sup> cation forming relatively weak hydrogen bonds. This matter is discussed in detail by Chukanov and Chervonnyi (2016). Thus the shoulders at 3395 and 3620 cm<sup>-1</sup> and enhanced integrated intensity of the IR spectrum of the Khibiny hydrated elpidite in the range of O–H stretching vibrations may be due to both H<sub>2</sub>O molecules and hydronium cations. The relatively high frequency of the band of Si–O stretching vibrations (at 1020 cm<sup>-1</sup>) in the IR spectrum indicates a medium-strength hydrogen bond formed by a species at the Ow2 site (i.e. H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup>) with O7 in the Si<sub>6</sub>O<sub>15</sub> ribbon with the Ow2–O7 distance of 2.811 Å (see below).

The IR spectrum of the 7–14–14 Å elpidite (Fig. 1c) differs significantly from those of 7–14–7 Å samples in additional splitting of some bands in the ranges 600–700 and 1000–1100 cm<sup>-1</sup>, which



**Fig. 1.** Powder infrared absorption spectra of (a) highly hydrated elpidite from Khibiny (this work), (b) 7–14–7 Å elpidite (space group *Pbm2*) from Khan Bogdo (see: Sapozhnikov and Kashaev, 1978) and (c) 7–14–14 Å elpidite (space group *Pbcm*) from Lovozero (see: Zubkova et al., 2011).

correspond to bending and stretching vibrations of the  $\text{Si}_6\text{O}_{15}$  ribbon. The integrated absorbance of the 7–14–14 Å sample from Lovozero in the range  $2800\text{--}3800\text{ cm}^{-1}$  is nearly the same as that of the 7–14–7 Å sample from Khan Bogdo.

### Chemical composition

The chemical composition of the highly hydrated elpidite from Khibiny was determined by electron microprobe analysis (EMPA) in the Laboratory of Analytical Techniques of High Spatial Resolution at the Department of Petrology, Moscow State University using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer. The analyses were carried out in WDS mode, with an acceleration voltage of 20 kV and a beam current of 20 nA. The electron beam was rastered to  $10\ \mu\text{m} \times 10\ \mu\text{m}$  to minimise damage of the mineral. The following standards were used: NaCl (Na), microcline (K), clinopyroxene (Ca), zircon (Si, Zr), Ti (Ti) and Nb (Nb). The results obtained were checked for the correctness of Na content measurement, in energy-dispersive mode at a low beam current (0.7 nA). The latter gave practically the same values for all measured constituents. The  $\text{H}_2\text{O}$  content was determined using thermogravimetric analysis.

The average chemical composition of the Khibiny hydrated elpidite [average of 12 spot analyses; wt.% (range)] is:  $\text{Na}_2\text{O}$  5.45 (5.12–5.78),  $\text{K}_2\text{O}$  0.67 (0.35–0.91),  $\text{CaO}$  0.05 (0.03–0.10),  $\text{SiO}_2$  60.32 (59.40–61.12),  $\text{TiO}_2$  1.34 (1.11–1.59),  $\text{ZrO}_2$  18.43 (17.66–18.92),  $\text{Nb}_2\text{O}_5$  0.65 (0.39–0.87),  $\text{H}_2\text{O}$  12.80, total 99.71. Contents of other elements with atomic numbers higher than carbon are below detection limits in the majority of analyses. Some analyses show very low concentrations, close to detection limits, of Fe, Y, Yb, Th and U. The empirical formula was calculated on the basis of 6 Si and 15 O atoms per formula unit (apfu) because of (1) the absence of  $\text{OH}^-$  groups and (2) the presence of both  $\text{H}_2\text{O}^0$  and  $\text{H}_3\text{O}^+$  groups in the mineral (see the crystal structure data below). The  $\text{H}_2\text{O}:\text{H}_3\text{O}$  ratio was calculated based on charge balance considerations after the atoms per formula units (apfu) were calculated for Si (6 apfu) and metal cations. The empirical formula is:  $[(\text{Na}_{1.05}\text{K}_{0.08}\text{Ca}_{0.01})_{\Sigma 1.14}(\text{H}_3\text{O})_{0.74}]_{\Sigma 1.88}(\text{Zr}_{0.89}\text{Ti}_{0.10}\text{Nb}_{0.03})_{\Sigma 1.02}\text{Si}_6\text{O}_{15}\cdot 3.47\text{H}_2\text{O}$ .

### X-ray crystallography and crystal-structure determination details

Single-crystal X-ray studies of the highly hydrated elpidite were carried out using an Xcalibur S diffractometer equipped with a

**Table 2.** Crystal data, data collection information and structure refinement details for highly hydrated elpidite.

Crystal data	
Formula	Na <sub>1.19</sub> (H <sub>3</sub> O <sub>0.81</sub> H <sub>2</sub> O <sub>0.08</sub> )(Zr <sub>0.95</sub> Ti <sub>0.05</sub> )Si <sub>6</sub> O <sub>15</sub> ·2.81H <sub>2</sub> O
Formula weight*	583.94
Radiation, wavelength	MoK $\alpha$ ; 0.71073 Å
Crystal system, space group, Z	Orthorhombic, <i>Pma</i> 2, 2
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.5916(6), 7.3294(3), 7.1387(2)
<i>V</i> (Å <sup>3</sup> )	763.47(5)
Density (calc.) (g/cm <sup>3</sup> )	2.54
$\mu$ (mm <sup>-1</sup> )*	1.32
<i>F</i> <sub>000</sub> *	571
Crystal size (mm)	0.05 × 0.08 × 0.80
Data collection	
Diffractometer	Xcalibur S CCD
Temperature (K)	293(2)
Absorption correction	Multi-scan
$\theta$ range (°)	2.779–28.277
Index ranges	−19 ≤ <i>h</i> ≤ 19, −9 ≤ <i>k</i> ≤ 9, −9 ≤ <i>l</i> ≤ 9
Reflections collected	12,230
Unique reflections	1883 ( <i>R</i> <sub>int</sub> = 0.0548)
Unique reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1654
Refinement	
Structure refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
No. of refined parameters	128
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0343, <i>wR</i> <sub>2</sub> ** = 0.0914
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0398, <i>wR</i> <sub>2</sub> ** = 0.0948
GoF	1.044
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ , e <sup>−</sup> /Å <sup>3</sup>	2.07 and −0.46

\*Calculated from structural data (i.e. no H atoms were inserted in the structure model).

\*\**w* = 1/[ $\sigma^2(F_o^2) + (0.0632P)^2 + 0.3999P$ ]; *P* = [(max of (0 or *F<sub>o</sub><sup>2</sup>)) + 2*F<sub>c</sub><sup>2</sup>]/3**

CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using *CrysAlisPro* Version 1.171.39.46 (Rigaku Oxford Diffraction, 2018). The data were corrected for Lorentz factor and polarisation effects. The crystal structure was solved by direct methods and refined in the frames of the orthorhombic space group *Pma*2 with the *SHELX* software package (Sheldrick, 2015) to *R*<sub>1</sub> = 0.0343 for 1654 unique reflections with *I* > 2 $\sigma$ (*I*). Crystal data, data collection information and structure refinement details are given in Table 2, the coordinates and thermal displacement parameters of atoms and site occupancies in Table 3 and selected interatomic distances in

**Table 3.** Coordinates, equivalent (*U*<sub>eq</sub>) and anisotropic (*U*) displacement parameters of atoms (in Å<sup>2</sup>), site occupancy factors (s.o.f.) and site multiplicities (*Q*) in the structure of highly hydrated elpidite.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	s.o.f.	<i>Q</i>	<i>U</i> <sup>11</sup>	<i>U</i> <sup>22</sup>	<i>U</i> <sup>33</sup>	<i>U</i> <sup>23</sup>	<i>U</i> <sup>12</sup>	<i>U</i> <sup>13</sup>
Zr	½	½	0.3796(5)	0.0085(2)	Zr <sub>0.947(10)</sub> Ti <sub>0.053(10)</sub>	2	0.0081(3)	0.0080(3)	0.0094(3)	0.000	0.000	−0.00062(19)
Si1	0.35847(8)	0.90579(16)	0.3768(7)	0.0114(3)	Si <sub>1.00</sub>	4	0.0113(6)	0.0102(6)	0.0126(6)	0.0027(14)	−0.0024(14)	0.0013(4)
Si2	0.35474(18)	0.2221(3)	0.6574(2)	0.0104(6)	Si <sub>1.00</sub>	4	0.0113(9)	0.0169(11)	0.0029(8)	−0.0026(5)	0.0016(5)	−0.0048(6)
Si3	0.35641(18)	0.2230(3)	0.1018(2)	0.0123(7)*	Si <sub>1.00</sub>	4						
Na1	¼	0.5357(7)	0.3255(9)	0.035(3)	Na <sub>0.41(6)</sub> H <sub>2</sub> O <sub>0.59(6)</sub>	2	0.038(4)	0.014(3)	0.054(6)	−0.006(2)	0.000	0.000
Na2	½	0.883(2)	0.0221(13)	0.0221(13)	Na <sub>0.78(4)</sub> H <sub>2</sub> O <sub>0.22(4)</sub>	2	0.0276(19)	0.0207(19)	0.0180(19)	0.000	0.000	−0.0027(13)
O1	0.3628(2)	0.1946(5)	0.8803(17)	0.0219(8)	O <sub>1.00</sub>	4	0.0285(18)	0.029(2)	0.0080(16)	0.007(4)	−0.007(4)	−0.0017(15)
O2	0.4199(5)	0.3770(10)	0.1767(11)	0.0195(18)	O <sub>1.00</sub>	4	0.020(4)	0.020(3)	0.018(4)	0.003(3)	−0.011(3)	0.003(3)
O3	0.4209(5)	0.3869(9)	0.5913(10)	0.0187(19)	O <sub>1.00</sub>	4	0.019(5)	0.017(3)	0.020(4)	0.005(3)	−0.002(3)	−0.014(2)
O4	¼	0.2683(17)	0.1619(17)	0.025(3)	O <sub>1.00</sub>	2	0.004(3)	0.059(6)	0.011(4)	−0.005(3)	0.000	0.000
O5	0.3821(8)	0.0297(11)	0.5605(16)	0.028(3)	O <sub>1.00</sub>	4	0.032(7)	0.030(5)	0.022(5)	−0.011(4)	0.010(4)	−0.006(4)
O6	0.3818(8)	0.0249(8)	0.1909(14)	0.019(2)	O <sub>1.00</sub>	4	0.033(7)	0.010(3)	0.014(5)	0.006(3)	0.004(3)	0.001(3)
O7	¼	0.2711(15)	0.6068(18)	0.025(3)*	O <sub>1.00</sub>	2						
O8	¼	0.8581(8)	0.381(2)	0.0286(15)	O <sub>1.00</sub>	2	0.011(2)	0.022(3)	0.053(4)	0.022(6)	0.000	0.000
O9	0.4129(2)	0.7201(4)	0.3745(17)	0.0206(8)	O <sub>1.00</sub>	4	0.0221(16)	0.0138(17)	0.026(2)	−0.004(4)	−0.003(5)	0.0079(13)
Ow1	0.4184(4)	0.7706(7)	0.890(2)	0.0448(14)	O <sub>1.00</sub>	4	0.052(3)	0.044(3)	0.039(4)	0.004(5)	0.007(5)	0.012(2)
Ow2	¼	0.6235(19)	0.762(2)	0.073(6)	O <sub>0.89(3)</sub>	2	0.052(8)	0.075(10)	0.091(11)	−0.040(8)	0.000	0.000

\**U*<sub>iso</sub>; Ow1 = H<sub>2</sub>O; Ow2 = H<sub>3</sub>O possibly with traces of H<sub>2</sub>O

**Table 4.** Selected interatomic distances (Å) in the structure of highly hydrated elpidite.

Zr–O9	2.054(3) ×2	Si3–O2	1.554(8)
Zr–O2	2.069(7) ×2	Si3–O1	1.597(13)
Zr–O3	2.074(7) ×2	Si3–O6	1.628(8)
<Zr–O>	2.066	Si3–O4	1.645(5)
		<Si3–O>	1.606
Si1–O9	1.576(3)		
Si1–O8	1.6211(16)	Na1–O4	2.281(13)
Si1–O6	1.625(11)	Na1–O8	2.396(9)
Si1–O5	1.632(12)	Na1–O9	2.756(5) ×2
<Si1–O>	1.614	Na1–O7	2.791(12)
		Na1–O2	2.937(8) ×2
Si2–O1	1.608(12)		
Si2–O7	1.611(5)	Na2–Ow1	2.314(5) ×2
Si2–O3	1.617(7)	Na2–O3	2.519(16) ×2
Si2–O5	1.620(9)	Na2–O2	2.565(17) ×2
<Si2–O>	1.614		

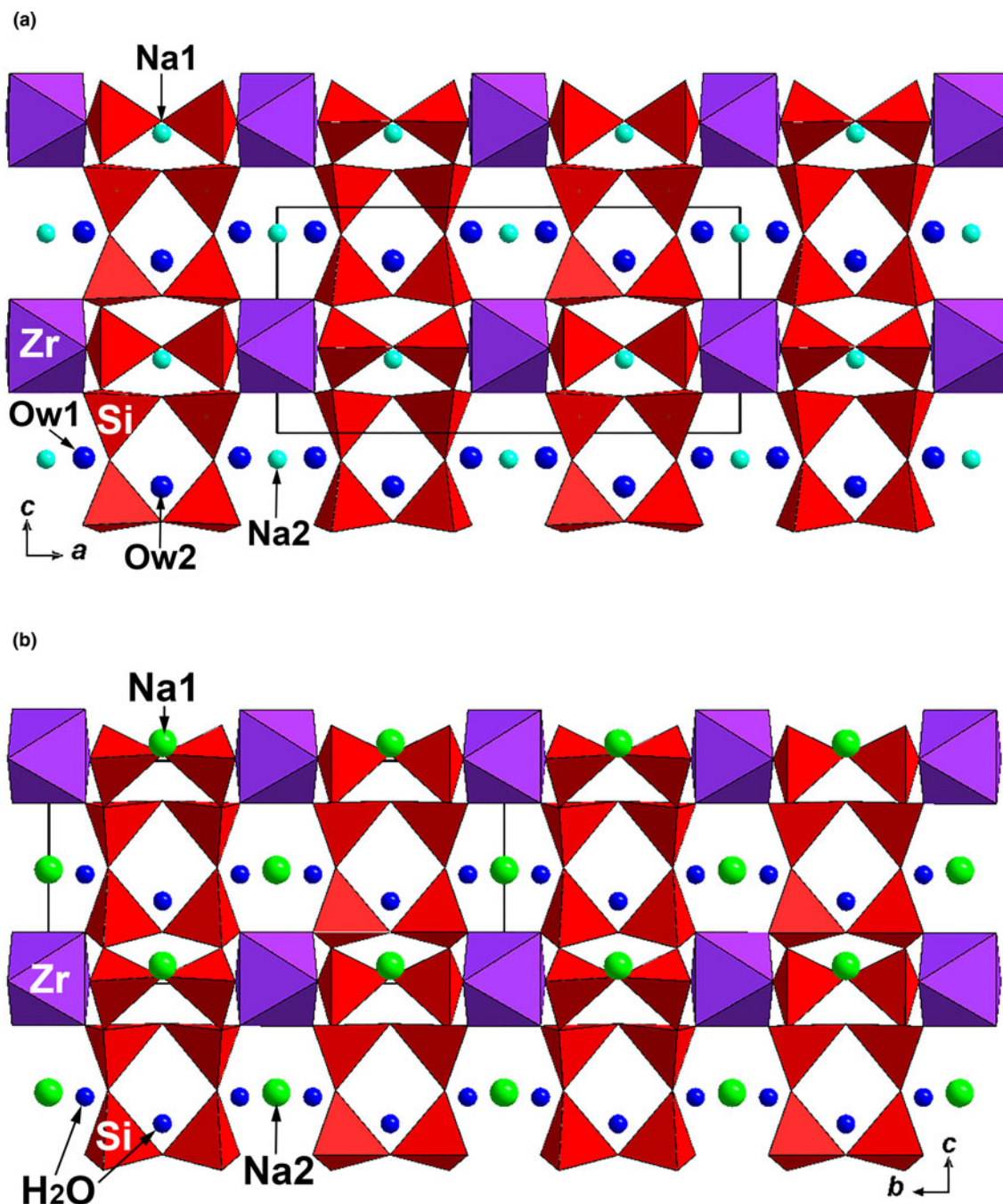
Table 4. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

The powder X-ray diffraction (PXRD) pattern of the sample studied (PXRD data were collected in an RKD camera with the diameter of 57.3 mm using Debye-Scherrer geometry, FeK $\alpha$  radiation) is typical for elpidite. The unit-cell parameters calculated from the PXRD data are: *a* = 14.553(5), *b* = 7.325(2), *c* = 7.135(2) Å and *V* = 760.6(7) Å<sup>3</sup>.

## Discussion

The crystal structure of the highly hydrated elpidite was refined in the space group *Pma*2 and thus with the 14–7–7 Å unit cell (in the standard setting; see Introduction). Although the refinement in centrosymmetric space group *Pmma* was successful [*R*<sub>1</sub> = 0.0412 for 1455 unique reflections with *I* > 2 $\sigma$ (*I*)], careful inspection of this refinement showed that the position of oxygen in the Ow2 site is split, and so is the Na1 site. The lowering of symmetry to *Pma*2 means splitting can be avoided: the O atom almost fully occupies one site (89%) and the Na1 site is not split and occupied fully by statistically substituting Na cations and H<sub>2</sub>O molecules.





**Fig. 2.** The crystal structure of highly hydrated elpidite projected along the *b* axis (a) and the crystal structure of elpidite drawn after Neronova and Belov (1964) in non-standard *Pbm2* space group (b). The unit cells are outlined.

The same symmetry lowering to *Pma2* was found for the elpidite sample studied by Neronova and Belov (1964), for Ca-enriched variety of elpidite (Sapozhnikov and Kashaev, 1978) and for elpidite from Lovozero reported by Zubkova *et al.* (2019) but in the latter only the Ow2 site was finally not split while the Na site was split.

In the structure of the highly hydrated elpidite (Fig. 2a), tetrahedral ribbons Si<sub>6</sub>O<sub>15</sub> are linked by isolated ZrO<sub>6</sub> octahedra to form the heteropolyhedral Zr–Si–O framework identical to that reported for all previously studied elpidite samples (Zubkova *et al.*, 2019). The most interesting feature of the sample studied

is the arrangement and the content of extra-framework sites. In all previously studied samples of elpidite with the same unit-cell metrics (14–7–7 Å) there are two crystallographically non-equivalent Na sites and two sites usually filled by O atoms representing H<sub>2</sub>O molecules. Sodium cations occur in the centre of octahedra and/or seven- and eight-fold polyhedra. Both Na sites in the Khibiny hydrated elpidite are occupied by Na statistically substituted by water molecules in the ratio Na<sub>0.41(6)</sub>H<sub>2</sub>O<sub>0.59(6)</sub> for the Na1 site and Na<sub>0.78(4)</sub>H<sub>2</sub>O<sub>0.22(4)</sub> for Na2 which occur in the centre of a seven-fold polyhedron and octahedron, respectively. The Ow1 site is fully occupied by H<sub>2</sub>O while the Ow2 site

contains an O atom with a site occupancy factor (s.o.f.) of 0.89 and this site is assumed to be filled dominantly by the hydronium cation  $\text{H}_3\text{O}^+$ . The calculated bond-valence sums range from 1.79 to 2.11 valence units for all O atoms forming the heteropolyhedral Zr–Si–O framework. This excludes the possibility that some of oxygen atoms in the framework are protonated to the charge balance in our Na-depleted sample. Thus, the placement of hydronium in the Ow2 site is the only available option to achieve charge balance. The environment of this site allows it to be filled by  $\text{H}_3\text{O}^+$ . The shortest distances from Ow2 to the nearest neighbours are all longer than 2.8 Å: 2.811(16) Å between the Ow2 and O7 sites (oxygen atom of the Zr–Si–O framework) and two distances of 2.834(11) Å between the Ow2 and Ow1 sites. The absence of Na1 site splitting in hydrated elpidite, which was reported for some other samples of elpidite, means avoiding a short distance between the Ow2 and Na. This splitting provides two possible sites for Na1 and it is worth noting that in the structure of elpidite reported by Neronova and Belov (1964) Na cations occupy another site compared with the structure of hydrated elpidite (Fig. 2a) reported here. In the structure reported by Neronova and Belov (1964), the  $\text{H}_2\text{O}$  site (marked as Ow2 and mainly filled with the O atom of  $\text{H}_3\text{O}^+$  in our sample) is included in the coordination sphere of Na1 site (Fig. 2b).

The highly hydrated variety of elpidite studied from Khibiny differs distinctly from 'ordinary' elpidite not only in crystal chemistry but also in its physical properties. Some distinctive features of this new variety of the mineral are: (1) the unusual character of its IR spectrum, especially in the area of vibrations of H-bearing groups (Fig. 1); (2) its lower density; (3) an uncommon, for elpidite, configuration of optical indicatrix: small difference between refractive indices  $\beta$  and  $\alpha$  ( $\sim 0.001$ ; Table 1); (4) very bright greenish-yellow fluorescence in UV light in contrast to 'ordinary' elpidite, which either does not fluoresces or, rarely, shows weak yellowish-white fluorescence.

The deficiency of Na and the presence of  $\text{H}_3\text{O}^+$  in the elpidite studied can be a sign that the mineral underwent ion exchange at the stage of hydrothermal alteration of the pegmatite. The first step of the natural ion exchange in sodium-bearing zeolites and hydrous zeolite-like silicates with heteropolyhedral frameworks is typically characterised by leaching of  $\text{Na}^+$  with partial replacement of  $\text{H}_2\text{O}$  by  $\text{H}_3\text{O}^+$ . Hydronium-rich forms of microporous silicates are in general less stable than those with extra-framework metal cations and can be easily replaced by the latter at further stages of ion exchange (Pekov *et al.*, 2008). In particular, this was reported for hydrous zeolite-like zirconosilicates of the hilairite group. The natural ion-exchange transformation of hilairite, ideally  $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ , to calciohilairite, ideally  $\text{CaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ , involves an intermediate stage, where a cation-deficient and hydronium-bearing form of the latter mineral is formed:  $2\text{Na}^+ + \text{H}_2\text{O} \rightarrow 0.5\text{Ca}^{2+} + 1.5\text{O} + \text{H}_3\text{O}^+$  (Pushcharovsky *et al.*, 2002; Pekov *et al.*, 2003). Two minerals closely related to elpidite in terms of crystal chemistry exist in nature, namely yusupovite ( $\text{Na, K, Cs}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$ ) (Agakhanov *et al.*, 2015) and armstrongite  $\text{CaZrSi}_6\text{O}_{15} \cdot 2\text{H}_2\text{O}$  (Kabalov *et al.*, 2000; Mesto *et al.*, 2014). For the latter Roelofsen and Veblen (1999) proposed the origin by natural ion-exchange reaction, which takes place in subsolidus alkaline-granite systems:  $\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O} + \text{Ca}^{2+} \rightarrow \text{CaZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O} + 2\text{Na}^+$ . Taking into account these data and the experimentally tested strong cation-exchange properties of elpidite (Turchkova *et al.*, 2006; Grigor'eva *et al.*, 2011; Zubkova *et al.*, 2019), we believe that elpidite can undergo ion exchange in Nature, under hydrothermal conditions. The Na-depleted and highly hydrated variety of the

mineral studied in the present work is interpreted here as an intermediate product of such natural ion-exchange reaction between 'ordinary' elpidite and a low-temperature hydrothermal fluid (solution). Taking into account the above-discussed experimental data and the presence of aluminosilicate zeolites including the wide-porous species chabazite (Pekov *et al.*, 2004) as overgrowths on our hydrated elpidite, we infer that the temperature of alteration did not exceed 150–200°C.

## Conclusions

A new highly hydrated and Na-depleted variety of elpidite was discovered in a hydrothermally altered peralkaline pegmatite at Mt. Yukspor in the Khibiny alkaline complex, Kola Peninsula, Russia. It differs from 'ordinary' elpidite in its crystal chemical features, IR spectrum, optical and fluorescent characteristics.

The highly hydrated elpidite studied is characterised by an undistorted heteropolyhedral Zr–Si–O elpidite-type framework with the 14–7–7 Å unit cell and space group *Pma*2. The choice of the acentric space group was determined by the possibility of avoiding splitting one of the Na sites and one O site representing the  $\text{H}_2\text{O}$  molecule. Both crystallographically non-equivalent Na sites are occupied by  $\text{Na}^+$  cations statistically substituted by  $\text{H}_2\text{O}$  molecules. In comparison with the two sites occupied by  $\text{H}_2\text{O}$  molecules in previously reported samples of 'ordinary' elpidite with the same unit-cell metrics, our additionally hydrated elpidite has one site fully occupied by  $\text{H}_2\text{O}$  while the other one is assumed to be dominantly filled by hydronium cations  $\text{H}_3\text{O}^+$ .

The deficiency of Na and the presence of  $\text{H}_3\text{O}^+$  in the variety of elpidite studied are interpreted to indicate that it underwent natural ion exchange at the stage of hydrothermal alteration of its host peralkaline pegmatite, and represents an intermediate product of natural ion-exchange reaction between 'ordinary' elpidite and a low-temperature (<150–200°C) hydrothermal fluid (solution).

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**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2020.96>

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