Dehydration and thermal stability of elpidite: an *in-situ* single crystal X-ray diffraction study

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Abstract

Elpidite $\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$ is a natural zirconosilicate with space group *Pbcm*. A sample from Mt. Saint Hilaire (Canada) was investigated between 25 and 350°C under different humidity conditions (RH = 0% and at RH = 100%). The largest structural channels are eight- and ten- rings delimited by corner-sharing SiO_4 tetrahedra and ZrO_6 octahedra.

Under dry conditions, the structure started liberating water at 75°C. At 100°C, when it lost one H_2O molecule, elpidite underwent a structural change from space group *Pbcm* to *Cmce*.

The structure continuously released water up to 225 °C until it became anhydrous. From 225°C to 350°C no structural changes were observed. Associated with the transition from *Pbcm* to *Cmce* symmetry, the unit-cell volume reduced by 2.7%. An additional decrease is observed up to 225°C when the contraction reached 3.4% of the starting volume. After release of all H_2O molecules, increase of temperature led to gradual expansion of the unit cell from 2940.79(7) Å³ at 225°C to 2947.4(5) Å³ at 350°C.

Supplementary *ex-situ* heating experiments showed that the structure was retained up to 950°C but after heating at 1200°C the sample melted.

Under humid conditions a similar dehydration-trend similar to that found under a dry N_2 -atmosphere was observed but the structural changes occurred at slightly higher temperatures. Immersion of a dehydrated sample in water for 30 days led to only marginal rehydration and the *Cmce* symmetry was preserved.

Keywords: elpidite, thermal stability, dehydration, X-ray diffraction

1. Introduction

Microporous zirconosilicates constitute an interesting class of materials owing to their potential applications such as catalysts, sorbents, and ion-exchangers [1,2,3,4]. They are usually referred as heteropolyhedral framework silicates with a “zeolite-like” structure made up of corner-shared SiO_4 tetrahedra and ZrO_6 octahedra.

Elpidite $\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$ is a natural zirconosilicate firstly reported by Lindström [5]. At room temperature the structure is described in *Pbcm* space group and consists of double sawtooth chains of SiO_4 tetrahedra parallel to [100] connected by ZrO_6 octahedra to a three-dimensional

framework [6,7]. The charge of this anionic framework is balanced by Na ions that occupy the zeolitic channels together with H₂O molecules.

The calculated framework density of elpidite is $FD = 18$ (SiO₄ tetrahedra and ZrO₆ octahedra) per 1000 Å³. Thus, extending the Brunner and Meier [8] diagram to heteropolyhedral frameworks, elpidite is classified as a “zeolite-like” material.

The largest structural windows are 10-membered rings of SiO₄ tetrahedra and ZrO₆ octahedra intersected by smaller six-ring bottle necks that subdivide the 10-rings into two puckered eight-membered rings (Fig. 1). According to this scheme, the maximum effective pore opening has dimension of approximately 4.64 x 4.41 Å. Thus, extraframework (EF) species may diffuse through the structural voids avoiding the narrow passages (3.40 Å) delimited by the six-membered rings.

Among zirconosilicates, elpidite received particular attention because of its pronounced cation-exchange properties [9]. The mineral exhibits high exchange capacity for K and Rb, accompanied by pronounced dehydration and structural modification, resulting in the doubling of the *a* parameter and change of symmetry from *Pbcm* (No. 57) to *Cmce* (No. 64) [10].

Elpidite can be completely dehydrated by a two-step calcination process at 240°C and at 300°C [11]. A detailed kinetics study of the dehydration process investigated by isothermal (110-254°C) and nonisothermal (20-600°C) thermogravimetry confirmed that during the first step (110-180°C) the elpidite sample rapidly loses 50-60 % of its water, whereas the second step is characterized by decrease of the activation energy [12]. The nature of this kinetic compensation was interpreted as a result of structural transformations accompanying the water release.

Elpidite under high-pressure conditions undergoes two different structural modifications [13]. The first transformation occurred at 1.2 GPa with the doubling of the *a* parameter similar to that observed during the dehydration experiments; however, the structure showed the different space group *Pbca*. Above 3.5 GPa, another phase transition was detected leading to the reduction of symmetry to the monoclinic space group *C2_{1/a}*.

Although many structural studies have been carried out on elpidite under non-ambient conditions, some points remain open: i) the structure of the partially-hydrated elpidite, ii) the rehydration behavior of the anhydrous structure and iii) the temperature at which the structure collapses. In order to answer these questions, we track the dehydration behavior of elpidite by performing some *in situ* single-crystal X-ray diffraction experiments. Moreover, we aim determining the hydrogen bond-system and the influence of the relative humidity on the dehydration process. Finally, the recovery of H₂O is monitored by rehydration experiments.

On the basis of our results we attempt to highlight the driving force of the *Pbcm*-*Cmce* transition. In addition, we search for a possible diffusion path of EF cations and H₂O within the elpidite structure in order to justify the pronounced exchange capacity of this mineral.

2. Experimental methods

2.1 Chemical analysis

The elpidite sample from Mt. St. Hilaire (Quebec, Canada) was kindly provided by the Natural History Museum of Bern (sample number B8404). The chemical composition was determined by EMPA (electron microprobe-analyses) in wavelength dispersive mode using a JEOL JXA-8230 instrument with following analytical conditions: excitation voltage 15KV, beam current 2nA, beam diameter 10 μm . The standards were: wollastonite (Si $K\alpha$ and Ca $K\alpha$), corundum (Al $K\alpha$), albite (Na $K\alpha$), rutile (Ti $K\alpha$), eskolaite (Cr $K\alpha$), $\text{Ca}_3(\text{VO}_4)_2$ (V $K\alpha$), hematite (Fe $K\alpha$), manganosite (Mn $K\alpha$), periclase (Mg $K\alpha$), K-feldspar (K $K\alpha$), $\text{SrBaNb}_4\text{O}_{12}$ (Sr $L\alpha$ and Ba $L\alpha$), NiO (Ni $K\alpha$), KTiOPO_4 (P $K\alpha$), fluorite (F $K\alpha$), halite (Cl $K\alpha$), $(\text{Zr},\text{Y})\text{O}_2$ (Zr $L\alpha$), and KTaO_3 (Ta $M\alpha$). The ZAF (atomic number -absorption - fluorescence) correction-method [14] was used for all elements.

2.2 Single crystal X-ray diffraction

A single crystal with approximately 100 x 300 x 500 μm dimensions was selected under an optical microscope and glued on the tip of a glass fiber mounted on a goniometer head. Single crystal X-ray diffraction data were collected on a Bruker APEXII diffractometer with a $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), equipped with a CCD area detector. The *in situ* dehydration process was investigated by means of a self-constructed temperature controlled hot-nitrogen blower (1.4 l/min), up to 350°C in steps of 25°C. The crystal was kept at each temperature for 40 minutes before starting the data collection, and each data collection required ca. 12 h. Under these experimental conditions the crystal was exposed to a dry N_2 atmosphere (RH = 0).

In order to collect temperature-dependent data under high humidity conditions (RH = 100%), another crystal belonging to the same sample was selected and a second set of *in-situ* experiments was performed using water-saturated nitrogen. The crystal was measured at 100, 225, 250, 275, and 300°C.

The data were integrated and an empirical absorption correction was applied using the Apex 2v. 2011.4-1 software package. Structures were solved by using Superflip [15].

Up to 75°C the structure was solved in the *Pbcm* space group [7,10,11]. Structural refinements were carried out by SHELXL-2013 [16], using neutral atomic scattering factors. We changed the labels of Si, O, and Na sites used in previous studies to allow a better comparison between the *Pbcm* and *Cmce* structure. Relabeling of the H_2O sites became necessary in order to make clear that the Ow2 site becomes empty above 100°C and the remaining water is distributed over two sites in special position, here labeled Ow1 and Ow11 in the *Cmce* data sets. These Ow1 and Ow11 sites correspond to Ow1 in space group *Pbcm*.

At room temperature and at 50°C the hydrogen positions were extracted from difference-Fourier maps. Restraints on bond distances $\text{H-O} = 0.97(2) \text{ \AA}$ were applied and the H positions were refined with fixed isotropic displacement parameters ($U = 0.05 \text{ \AA}^2$). Structural data obtained above

100°C up to 350°C were solved in space group *Cmce* [11]. At 250°C the Na1 site showed positional disorder and was split in three sites refined by imposing equivalent displacement parameters.

The 100°C data set obtained under high humidity conditions was affected by a structural transformation from space group *Pbcm* to *Cmce* occurring during data collection. The unit cell obtained at the beginning of the measurement indicated a *P* lattice whereas the final runs of the data set could be solved and refined in the *Cmce* space group.

A corresponding time dependent transformation, though less pronounced, also occurred in the 100°C data set measured under dry conditions as indicated by the higher R_{int} value compared to the other sets (Table 1).

An additional crystal was selected and heated up to 1200°C in order to evaluate the temperature at which the structural collapse occurred. The crystal was analyzed *ex-situ* after it was kept for 1 hour at the following temperatures: 450, 650, 850, 950, 1200°C.

Moreover, the rehydration of elpidite was investigated. The crystal used in the series of dry experiments was removed from the diffractometer, immersed in water (25°C) and measured after 15 and 30 days.

Data collections parameters and refinements for the different sets of experiments are reported in Table 1. Bond valence calculations were performed using the parameters by Breese and O’Keeffe [17] and Ferraris and Ivaldi [18].

3. Results and discussion

The measured chemical composition of Mt. St. Hilaire elpidite (Table 2) $\text{Na}_{1.96}\text{ZrSi}_{5.97}\text{O}_{15} \cdot 3\text{H}_2\text{O}$ is in agreement with previous reference data from the same locality [19].

Structural data, bond distances and angles, and bond-valence analysis of the elpidite structure under ambient conditions are reported in Table S1, S2, and S10. The hydrogen bond system determined at room temperature and at 50°C is shown in Table 3. Table S3 and S4 reported atomic parameters and bond distances and angles of elpidite structures at 100°C. Corresponding data of structures obtained at 175 and 250°C are shown in Table S5-S7. Structural data obtained at 225°C (RH = 100%) are reported in Table S8 and those of partially rehydrated elpidite in Table S9. Table 4 reports the dehydration degree of elpidite as obtained in our study compared with that observed by reference data [12]. Tables S11 and S12 show the bond-valence sums of the elpidite structure at 100 and 250°C.

CIF files have been submitted as supplementary material.

3.1 Structure at room temperature

The crystal structure of elpidite under ambient conditions ($T = 25^\circ\text{C}$ and $\text{RH} = 35\%$) was in agreement with previous studies [7,11]. The heteropolyhedral framework is built of double $[\text{SiO}_4]$

chains parallel to [100] linked by [ZrO₆] octahedra (Fig. 2a-b). The resulting channels are occupied by two symmetry independent Na sites (Na1 and Na2) and by H₂O at Ow1 and Ow2 sites (Table S1). The Na1 site links to four framework oxygen-atoms and two Ow1 sites, forming octahedra stacked along [100]. Na2 is coordinated by eight O, seven contact distances to framework O and the shortest one (2.349 Å) to H₂O at Ow2. The distances range from 2.349(2) to 2.9076(10) Å (Table S2).

Our experimental data allowed refinement of hydrogen positions and evaluation of the hydrogen-bond system. The oxygen at Ow2 resides on the mirror plane perpendicular to [001]. As a consequence it forms a bond to H2 at (x, y, z) and to the symmetry equivalent site at (x, y, -z+1/2). The hydrogen bonds (Table 3) are fairly strong with H $\cdots$ O acceptor distances between 2.03 and 2.15 Å and donor-acceptor distances O $\cdots$ O between 2.84 and 2.92 Å. The Ow1 site is linked to the framework by two hydrogen interactions Ow1-H1A $\cdots$ O7 and Ow1-H1B $\cdots$ O4 and acts as acceptor in the interaction Ow2-H2 $\cdots$ Ow1, responsible for the interconnection between the H₂O molecules inside the channels. The O-H stretching region in the IR spectrum of elpidite [11] is characterized by a triplet at 3435, 3490, and 3540 cm⁻¹. According to the hydrogen-bond-length versus IR frequency correlation [20] absorption between 3450 and 3550 cm⁻¹ corresponds to H $\cdots$ O distances of ca. 1.9 - 2.10 Å, which agrees with distances reported in Table 3.

3.2 Dehydration behavior under RH = 0

The dehydration of the elpidite structure began at 75°C as demonstrated by the occupancy of Ow1 and Ow2 sites that decreased from full occupancy to 0.978(8) and 0.953(5), respectively. Up to this temperature the structure remained essentially unchanged, slightly increasing the unit cell volume from 1524.84(4) Å³ at RT to 1525.19(4) Å³ at 50°C.

At 100°C, when the structure lost one H₂O molecule (Ow2), elpidite underwent a structural change from space group *Pbcm* to *Cmce*. This transformation is accompanied by doubling of the *a* parameter from 7.1134(4) Å at RT to 14.1260(5) Å at 100°C. The *C*-centered structure corresponds to that reported by Grigor'eva et al. [10] for Rb- and K-exchanged elpidite. The framework topology is maintained, but the framework polyhedra are tilted from their original orientations (Fig. 3a-b). The unit-cell volume dropped to 2966.10(18) Å³ corresponding to ca. 3%, taking the doubled volume at 50°C as reference. In this partially dehydrated structure the Na2 site is bonded only to framework oxygen atoms, whereas Na1 is coordinated by framework oxygen as well as Ow1 and Ow11 (Table S3, S4). At this step, the H₂O sites are affected by strong anisotropic displacement parameters (*U*^{eq} Ow1 = 0.086(2) Å² and *U*^{eq} Ow2 = 0.127(4) Å²).

This partially hydrated intermediate phase agrees with the one obtained in argon at 155°C for 2 hours, for which Zubkova et al. [11] presented IR spectra with H₂O characteristic bands at 1605, 1640, and 3600 cm⁻¹.

At 175°C the H₂O at the Ow1 site displayed positional disorder and was split in Ow1 and Ow1a subsites, 0.57(4) Å apart. In contrast, the Ow11 site appeared smeared and thus probably

dynamically disordered as demonstrated by the ADP values (Table S5). The occupancy of the H₂O sites continued decreasing up to 225 °C, at which the structure became anhydrous. The loss of the remaining water is accompanied by reduction of the unit-cell volume to 2940.79(6) Å³.

At 250°C the Na1 site was split in three sites Na1, Na1a, and Na1b in order to model the strong disorder (Table S6). The distances between these subsites were in the range of 0.306(19)-0.818(8) Å. The disorder was suggested by inspection of the calculated electron density corresponding to Na1 sub-sites. As reported in Fig. 4a the electron density is rather featureless as characteristic for Na if randomly distributed over a large volume. Furthermore, Na1 occupies the center of a distorted six-membered ring of four SiO₄ tetrahedra and two ZrO₆ octahedra and bonds laterally to five O of the ring with no additional bonds perpendicular to the ring. Thus Na1 is allowed to strongly vibrate through the ring (Fig.4b). From 225°C to 350°C no structural modifications were observed and the unit-cell volume slightly expanded up to 2947.40(5) Å³.

The variation of the unit-cell volume upon heating (Fig. 5) was characterized by a sharp drop occurring at 100°C accompanied by the transition from *Pbcm* to *Cmce*. The decreasing trend was maintained up to 225°C when the contraction reached 3.4% of the starting volume. In contrast, after the release of all H₂O molecules, increase of temperature led to gradual expansion of the unit cell (Fig. 5).

Elpidite crystals heated to 950°C remained crystalline but when fired at 1200°C melting occurred.

3.3 Dehydration under RH = 100%

Under humid conditions a similar dehydration-trend as observed under dry N₂-atmosphere was analyzed. Our data at 100°C showed that the transformation from the primitive cell to the C-centered one was only slightly shifted toward higher temperatures. At 225°C the structure still contained a small amount of water at Ow1 and Ow11 sites (sof = 0.113(11) and 0.112(3) respectively). At this temperature the Na1 site already displayed strong disorder and we modeled it by applying the same strategy used for the data collected at 250°C under dry conditions (Table S8).

The structure became anhydrous at 250°C and at higher temperatures no significant differences were observed relative to the previous experimental set-up.

3.4 Rehydration

Data collected on elpidite after 15 and 30 days immersion in water indicated that the rehydration process is extremely slow. After 15 days the structure marginally rehydrated with Ow1 and Ow11 occupancies of 0.124(10) and 0.076(12), respectively. After 30 days the corresponding values slightly increased to 0.190(9) and 0.138(11) (Table S9). Most important, the structure preserved the *Cmce* symmetry with the doubled *a* parameter, suggesting that the activation energy at room temperature is not sufficient to induce the inverse transition to the *Pbcm* symmetry.

3.5 Driving force for the *P-C* transition

The framework modification occurring after the loss of one H₂O molecule (Ow2) is interpreted as a rotation of rigid framework units (i.e. ZrO₆ octahedra and SiO₄ tetrahedra) and not a distortion in terms of strain or compression. Indeed, the *Cmce* phase has favorable T-O-T angles and at high temperatures the ZrO₆ units were still regular octahedra (Table S4). The modification accompanying the *P - C* transformation mainly involves the T-O-T angles. Comparing the corresponding T-O-T angles at RT and at 100°C (Fig. 6) the variation mostly affects the Si3-O1-Si2 angle that bends from 163.01(13)° at RT to 146.6(3)° (Si3-O1-Si3) and 156.0(3)° (Si2-O8-Si2) at 100°C. The angles Si3-O1-Si3 and Si2-O8-Si2 in space group *Cmce* are topological equivalent to Si3-O1-Si2 in space group *Pbcm* at RT (Fig. 6).

Such modifications are initiated by the rearrangement of the Na2 bonds after the partial dehydration of the structure. As already mentioned, at room temperature Na2 is coordinated by Ow2 at 2.349(2) Å and framework oxygen belonging to the six-ring. The longest bond-distances are those formed with the oxygen of ZrO₆, that is Na2-O6 at 2.7342(10) Å and Na2-O9 at 2.9076(10) Å. When the H₂O at Ow2 is expelled, these distances (Na2-O3 and Na2-O6 at 100°C) shorten to 2.5535(18) and 2.7756(20) Å, causing the rotation of the ZrO₆ octahedra and as a consequence the attached SiO₄ tetrahedra are also affected. The bond-valence sums of fully hydrated elpidite (Table S10) indicated that the Na2 site is well balanced with 0.962 v.u. (valence units); the release of Ow2 and retaining *Pbcm* symmetry would lead to the unfavorable situation of only 0.73 v.u. This is prevented by modification of the structure in space group *Cmce* , in which Na atoms become electrostatically well balanced (Table S11). In the partially hydrated structure, the remaining H₂O at Ow1 and Ow11 bond to the Na1 site. The complete dehydration of the structure reduces the bond-valence sum at Na1 to ca. 0.79 v.u. (Table S12). This value is obtained by the shortening of Na1-O8 and Na1-O9 distances from 2.3750(20) and 2.533(3) at 100°C to 2.328(12) and 2.465(20) at 250°C whereas the Na-O3 distance remains almost unvaried (Table S4, S7).

3.6 Diffusion path within the elpidite structure

Diffusion within the elpidite structure proceeds via a zigzag track along the *c* axis (Fig. 7). EF occupants access to the adjacent channels by passing through the eight-membered rings (Fig. 1) that at room temperature have an aperture of ca. 4.64 x 4.41 Å. Increasing temperature and subsequent transformation to *Cmce* leads to necking of the channels. In the *Cmce* structure the eight-membered rings are no longer symmetry equivalent as for *Pbcm* . The rotation of the ZrO₆ octahedra gives rise to two systems of channels characterized by more compressed elliptical shape (3.43 x 5.48 Å and 3.70 x 5.28 Å). Thus, the dehydration process can be described as a fast loss of the first H₂O molecule situated at Ow2 site (space group *Pbcm*). Subsequently, further dehydration is slowed down [12] by the decrease of the channel dimension (space group *Cmce*). The narrowing of the structural windows

remains preserved after complete dehydration. For this reason the rehydration of elpidite is also very slow compared to that normally reported for natural zeolites.

In general, our findings are in agreement with the structural modifications reported in previous studies [10,11].

The main difference concerns the lower transformation temperatures recorded in our study compared to Zubkova et al. [11] and Nedel'ko et al. [12]. In our experiment the dehydration started at 75°C and at 100°C the mineral lost approximately 40% of its total water content. The thermogravimetric curve [12] indicated the onset of dehydration at 130°C and only at 190°C the structure released 50% of the water. Under isothermal conditions elpidite converted already at 110°C to a partially dehydrated structure [12] although the structure retained 75% of its original water content. The isothermal curves collected in the temperature range 110-180°C [12] can be easily compared to our data. The curves represent the degree of dehydration as a function of time (from 0 to 10 hours) at 110, 123, 140, 155, and 180°C. In our experimental set-up the crystal was kept at the measured temperature for ca. 12 hours, the necessary time for completion of data collection, similarly to isothermal conditions (10 h) applied by Nedel'ko et al. [12]. Nevertheless, the degree of dehydration observed in our experiments is considerably higher compared to the results of Nedel'ko et al. [12] at the corresponding temperatures (Table 4). The reason for the difference is not obvious because the two elpidite samples have similar chemical composition and, most important, the dry-environment used for the experiments was analogous. One possible explanation could be related to the average particle size (0.05 x 1.0 mm) of the sample used for thermal analysis [12] compared to our single crystal (0.03 x 0.01 x 0.05 mm). Further, the elpidite sample investigated by Nedel'ko et al [12] originates from Lovozero, Kola Peninsula, Russia that differs from the Mt. St. Hilaire occurrence because of imperfect and twinned crystals [6,7]. Our suggestion is that such twinning could cause an offset of the channels entrances leading to different dehydration kinetics.

References

- [1] D. M. Poojary, A. I. Bortun, L. N. Bortun, A. Clearfield, *Inorg. Chem.* 36 (1997) 3072-3079.
- [2] A. I. Bortun, L. N. Bortun, A. Clearfield, *Chem. Mater.* 9 (1997) 1854-1864.
- [3] C.B. Lopes, J.Coimbra, M. Otero, E. Pereira, A. C. Duarte, *Quim. Nova* 31 (2) (2008) 321-325.
- [4] Y. Kuwahara, D. Kang, J. R. Copeland, N. A. Brunelli, S. A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, C. W. Jones, *J. Am. Chem. Soc.* 134 (2012) 10757-10760.
- [5] G. Lindström, *Geologiska Föreningens i Stockholm Förhandlingar* 16 (1894) 330-335.
- [6] N. N. Neronova, N. V. Belov, *Sov. Phys. Crystallogr.* 9 (6) (1965) 700-705.
- [7] E. Cannillo, G. Rossi, L. Ungaretti, *Am. Miner.* 58 (1973) 106-109.
- [8] G. Brunner, W. Meier, *Nature* 337 (1989) 146-147.

- 294 [9] A. G. Turchova, I. V. Pekov, I. A. Bryzgalov, 19th General Meeting of IMA, Kobe, 2006, p. 280.
- 295 [10] A. A. Grigor'eva, N. V. Zubkova, I. V. Pekov, U. Kolitsch, D. Yu Pushcharovsky, M. F.
- 296 Vigasina, G. Giester, T. Dordevic, E. Tillmanns, N. V. Chukanov, *Crystallog. Rep.* 56 (5) (2011) 832-
- 297 841.
- 298 [11] N. V. Zubkova, D. A. Ksenofontov, Yu K. Kabalov, N. V. Chukanov, V. V. Nedel'ko, I. V.
- 299 Pekov, D. Yu Pushcharovsky, *Inorg. Mater.* 47 (5) (2011) 506-512.
- 300 [12] V. V. Nedel'ko, N. V. Chukanov, I. V. Pekov, *Inorg. Mater.* 47 (5) (2011) 502-505.
- 301 [13] Yu V. Seryotkin, V. V. Bakakin, I. V. Pekov, *J. Struct. Chem.* 55 (7) (2014) 1252-1259.
- 302 [14] J. L. Pouchou, F. Pichoir, *Microbeam Analysis 1988*, Newbury D. ed., San Francisco Press 1988.
- 303 [15] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* 40 (2007) 786-790.
- 304 [16] G. M. Sheldrick, *Acta Cryst. A* 64 (2008), 112-122.
- 305 [17] N.E. Breese and M. O'Keeffe, *Acta Cryst. B* 47 (1991) 192–197.
- 306 [18] G. Ferraris and G. Ivaldi, *Acta Cryst. B* 44 (1988) 341-344.
- 307 [19] J. A. Mandarino, V. Anderson, *Monteregian Trasures: The Minerals of Mont Saint-Hilaire,*
- 308 *Quebec*, Cambridge University Press 1989.
- 309 [20] E. Libowitzky, *Monatsh. Chem.* 130 (1999) 1047–1059.

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Table 1. Crystal data and refinement parameters for elpidite at room temperature (RT), 50°C (RH = 0), 100°C (RH = 0), 250°C (RH = 0), and rehydrated structure after 30 days (RH = 100%).

Crystal data	Elpidite RT	Elpidite 50°C	Elpidite 100°C	Elpidite 250°C	Rehydrated Elpdite 30 d	Elpidite 225°C RH = 100%
<i>a</i> -axis	7.11340(10)	7.11430(10)	14.1260(5)	14.1271(4)	14.0906(4)	14.1244(3)
<i>b</i> -axis	14.6796(2)	14.6792(2)	14.5734(5)	14.5110(4)	14.5128(5)	14.5173(2)
<i>c</i> -axis	14.6030(2)	14.6046(2)	14.3627(5)	14.3533(4)	14.3471(4)	14.3535(2)
Cell volume (Å ³)	1524.87(4)	1525.19(4)	2956.76(18)	2942.40(14)	2933.90(15)	2943.16(9)
Z	4	4	8	8	8	8
Space Group	<i>Pbcm</i>	<i>Pbcm</i>	<i>Cmce</i> *	<i>Cmce</i> *	<i>Cmce</i> *	<i>Cmce</i> *
Chemical formula	Na ₂ ZrSi ₆ O ₁₅ ·3H ₂ O	Na ₂ ZrSi ₆ O ₁₅ ·3H ₂ O	Na ₂ ZrSi ₆ O ₁₅ ·1.8H ₂ O	Na ₂ ZrSi ₆ O ₁₅	Na ₂ ZrSi ₆ O ₁₅ ·0.32H ₂ O	Na ₂ ZrSi ₆ O ₁₅ ·0.23H ₂ O
Intensity measurement						
Diffractionmeter	APEX II SMART					
X-ray radiation	MoK α λ =0.71073 Å					
X-ray power	50 kV, 30 mA					
Monochromator	Graphite					
Temperature	25°C	50°C	100°C	250°C	25°C	225°C
Time per frame	10s	10s	10s	10s	10s	10s
Max. 2 θ	72.64	72.63	72.63	72.64	72.61	66.12
Completeness of data	99.9%	99.9%	99.8%	99.8%	100%	99.2%
Index ranges	-11 ≤ <i>h</i> ≤ 11	-11 ≤ <i>h</i> ≤ 11	-22 ≤ <i>h</i> ≤ 23	-23 ≤ <i>h</i> ≤ 22	-23 ≤ <i>h</i> ≤ 23	-21 ≤ <i>h</i> ≤ 20
	-24 ≤ <i>k</i> ≤ 21	-24 ≤ <i>k</i> ≤ 21	-21 ≤ <i>k</i> ≤ 24	-24 ≤ <i>k</i> ≤ 21	-23 ≤ <i>k</i> ≤ 24	-22 ≤ <i>k</i> ≤ 22
	-23 ≤ <i>l</i> ≤ 24	-23 ≤ <i>l</i> ≤ 24	-23 ≤ <i>l</i> ≤ 23	-23 ≤ <i>l</i> ≤ 23	-23 ≤ <i>l</i> ≤ 23	-21 ≤ <i>l</i> ≤ 22
No. of measured reflections	62322	62505	44910	53211		36982
No. of unique reflections	3807	3808	3690	3667	3666	2866
No. of observed reflections <i>I</i> > 2 σ (<i>I</i>)	3024	3001	2980	3037	3187	2195
Structure refinement						
No. of parameters used in the refinement	140 + 3 restraints	140 + 3 restraints	130	122	127	128
<i>R</i> (int)	0.0329	0.0331	0.0733	0.0406	0.0373	0.0747
<i>R</i> (σ)	0.0147	0.0148	0.0402	0.0178	0.0163	0.0298
GooF	1.048	1.073	1.092	1.067	1.060	1.059
<i>R</i> 1, <i>I</i> > 2 σ (<i>I</i>)	0.0213	0.0217	0.0382	0.0232	0.0219	0.0303
<i>R</i> 1, all data	0.0316	0.0331	0.0499	0.0323	0.0282	0.0491
w <i>R</i> 2 (on <i>F</i> ²)	0.0599	0.0659	0.1087	0.0621	0.0572	0.0761
$\Delta\rho_{min}$ (-eÅ ⁻³) close to	-0.60 Na2	-0.84 Na2	-0.82 Si3	-0.69 Na1b	-0.86 Na1	-0.77 Na2
$\Delta\rho_{max}$ (eÅ ⁻³) close to	0.54 O8	0.61 O8	1.43 Si3	0.86 Na1b	0.61 Na1	0.60 O7

*Transformation matrix from *Pbcm* to *Cmce*: [200 010 001]

Table 2. Results of quantitative chemical analyses of elpidite as obtained from EMPA.

Mean values from 16 analytical points			
	wt. %		<i>a.p.f.u.*</i>
SiO ₂	58.45(53)	Si	5.97(1)
TiO ₂	0.13(10)	Ti	0.01(1)
Al ₂ O ₃	0.04(6)	Al	0.01(1)
Cr ₂ O ₃	0.06(8)	Cr	0.00(1)
V ₂ O ₃	0.03(5)	V	0.00
Fe ₂ O ₃	0.08(9)	Fe	0.01(1)
MnO	0.06(6)	Mn	0.01(1)
MgO	0.01(1)	Mg	0.00
CaO	0.01(1)	Ca	0.00
SrO	0.03(4)	Sr	0.00
BaO	0.18(23)	Ba	0.01(1)
Na ₂ O	9.92(11)	Na	1.96(2)
K ₂ O	0.02(3)	K	0.00
NiO	0.03(6)	Ni	0.00
P ₂ O ₅	0.01(3)	P	0.00
ZrO ₂	20.01(38)	Zr	1.00(2)
Nb ₂ O ₅	0.24(19)	Nb	0.01(1)
F	0.04(7)	F	0.01(2)
Cl	0.01(2)	Cl	0.00
Total	89.38		8.99

*atoms per formula unit calculated on the basis of 15 O

Table 3 Hydrogen bond system of elpidite at room temperature and at 50°C. Bond distances (Å), O-H...O, O-H-O and H-O-H angles (°) are reported.

Hydrogen bond	D-H	H...A	D...A	< (DHA)	<(HOH)
RT					
Ow1-H1A....O7	0.912(16)	2.031(3)	2.9183(15)	163.9(8)	105.2(8)
Ow1-H1B....O4	0.898(16)	2.140(3)	3.0040(15)	161.1(8)	
Ow2-H2....Ow1	0.914(14)	1.956(19)	2.8380(17)	159.5(8)	104.4(8)
50°C					
Ow1-H1A....O7	0.930(16)	2.008(3)	2.9185(14)	166.5(8)	107.6(8)
Ow1-H1B....O4	0.900(16)	2.138(3)	3.0068(15)	161.9(8)	
Ow2-H2....Ow1	0.928(15)	1.956(19)	2.8376(18)	158.1(8)	102.0(7)
Symmetry codes:					
O7 = -x, y-1/2, z					
O4 = -x+1, y-1/2, z					
Ow1 = x, y, -z+3/2					

Table 4 Dehydration degree of elpidite at different temperatures as reported in Nedel'ko et al. (2011) [12] compared to our findings.

Nedel'ko et al. (2011) [12]					
T (°)	110	125	140	155	180
Degree of dehydration ¹	28%	35%	48%	55%	60%
This study					
T (°)	100	125		150	175
Degree of dehydration	40%	50%		70%	84%

¹Maximum degree of dehydration

Figure 1

RT *Pbcm*

a)

b)

100°C *Cmce*

a)

b)

250°C *Cmce*

Figures Caption

Figure 1 System of n -membered rings in elpidite structure at room temperature (space group $Pbcm$) emphasizing the interconnection of six- and eight-membered rings. The blue and yellow polyhedra represent SiO_4 tetrahedra belonging to the lower and upper 8-rings, respectively. Such rings are not symmetry equivalent in the $Cmce$ structure. ZrO_6 octahedra are depicted in green. Channel dimension are reported in Å.

Figure 2 Elpidite structure at room temperature. The polyhedra are presented by blue SiO_4 tetrahedra and green ZrO_6 octahedra. Na atoms are depicted in yellow (Na1 site) and in dark yellow (Na2 site). Oxygen of H_2O molecules are shown in red (Ow1 site) and in dark red (Ow2 site) with corresponding hydrogen atoms reported as small grey spheres. Hydrogen-bond interactions are reported as grey dotted lines. (a) Projection along the c -axis showing the cavities containing Na1 sites and (b) projection along the a -axis highlighting the other system of channels hosting the Na2 sites.

Figure 3 Elpidite structure at 100°C in space group $Cmce$. The occupancy of H_2O molecules is shown by partially colored sites; atom colors as reported in Fig.1.

Figure 4 Crystal structure of elpidite at 250°C. (a) The calculated electron-density of Na1, Na1a, and Na1b sites is displayed. Orange isosurfaces correspond to electron density $< 0.9 \text{ e}/\text{\AA}^3$. Atoms colors as reported in Fig.1. (b) Na1 coordination within the six-rings cavity.

Figure 5 Temperature dependence of unit-cell volume of elpidite. Volume data (light and dark blue) of the partly rehydrated structures after 15 and 30 days are also reported. The trend for experiments under high humidity conditions ($\text{RH} = 100\%$) at 225, 250, 275, and 300°C is shown by red dots.

Figure 6 SiO_4 chains in elpidite structure at room temperature and at 100°C. Red arrows represent lattice translation along $[100]$, green symbols indicate mirror planes parallel to (001) in $Pbcm$ space group and (100) in $Cmce$.

Figure 7 Diffusion path (black arrow) within the elpidite structure. Interconnection of ten-membered rings with six-membered rings (a). Detail of ten-membered rings units stacked along c -axis (b).