

Zvyaginite, $\text{NaZnNb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}(\text{OH},\text{F})_3(\text{H}_2\text{O})_{4+x}$ ($x < 1$), a New Mineral of the Epistolite Group from the Lovozero Alkaline Pluton, Kola Peninsula, Russia¹

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Abstract—A new mineral, zvyaginite, a member of the epistolite group, has been found at Mt. Malyi Punkaruaiv, Lovozero Alkaline Complex, Kola Peninsula, Russia. It occurs in a hydrothermally altered peralkaline pegmatite and is associated with ussingite, microcline, aegirine, sphalerite, vigrishinite, and saucornite. Zvyaginite forms rectangular or irregular-shaped lamellae up to $0.1 \times 1 \times 2$ cm in size when flattened [001]. The mineral is translucent to transparent and colorless, pearly-white, yellowish brownish, pale pink, or violet pink. The luster is nacreous on crystal faces and greasy on broken surfaces. Its Mohs' hardness is 2.5–3. Zvyaginite is brittle. The cleavage parallel to {001} is perfect. $D_{\text{meas}} = 2.88(3)$, $D_{\text{calc}} = 2.94 \text{ g/cm}^3$. The mineral is optically biaxial (–), $\alpha = 1.626(5)$, $\beta = 1.714(3)$, $\gamma = 1.740(5)$, $2V_{\text{meas}} = 45(15)^\circ$, $2V_{\text{calc}} = 55^\circ$. The IR spectrum is given. Chemical composition is as follows (wt %; average of five point analyses; H_2O was determined using the modified Penfield method): 4.74 Na_2O , 0.22 K_2O , 0.77 CaO , 1.36 MnO , 0.24 FeO , 9.61 ZnO , 0.19 Al_2O_3 , 29.42 SiO_2 , 12.33 TiO_2 , 27.22 Nb_2O_5 , 1.94 F , 12.65 H_2O , $-0.82 - \text{O} = \text{F}_2$, for a total of 99.87. The empirical formula calculated on the basis of $\text{Si} + \text{Al} = 4$ is: $\text{Na}_{1.24}\text{K}_{0.04}\text{Ca}_{0.11}\text{Mn}_{0.16}\text{Fe}_{0.03}\text{Zn}_{0.96}\text{Nb}_{1.66}\text{Ti}_{1.25}(\text{Si}_{3.97}\text{Al}_{0.03})_{\Sigma 4}\text{O}_{15.07}(\text{OH})_{2.10}\text{F}_{0.83}(\text{H}_2\text{O})_{4.64}$. The simplified formula is: $\text{NaZnNb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}(\text{OH},\text{F})_3(\text{H}_2\text{O})_{4+x}$ ($x < 1$). Zvyaginite is triclinic, $P\bar{1}$, $a = 8.975(3)$, $b = 8.979(3)$, $c = 12.135(4) \text{ \AA}$, $\alpha = 74.328(9)^\circ$, $\beta = 80.651(8)^\circ$, $\gamma = 73.959(8)^\circ$, $V = 900.8(6) \text{ \AA}^3$, $Z = 2$. The strongest reflections in the X-ray powder pattern (d , Å – $|hkl|$) are: 11.72–100[001], 5.83–40[002], 5.28–53[–1–11, 112], 4.289–86[200, 021], 3.896–36[–1–12, –201, 003, 022, 113], 2.916–57[310, 132, 004], 2.862–72[130, 312]. The model of the crystal structure was obtained on a single crystal, $R = 0.159$. Zvyaginite and epistolite are similar in the structure of the NbTiSiO motif, but differ from each other in composition of O layer in HOH block. Zvyaginite is named in honor of Boris B. Zvyagin (1921–2002), Russian crystallographer, crystal chemist and physicist. The type specimen is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

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INTRODUCTION

A specimen with a mineral visually not distinguished from the brownish pink variety of abundant layered titanosilicate murmanite, $\text{Na}_4\text{Ti}_4\text{Si}_4\text{O}_{14}(\text{OH})_4\text{O}_2(\text{H}_2\text{O})_2$ was found in 2009 while studying peralkaline pegmatite no. 71 (according to Semenov's (1972) numeration) at Mt. Malyi Punkaruaiv in the southeastern part of the Lovozero alkaline pluton, Kola Peninsula, Rus-

sia. Laboratory investigation revealed that this mineral is indeed cognate to murmanite in crystallographic parameters, but strongly depleted in Na (no higher than 1.6 wt % Na_2O) and strongly enriched in Zn up to 15.8 wt % ZnO . No significant amount of Zn had been reported at that time in the composition of known heterophyllosilicates of the bafertsite polysomatic series, to which murmanite belongs (Ferraris and Gula, 2005); therefore this mineral attracted interest and was examined in detail. It turned out to be a new mineral species and was described as vigrishinite with the simplified formula $\text{Zn}_2\text{Ti}_{4-x}\text{Si}_4\text{O}_{14}(\text{OH},\text{H}_2\text{O},\square)_8$. In its structure, Zn atoms occupy sites similar to those occupied by Na atoms and H_2O molecules in murmanite. We drew attention to the fact that in the holotype sam-

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¹ A new mineral, zvyaginite, and its name, considered by the Commission on New Minerals and Mineral Names, Russian Mineralogical Society and approved by the Commission on New Minerals, Nomenclature, and Classification of Minerals International Mineralogical Association, October 2, 2013, IMA no. 2013-071.

ple vigrishinite occurs in immediate contact with cavities of leached sphalerite and suggested that it could be a product of a natural ion exchange, i.e., the substitution of Na in murmanite by Zn mobilized from dissolved sphalerite under late hydrothermal or supergene conditions (Pekov et al., 2012). To verify this suggestion, in the summer of 2012 we gathered a representative collection of 52 specimens with minerals megascopically appearing similar to murmanite or the related epistolite $\text{Na}_4\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_2(\text{OH},\text{F})_2(\text{H}_2\text{O})_4$, which is also abundant here (Semenov, 1972; Pekov, 2000). In 37 specimens these minerals neighbored leached cavities of sphalerite, which contain its relics (“licked lollipops”) and the newly formed Zn–Al smectites of the sauconite–Zn-bearing montmorillonite solid solution series; in the other 15 specimens, pockets of sphalerite remained fresh without the attributes of dissolution. The electron microprobe data of these samples unequivocally confirmed the cation-exchange origin of vigrishinite: in 24 of 37 samples with leached cavities of sphalerite, the murmanite-like mineral was identified as vigrishinite; in one sample, it was Zn-bearing murmanite. In the other 12 samples with cavities, there was a mineral appearing to be epistolite rather than murmanite, which was strongly enriched in Zn (up to 11.3 wt % ZnO) with comparable atomic amounts of Na and Zn and ratios of high-valence constituents Nb : Ti : Si ~ 2 : 1 : 4 corresponding to epistolite. In all 15 specimens without leached cavities of sphalerite, heterophyllosilicates were murmanite or epistolite of the usual composition with Zn concentration below detection limit of electron microprobe (0.1 wt %).

Detailed study of Zn-rich epistolite-like mineral revealed Zn and Na ordering in it. Species-defining Zn and differences from epistolite in the unit-cell dimensions caused by the structural features allowed us to consider this heterophyllosilicate as a separate mineral species of the epistolite group. It was named *zvyaginite* in honor of Boris Borisovich Zvyagin (1921–2002), outstanding Russian crystallographer, crystal chemist, physicist, and specialist in the electron diffraction method. For many years he was a Head of the Laboratory of High Voltage Electronography in the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Moscow. Zvyagin carried out pioneering work in the field of electron diffraction studies of minerals with layered structures and made a significant contribution to this complex complex field of structural mineralogy and crystallography. The type specimen of zvyaginite is deposited in the systematic collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, catalogue no. 94140.

OCCURRENCE AND GENERAL CHARACTERISTICS

Pegmatite no. 71 is a large (size of opened part is 15×6 m) lenticular peralkaline body with ussingite

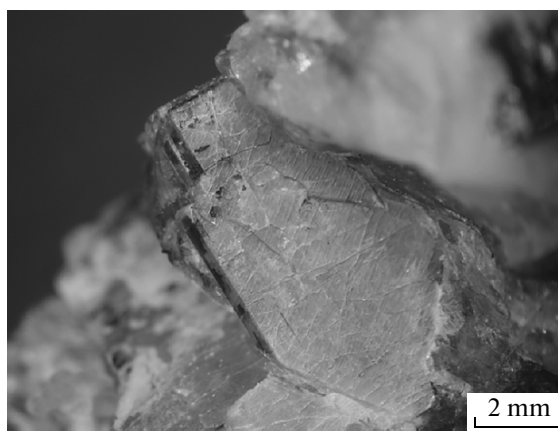


Fig. 1. Lamellar crystals of zvyaginite – supposed homoaxial pseudomorphs after vuonnemite/epistolite in ussingite. Width of field is 11.4 mm. Photo by I.V. Pekov and A.V. Kasatkin.

core hosted in the foyaite and lujavrite of layered complex at the eastern slope of Mt. Malyi Punkaruai. This remarkable mineralogical locality, known since 1932, is characterized in detail by Gerasimovsky (1936), Vlasov et al. (1959), Semenov (1972), and Pekov (2000). Specimens containing zvyaginite come from the contact of ussingite core of pegmatite with the marginal aegirine–eudialyte zone. Ussingite and microcline are the major minerals there; sodalite, aegirine, arfvedsonite, eudialyte, yellow-brown sphalerite, and intermediate members of the pectolite–sérandite series are minor minerals; manganon-eptunite, murmanite, vigrishinite, epistolite, belovite-(Ce), steenstrupine-(Ce), chkalovite, tugtupite, polyolithionite, and galena occur in small amounts. This zone is strongly altered by late low-temperature hydrothermal processes. Ussingite and sodalite are frequently replaced with aggregates of zeolites, analcime, natrolite, gmelinite-Na, gmelinite-K, and chabazite-Ca. Complete pseudomorphs of rhabdophane-(Ce) and monazite-(Ce) after vitusite-(Ce), “erikite” (Pekov et al., 1997), leucoxene after kazakovite (?) crystals, and partial to complete pseudomorphs of sooty Mn oxides (takanelite, rancieite) after the pectolite–sérandite series minerals, catapleiite and “zirconite” after eudialyte, and gerasimovskite after epistolite are common. In many places, sphalerite was partially or completely dissolved to form characteristic tetrahedral or firlike (in the case of skeletal crystals) cavities, where white, yellow, or rusty-brown clay and cracker-like masses of the aforementioned Zn–Al smectites are frequent along with sphalerite relics.

Zvyaginite occurs as lamellar rectangular (Fig. 1) or irregular-shaped crystals flattened on [001]. They reach 1×2 cm in area and up to 1 cm in thickness. Its faces {001} are smooth and lustrous, whereas its lateral faces are commonly poorly developed; only in one

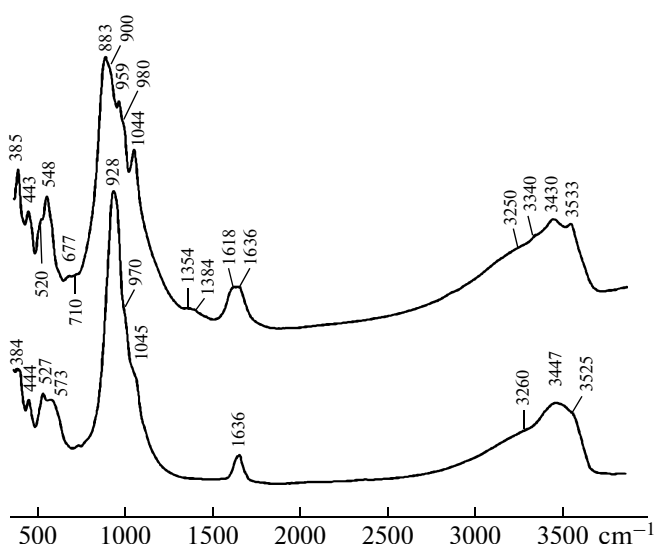


Fig. 2. IR spectra of (1) zvyaginite and (2) epistolite from Mt. Kedykverpakhhk, Lovozero alkaline pluton.

case, a sheet with pronounced lateral faces was encountered (Fig. 1) approximately corresponding to faces {100}, {012}, and {0 $\bar{1}2$ } in angle parameters of vuonnemite, $\text{Na}_5\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_3(\text{F},\text{OH}) \cdot 2\text{Na}_3\text{PO}_4$ crystals, as they were reported by Khomyakov (1990). This is an additional argument indicating that crystals of zvyaginite are homoaxial pseudomorphs after vuonnemite (see below). Those crystals appearing to be single actually are mosaic. Like vigrishinite (Pekov et al., 2012), they show microcracking and are in fact near-parallel aggregates of lamellar individuals up to a few dozen microns in thickness.

Usually, zvyaginite as isolated lamellae of their near-parallel or chaotic intergrowths is embedded in massive ussingite or occurs within replacing aggregates of zeolites. Occasionally, lamellae of the new mineral are observed at the boundary between ussingite and microcline or partially dissolved sphalerite. Parallel intergrowths (“sandwiches”) of zvyaginite and vigrishinite adjoining on their faces {001} are similar to the intergrowths of epistolite and murmanite previously described from this pegmatite (Semenov, 1972; Pekov, 2000) and to the syntactic intergrowths of lomonosovite, $\text{Na}_4\text{Ti}_4[\text{Si}_2\text{O}_7]_2\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4$, and vuonnemite found in peralkaline Palitra pegmatite discovered in the underground works at Mt. Kedykverpakhhk, in the Lovozero pluton.

PHYSICAL PROPERTIES AND OPTICAL PARAMETERS

Zvyaginite is translucent to transparent, colorless, pearly white, creamy, yellowish-brownish, and less frequently pale pink or violet-pink. Its streaks are white. The luster is nacreous on its faces or cleavage

surface and greasy on broken surface. Its Mohs' hardness is 2.5–3. Zvyaginite is brittle, with perfect cleavage parallel to {001}; two directions of distinct cleavage, which are nearly perpendicular to each other and to {001}, can be observed under a microscope. Fracture is stepped. The density measured by flotation in heavy liquids is 2.88(3) g/cm³; the density calculated from structural data is 2.94 g/cm³.

In transmitted light, zvyaginite is colorless and devoid of pleochroism. The mineral is optically biaxial, negative. The refractive indices measured in immersion liquids ($\lambda = 589$ nm) are: $N_p = 1.626(5)$, $N_m = 1.714(3)$, $N_g = 1.740(5)$, $2V_{\text{meas}} = 45(15)^\circ$. $2V$ estimated from the degree of curvature of isogyre in the section perpendicular to optical axis is $45(10)^\circ$; $2V_{\text{calc}} = 55^\circ$. The dispersion of the optical axes is weak, $r < v$. Orientation: Y and Z lie in the ab plane.

INFRARED SPECTROSCOPY

The infrared absorption spectrum of zvyaginite was measured on an ALPHA FTIR spectrometer (Bruker Optics) in the absorption band range of 360 to 3800 cm⁻¹, with a resolution of 4 cm⁻¹ and over 16 scans. The sample was prepared as an anhydrous KBr pellet. A similar pellet of pure KBr was used as a reference sample.

The wavenumbers of absorption bands and their assignments in the IR spectrum of zvyaginite (Fig. 2) are (cm⁻¹; s is strong band, sh is shoulder): 3525sh, 3447, 3260sh (O–H stretching vibrations), 1636 (H–O–H bending vibrations of H₂O molecules), 1045sh, 970sh (Si–O stretching vibrations of Si–O–Si bridges in Si₂O₇ groups), 928s (Si–O stretching vibrations involving apical O atoms of Si₂O₇ groups), 573, 527 (combination of Ti...O, Nb...O, and Zn...O stretching vibrations), 444, 384 (lattice modes involving Si–O–Si bending vibrations). Bands, which could correspond to CO₃²⁻, NO₃⁻, and NH₄⁺ groups (in the range of 1300–1550 cm⁻¹), B–O (1200–1500 cm⁻¹) or Be–O (680–820 cm⁻¹) bonds are absent in the IR spectrum of new mineral.

The IR spectrum of epistolite is generally similar, but better resolved (Fig. 2) and differs from that of zvyaginite in the notably lower frequency of the major absorption maximum in the region of Si–O stretching vibrations (at 888 cm⁻¹) and the higher intensity of bands corresponding to H-bearing groups.

CHEMICAL COMPOSITION

The chemical composition of zvyaginite was determined on a JEOL JSM-6480LV SEM equipped with a combined electron microprobe system. The analysis was carried out in coupled mode: the contents of F and Na were measured with an INCA-Wave 500 WDS, whereas other elements were determined using an

INCA-Energy 350 EDS (window ATW-2). The operating conditions were: accelerating voltage 20 kV, current intensity 6.5 nA, and beam diameter 5 μ m. The following standards were used: lozenzenite (Na, Si, Ti), feldspar MAD-10 (K), CaMoO₄ (Ca), Mn (Mn), ZnS (Zn), FeAsS (Fe), Al₂O₃ (Al), Rb₂Nb₄O₁₁ (Nb), and MgF₂ (F). Special attention was paid to the correctness of Na content determination, because of the partial overlap of its analytical line K_{α} and line L_{α} of Zn. The count time was long: 60 s for peak Na and 30 s for background on each side to compensate for the relatively low WDS current intensity (to avoid the well-known effect of the electron-beam-induced migration of Na at high current intensities). The correctness of the Na determination was controlled at a low current intensity (0.5 nA). The content of Na₂O 4.9 ± 0.5 wt % for the holotype sample measured at these conditions covers the concentration range determined on WDS (see below). The H₂O content in zvyaginite was determined by the Alimarin method with selective sorption from gaseous products obtained by heating the mineral to 1080°C in an oxygen flow; absorbing tubes filled with Mg(ClO₄)₂ were used.

The average chemical composition of the holotype zvyaginite sample derived from five point analyses is as follows, wt % (range is in parentheses): 4.74 (4.64–4.79) Na₂O, 0.22 (0.18–0.28) K₂O, 0.77 (0.74–0.80) CaO, 1.36 (1.30–1.49) MnO, 0.24 (0.16–0.34) FeO, 9.61 (9.17–10.16) ZnO, 0.19 (0.18–0.21) Al₂O₃, 29.42 (29.02–30.30) SiO₂, 12.33 (12.05–12.46) TiO₂, 27.22 (26.61–27.55) Nb₂O₅, 1.94 (1.88–2.06) F, 12.65 H₂O, $-0.82 - O = F_2$, total is 99.87. The contents of other elements with atomic numbers higher than that of oxygen are below detection limits. The absence of Be, B, C, and N was supported by IR spectroscopy.

The empirical formula of zvyaginite, calculated on the basis of Si + Al = 4, is

Na_{1.24}K_{0.04}Ca_{0.11}Mn_{0.16}Fe_{0.03}Zn_{0.96}Nb_{1.66}Ti_{1.25}(Si_{3.97}Al_{0.03})_{Σ4}O_{15.07}(OH)_{2.10}F_{0.83}(H₂O)_{4.64}. The basis of the calculation is adopted according to the general crystal chemical features of minerals from the bafertisite mero-plesiotype series (Ferraris and Gula, 2005): the disilicate group [Si₂O₇] is the basic structural invariant of these heterophyllosilicates, while the ratios and structural position of other constituents, both cations and anions, are significantly variable. The O : OH value was calculated from the charge balance constraints and the structure data showing that the anionic composition of the formula is O₁₅(OH,O,F)₃.

The simplified formula of zvyaginite is NaZnNb₂Ti[Si₂O₇]₂O(OH,F)₃(H₂O)_{4+x}, where $x < 1$. The idealized formula NaZnNb₂Ti[Si₂O₇]₂O(OH)₃(H₂O)₄ requires, wt %: 3.89 Na₂O, 10.20 ZnO, 30.13 SiO₂, 10.02 TiO₂, 33.33 Nb₂O₅, 12.43 H₂O, total is 100.00.

X-RAY DIFFRACTION DATA AND MODEL OF CRYSTAL STRUCTURE

X-ray powder diffraction data for zvyaginite (Table 1) were collected with a STOE IPDS II single-crystal diffractometer equipped with an image plate detector using the Gandolfi method (MoK α radiation, at a distance from sample to IP detector of 200 mm). The triclinic unit-cell dimensions calculated taking into account single-crystal X-ray data are as follows: $a = 8.99(3)$, $b = 8.97(3)$, $c = 12.14(4)$ Å, $\alpha = 74.24(8)^\circ$, $\beta = 80.84(8)^\circ$, $\gamma = 74.08(8)^\circ$, $V = 902(2)$ Å³. The X-ray powder diffraction pattern of the new mineral is similar to that of epistolite (JCPDS-ICDD database, card no. 39-0407).

A single crystal X-ray diffraction study of zvyaginite was performed on a Bruker Kappa APEX DUO diffractometer equipped with a CCD detector. The mineral is triclinic, space group $P\bar{1}$, $a = 8.975(3)$, $b = 8.979(3)$, $c = 12.135(4)$ Å, $\alpha = 74.328(9)^\circ$, $\beta = 80.651(8)^\circ$, $\gamma = 73.959(8)^\circ$, $V = 900.8(6)$ Å³, $Z = 2$. The crystal structure of zvyaginite was solved by direct methods and refined on the basis of 2947 unique reflections with $I > 2\sigma(I)$ using the program package SHELX-97 (Sheldrick, 2008). The crystallographic parameters, single-crystal X-ray diffraction data, and refinement parameters of the crystal structure of zvyaginite are given in Table 2; atom coordinates, equivalent displacement parameters, and site occupancy factors are shown in Table 3; interatomic distances are given in Table 4; and bond order calculations are shown in Table 5.

Unfortunately, even the best of the examined single zvyaginite crystals is low-qualitative: a certain splitting has caused a broadening of reflections and affected the divergence value $R = 15.9\%$. Thus, we may only consider our data as a structural model of the new mineral. However, reasonable e_{ref} values, atom displacement parameters (Table 3), interatomic distances (Table 4), bond valence sums on anions and cations (Table 5), and a good correspondence between reflection intensities of the measured and calculated X-ray powder patterns (Table 1) testify to the correct structure model of zvyaginite.

Zvyaginite is a member of the epistolite group (Back and Mandarino, 2008) belonging to the bafertisite mero-plesiotype series (Ferraris and Gula, 2005). Like other heterophyllosilicates of this series, the structure of the new mineral (Fig. 3, Table 3) is based on the three-layer *HOH*-block. The central part of this block in zvyaginite is an octahedral *O*-layer formed by chains of the Zn-centered [Zn(1) and Zn(2)] octahedra and chains of alternating Ti-centered [Ti(1) and Ti(2)] and Na(1)-centered octahedra (Fig. 4a). This *O*-layer is sandwiched between two heteropolyhedral (*H*) layers consisting of the Si₂O₇ disilicate groups, Nb(1)- and Nb(2)-centered octahedra and hexagonal bipyramids centred by Na(2) and

Table 1. X-ray powder diffraction pattern for zvyaginite

I_{obs}	$d_{\text{obs}}, \text{\AA}$	I_{calc}^*	$d_{\text{obs}}^{**}, \text{\AA}$	hkl
100	11.72	100	11.631	001
3	8.59	1	8.587	100
3	6.90	2	6.901	110
40	5.83	46	5.816	002
53	5.28	22, 18	5.333, 5.197	$\bar{1}\bar{1}1, 112$
1	4.733	1	4.716	$1\bar{1}1$
86	4.289	28, 27	4.293, 4.281	200, 021
36	3.896	7, 10, 11, 6, 5	3.949, 3.909, 3.877, 3.863, 3.857	$\bar{1}\bar{1}2, \bar{2}01, 003, 022, 113$
12	3.648	9, 6	3.674, 3.622	$0\bar{2}1, 202$
4	3.440	3	3.451	220
5	3.396	2	3.401	222
9	3.278	6, 5	3.307, 3.256	023
10	3.034	3, 1, 4	3.071, 3.045, 3.024	$0\bar{2}2, \bar{1}\bar{1}3, 203$
57	2.916	10, 7, 41	2.937, 2.914, 2.908	310, 132, 004
72	2.862	32, 30	2.872, 2.836	130, 312
23	2.674	4, 4, 14	2.690, 2.688, 2.674	$133, \bar{2}20, \bar{2}21$
17	2.606	12	2.625	$\bar{1}\bar{3}1$
18	2.536	4, 14, 4	2.559, 2.531, 2.521	$0\bar{2}3, \bar{2}22, 204$
8	2.428	9, 8	2.450, 2.401	$3\bar{1}2, 134$
6	2.320	2	2.326	005
8	2.308	3, 3	2.312, 2.308	$\bar{2}23, \bar{2}04$
20	2.144	5, 2, 6, 1, 2	2.154, 2.148, 2.148, 2.147, 2.140	$041, \bar{3}\bar{3}1, 401, 400, 042$
7	2.093	5, 1, 2, 1	2.119, 2.105, 2.104, 2.087	$2\bar{2}3, \bar{3}13, 334, \bar{1}34$
4	2.033	2, 1	2.043, 2.023	$\bar{1}\bar{1}5, \bar{4}\bar{2}1$
3	2.015	2	2.014	116
4	1.966	2, 1	1.968, 1.958	$\bar{2}\bar{4}1, 403$
7	1.936	4, 2	1.939, 1.932	006, 044
5	1.844	6	1.846	$\bar{2}25$
24	1.782	11, 1, 2, 6	1.792, 1.789, 1.778, 1.778	442, 511, 441, 151
3	1.696	1	1.694	531
9	1.668	2, 2, 1, 2	1.676, 1.668, 1.662, 1.662	$\bar{2}43, 2\bar{4}1, 4\bar{2}2, 007$
7	1.654	2, 1, 4, 5, 2	1.658, 1.654, 1.649, 1.647, 1.646	$405, \bar{4}04, 137, 2\bar{2}6, \bar{1}\bar{5}1$
21	1.604	4, 9, 1, 2, 5	1.605, 1.605, 1.604, 1.604, 1.601	$\bar{1}52, \bar{1}51, \bar{1}35, 155, 5\bar{1}1$
4	1.545	4	1.504	$\bar{4}\bar{4}2$
4	1.507	3, 4	1.508, 1.507	446, $2\bar{2}6$
7	1.483	4	1.487	263

Table 1. (Contd.)

<i>I</i> _{obs}	<i>d</i> _{obs} , Å	<i>I</i> _{calc} *	<i>d</i> _{obs} **, Å	<i>hkl</i>
5	1.464	4, 3, 2	1.471, 1.469, 1.462	138, 620, $\bar{5}$ 13
5	1.452	3, 2	1.454, 1.450	008, $\bar{3}$ $\bar{3}$ 5
3	1.415	2, 2, 1	1.418, 1.415, 1.415	624, 516, 338
5	1.376	2, 1	1.380, 1.375	$\bar{2}$ $\bar{6}$ 1, $\bar{4}$ 06
4	1.356	3, 1	1.358, 1.355	$\bar{2}$ $\bar{2}$ 7, 048
4	1.350	2, 2	1.350, 1.350	5 $\bar{1}$ 5, $\bar{4}$ 41
3	1.324	4	1.321	4 $\bar{4}$ 1
3	1.310	3	1.308	$\bar{4}$ 43
2	1.271	2	1.274	267
1	1.241	1	1.239	5 $\bar{3}$ 3
1	1.229	2	1.225	$\bar{6}$ $\bar{2}$ 4
2	1.202	1	1.197	159
2	1.178	2	1.179	4 $\bar{4}$ 4

* Only reflections with *I*_{calc} ≥ 1 are given for calculated X-ray powder pattern.

** Calculated for the unit-cell dimensions from single-crystal data.

Na(3) cations (Fig. 4b). The Nb(1) site contains admixtures of light cations with lower valency, mainly Ti (Tables 3, 4 5). All Zn and Na sites contain vacancies (Tables 3 and 5). Three of the four O-positions are not bound to Si, namely O(6), O(11) and O(12), are mainly occupied by OH groups ($\pm$ F), and only one [O(18)] is O²⁻ dominant (Tables 3 and 5). Four fully occupied H₂O sites O(19–22) are located in the inter-layer space between the *HOH* blocks. They are vertices of the Nb(1)-, Nb(2)-, Na(2)- and Na(3)-centred polyhedra (Tables 3, 5; Fig. 3). Electron density maps also show some weak peaks (up to 2.1 e/Å³) in the interlayer space that can be assigned to additional, low-occupied H₂O sites. This fact is consistent with the chemical data showing the presence of 4.64 H₂O molecules per formula, instead of the idealized value 4 H₂O corresponding to the fully occupied major sites O(19–22) of water molecules.

DISCUSSION

Zvyaginite, NaZnNb₂Ti[Si₂O₇]₂O(OH,F)₃(H₂O)_{4+x}, is structurally related to epistolite, Na₄Nb₂Ti[Si₂O₇]₂O₂(OH,F)₂(H₂O)₄. The structures of the both minerals are topologically identical. These minerals are different in the *O*-layers (Fig. 5; Table 6), whereas the *H*-layers in epistolite and zvyaginite are the same (Fig. 4b). The major crystal chemical difference between epistolite and zvyaginite is the ordered partial substitution of Na⁺ for Zn²⁺ in the *O* layer.

Table 2. Crystallographic characteristics, single-crystal experiment data, and refinement parameters of the structure of zvyaginite

Symmetry, space group, <i>Z</i>	Triclinic, <i>P</i> $\bar{1}$, 2
Unit-cell dimensions	$\alpha = 8.975(3)$ Å $\alpha = 74.328(9)^\circ$ $b = 8.979(3)$ Å $\beta = 80.651(8)^\circ$ $c = 12.135(4)$ Å $\gamma = 73.959(8)^\circ$
<i>V</i> , Å ³	900.8(6)
Temperature	293(2) K
Diffractionmeter	Bruker Kappa APEX DUO CCD
Radiation, λ	MoK α ; 0.71073 Å
$\theta_{\min/\max}$, °	1.75/26.37
Scanning ranges	$-11 \leq h \leq 11$, $-9 \leq k \leq 11$, $-14 \leq l \leq 15$
Number of measured/unique reflections	12773/3644
Number of unique reflections with $I > 2\sigma(I)$	2947
Method of refinement	Least square method for F^2
Number of refined parameters	234
R [$I > 2\sigma(I)$]	0.159
$\Delta\rho_{\max/\min}$, e/Å ³	5.542/–2.631

Table 3. Atom coordinates, equivalent displacement parameters (U_{eq} , Å²), and site occupancy factors (s.o.f.) in the structure of zvyaginite

Atom	x	y	z	U eq	S.o.f.***
Nb(1)	0.9576(4)	0.6613(4)	0.2409(2)	0.0287(11)	[32.6]Nb _{0.56} Ti _{0.44}
Nb(2)	0.45733(19)	0.1598(2)	0.24176(17)	0.0101(6)	Nb
Zn(1)	0.6200(4)	0.1195(4)	0.4999(3)	0.0071(14)	[22.8]Zn _{0.58}
Zn(2)	0.8635(5)	0.3626(5)	0.4991(4)	0.0239(16)	[24.8]Zn _{0.62}
Ti(1)**	0.5	0.5	0.5	0.014(2)	[20.0]0.91(3)
Ti(2)**	0.0	0.0	0.0	0.0161(19)	[22.2]1.01(3)
Na(1)	0.251(2)	0.250(2)	0.4961(19)	0.023(7)	[5.1]Na _{0.46}
Na(2)	0.201(2)	0.909(2)	0.1999(17)	0.026(7)	[5.4]Na _{0.49}
Na(3)	0.715(2)	0.438(2)	0.2092(15)	0.027(7)	[5.3]Na _{0.48}
Si(1)	0.0586(6)	0.2566(7)	0.2654(5)	0.0151(12)	Si
Si(2)	0.8491(7)	0.0468(7)	0.2650(5)	0.0149(12)	Si
Si(3)	0.5577(6)	0.7579(6)	0.2642(5)	0.0143(12)	Si
Si(4)	0.3486(6)	0.5489(7)	0.2645(5)	0.0162(12)	Si
O(1)	0.2366(17)	0.2000(18)	0.2202(13)	0.019(3)*	
O(2)	0.737(3)	0.704(3)	0.217(2)	0.058(6)*	
O(3)	0.0344(17)	0.2044(18)	0.4055(13)	0.019(3)*	
O(4)	0.4899(19)	0.944(2)	0.2186(14)	0.024(3)*	
O(5)	0.8377(19)	0.007(2)	0.4052(14)	0.025(3)*	
O(6) = (OH,O)	0.977(4)	0.645(4)	0.3972(11)	0.084(9)*	
O(7)	−0.012(2)	0.440(3)	0.220(2)	0.054(6)	
O(8)	0.459(2)	0.671(2)	0.2124(16)	0.033(4)*	
O(9)	0.664(2)	0.490(2)	0.5965(15)	0.028(4)*	
O(10)	0.923(3)	0.886(3)	0.224(2)	0.053(6)*	
O(11) = OH	0.1651(18)	0.8810(19)	0.4077(13)	0.021(3)*	
O(12) = OH	0.6606(18)	0.3749(19)	0.4103(14)	0.023(3)*	
O(13)	0.4657(18)	0.293(3)	0.5965(15)	0.035(5)	
O(14)	0.179(2)	0.633(3)	0.2228(18)	0.042(5)*	
O(15)	0.4308(19)	0.389(2)	0.2159(15)	0.027(4)*	
O(16)	0.6805(19)	0.139(2)	0.2162(14)	0.026(4)*	
O(17)	0.963(2)	0.167(2)	0.2111(16)	0.035(4)*	
O(18) = (O,OH)	0.4388(18)	0.1056(18)	0.4028(7)	0.021(3)*	
O(19) = H ₂ O	0.986(2)	0.728(2)	0.0430(15)	0.036(4)	
O(20) = H ₂ O	0.479(4)	0.221(5)	0.044(3)	0.101(17)*	
O(21) = H ₂ O	0.248(3)	1.000(3)	0.033(3)	0.073(8)	
O(22) = H ₂ O	0.738(4)	0.474(4)	0.0384(16)	0.083(9)*	

* U_{iso} .

** Multiplicities of the Ti(1) and Ti(2) sites are 1, multiplicities of all other sites are 2.

*** S.o.f is based on the refined electron content of sites (eref given in brackets), coordination polyhedra characteristics, interatomic distances, U_{eq} and electron microprobe data; values 0.91 and 1.01 for sites Ti(1) and Ti(2), respectively are formally calculated on the basis of 1.00 Ti at $e_{ref} = 22$.

The crystal structure of epistolite was studied by Khalilov et al. (1965), Sokolova and Hawthorne (2004), and Nemeth et al. (2005); their final *R* values were 22, 9.8 and 13.6%, respectively. According to

these studies, the *O*-layer in epistolite consists of alternating chains of Na-centered octahedra ...Na–Na–Na–Na... and mixed octahedral chains ...Ti–Na–Ti–Na... (Fig. 5b). In zvyaginite, the chains of dis-

torted octahedra ...Zn(1)—Zn(1)—Zn(2)—Zn(2)... are present, whereas the Ti,Na chains are retained; there are octahedral chains ...—Ti—Na(1)—Ti—Na(1)—.... The notable differences in ionic radii and other characteristics between Na^+ and Zn^{2+} cause the distortion of the *HOH* block, as a result of which the structure of zvyaginite cannot be described within the small, epistolite-type unit cell; similar differences were revealed for the pair murmanite, $\text{Na}_4\text{Ti}_4[\text{Si}_2\text{O}_7]_2\text{O}_4(\text{H}_2\text{O})_4$ — vigrishinite, $\text{Zn}_2\text{Ti}_{4-x}[\text{Si}_2\text{O}_7]_2(\text{OH},\text{H}_2\text{O},\square)_8$ (Table 6).

The unit cell of zvyaginite can be derived from the epistolite unit cell using the transformation matrix $(\bar{1} \ 1 \ 0 / 1 \ 1 \ 0 / 0 \ 0 \ \bar{1})$. If we apply this transformation to the unit cell reported for epistolite by Sokolova and Hawthorne (2004) (see Table 6), then it gives the following values $a = 9.011$, $b = 9.014$, $c = 12.041$ Å, $\alpha = 75.47^\circ$, $\beta = 82.87^\circ$, $\gamma = 74.58^\circ$. These dimensions are close to those derived from single-crystal X-ray diffraction data for zvyaginite. Thus, the a and b parameters of zvyaginite correspond to the ab face diagonals of the epistolite unit cell (Fig. 5). The unit cell of murmanite is transformed to the unit cell of vigrishinite (Table 6) with $(\bar{1} \ \bar{1} \ 0 / \bar{1} \ 1 \ 0 / 0 \ 0 \ \bar{1})$.

The *HOH*-blocks in zvyaginite, epistolite, and murmanite are uncharged and linked to each other by relatively weak hydrogen bonds (the low hardness of these minerals is probably caused by the absence of charged interlayer particles, which are able to form ionic bonds). The distances between the oxygen atoms of water molecules O(19–22) revealed as a result of the structure study, which form interblock hydrogen bonds, are: $d[\text{O}(19)\cdots\text{O}(21)] = 2.79$, $d[\text{O}(19)\cdots\text{O}(22)] = 2.85$, $d[\text{O}(20)\cdots\text{O}(21)] = 2.89$, and $d[\text{O}(20)\cdots\text{O}(22)] = 2.91$ Å. These values are consistent with the IR spectroscopic data. Previously, the following empirical correlation between the O...O distances and frequencies ν (cm^{-1}) of O—H stretching vibrations for hydrogen bonds in minerals were: $\nu(\text{cm}^{-1}) = 3592 - 304 \times 10^9 \exp[-d(\text{O}\cdots\text{O})/0.1321]$ (Libowitzky, 1999). The frequencies corresponding to the aforementioned O...O distances calculated from this equation are 3390, 3463, 3499, and 3513 cm^{-1} , respectively. These values are matched with absorbance bands (taking into account their significant broadness and probable overlapping) in the IR spectrum of zvyaginite in the range of 3400 to 3550 cm^{-1} . The shoulder at 3260 cm^{-1} in the IR spectrum of this mineral corresponding to the stronger hydrogen bonds is evidently assigned to the vibrations of additional interblock water molecules, whose number is determined by the x value in formula $\text{NaZnNb}_2 \cdot \text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}(\text{OH},\text{F})_3(\text{H}_2\text{O})_{4+x}$. The distances between them and water molecules coordinating cations Nb and Na in the outer parts of the H layers [O(19–22)] is clearly shorter than those between the H_2O apices of Nb- and Na-centered octahedra of nearby blocks (2.79–2.91 Å: see above), and this favors

Table 4. Selected interatomic distances (Å) in the structure of zvyaginite

Nb(1)—O(6) 1.895(10)	Na(2)—O(21) 1.99(4)
—O(10) 1.91(2)	—O(11) 2.44(2)
—O(14) 1.92(2)	—O(14) 2.48(3)
—O(2) 1.96(3)	—O(10) 2.53(3)
—O(7) 2.01(3)	—O(8) 2.68(3)
—O(19) 2.302(17)	—O(17) 2.70(3)
Mean 2.00	—O(4) 2.75(3)
Nb(2)—O(18) 1.873(9)	—O(1) 2.80(2)
—O(16) 1.940(16)	Mean 2.55
—O(15) 1.947(17)	Na(3)—O(22) 1.994(10)
—O(1) 1.961(15)	—O(12) 2.35(2)
—O(4) 1.965(16)	—O(7) 2.48(3)
—O(20) 2.31(4)	—O(2) 2.48(3)
Mean 2.00	—O(8) 2.48(3)
Ti(1)—O(12) 1.944(16) $\times 2$	—O(15) 2.69(3)
—O(13) 1.983(19) $\times 2$	—O(16) 2.76(3)
—O(9) 1.997(17) $\times 2$	—O(17) 2.81(3)
Mean 1.97	Mean 2.53
Ti(2)—O(11) 1.956(15) $\times 2$	Si(1)—O(7) 1.57(2)
—O(3) 1.959(15) $\times 2$	—O(1) 1.590(16)
—O(5) 1.976(16) $\times 2$	—O(17) 1.63(2)
Mean 1.96	—O(3) 1.632(16)
Zn(1)—O(18) 2.204(15)	Mean 1.61
—O(18) 2.205(14)	Si(2)—O(10) 1.59(3)
—O(5) 2.228(17)	—O(16) 1.631(17)
—O(13) 2.24(2)	—O(17) 1.631(19)
—O(12) 2.358(17)	—O(5) 1.633(17)
—O(11) 2.382(16)	Mean 1.62
Mean 2.27	Si(3)—O(4) 1.589(17)
Zn(2)—O(6) 2.03(2)	—O(2) 1.61(3)
—O(3) 2.182(16)	—O(8) 1.618(19)
—O(9) 2.193(18)	—O(13) 1.622(18)
—O(12) 2.226(17)	Mean 1.61
—O(11) 2.238(16)	Si(4)—O(14) 1.60(2)
—O(6) 2.88(3)	—O(8) 1.614(19)
Mean 2.29	—O(9) 1.618(18)
Na(1)—O(18) 2.18(2)	—O(15) 1.639(18)
—O(6) 2.35(4)	Mean 1.62
—O(9) 2.56(3)	
—O(3) 2.56(3)	
—O(5) 2.57(3)	
—O(13) 2.60(3)	
Mean 2.47	

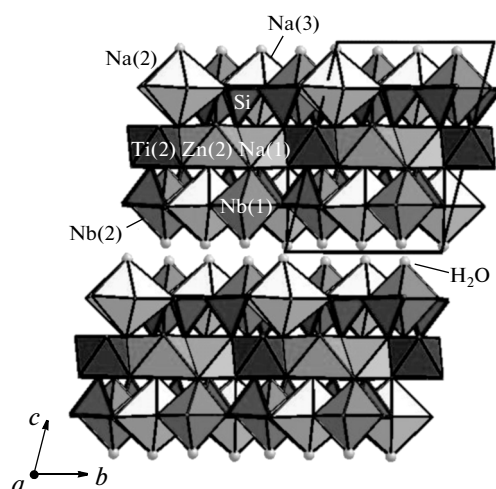


Fig. 3. Crystal structure of zvyaginite: general view. Unit cell is shown.

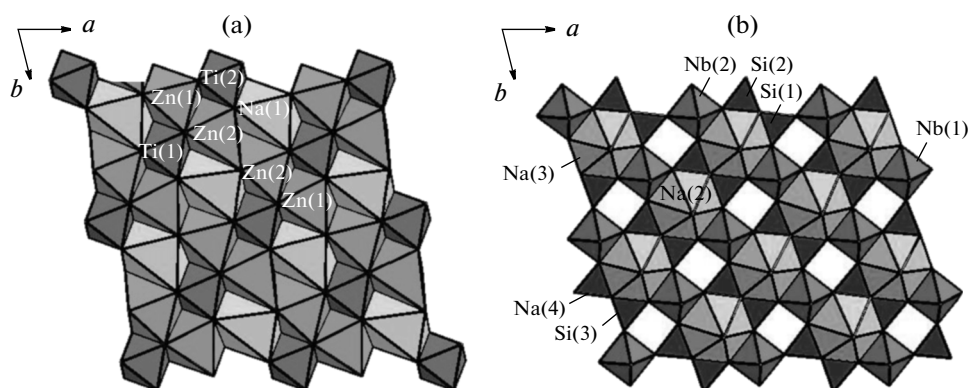


Fig. 4. (a) *O*- and (b) *H*-layers in the structure of zvyaginite. *H*-layer of epistolite is identical to that of zvyaginite

stronger hydrogen bonding, in which these additional H_2O molecules are involved.

It is well known that lomonosovite is unstable in low-alkali aqueous media (in nature these are hydrothermal and supergene conditions) and is easily altered by leaching of Na_3PO_4 and hydration. This process was repeatedly observed in nature and reproduced experimentally. The final silicate phase of these transformations is murmanite² (Borneman-Starynkevich, 1946; Vlasov et al., 1959; Zabavnikova, 1967; Khomyakov, 1995): $\text{Na}_4\text{Ti}_4(\text{Si}_4\text{O}_{14})\text{O}_4 \cdot 2\text{Na}_3\text{PO}_4 + 4\text{H}_2\text{O} \rightarrow \text{Na}_{4-x}\text{Ti}_4\text{Si}_4\text{O}_{14}(\text{OH})_{4-x}\text{O}_2(\text{H}_2\text{O})_{2+x} + (6+x)\text{Na}^+ + 2(\text{PO}_4)^{3-}$. Under similar conditions, vunnemite is transformed to epistolite (Khomyakov, 1995) and this process can be schematically described as follows:

² Recent experiments including our own data indicate that the hydrolysis of lomonosovite and vunnemite is a rather complex process, but there are no doubts that its products in nature are murmanite and epistolite, respectively

$\text{Na}_5\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_3(\text{F}_x\text{OH}_{1-x}) \cdot 2\text{Na}_3\text{PO}_4 + 4\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Na}_4\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_2(\text{OH}_{2-x}\text{F}_x)_{\Sigma 2}(\text{H}_2\text{O})_4 + 7\text{Na}^+ + 2(\text{PO}_4)^{3-}$. Khomyakov (1995) referred murmanite and epistolite to the special genetic group of transformation minerals: no evidence for their individual crystallization from melt, solution, or gas has been yet found.

In our opinion, zvyaginite and vigrishinite are typical transformation mineral species. Zvyaginite results from cation exchange with partial substitution of Na^+ by Zn^{2+} . The intermediate phase of this evolutionary series is most likely epistolite. Accordingly, crystals (individuals) of zvyaginite (Fig. 1) are homoaxial pseudomorphs after these minerals: all three TiNb-silicates show an identical topology of the major structural units, i.e., *HOH*-blocks.

We suggest that zvyaginite is a product of the cation-exchange reaction of epistolite with low-alkali aqueous (late hydrothermal) solution enriched in Zn^{2+}

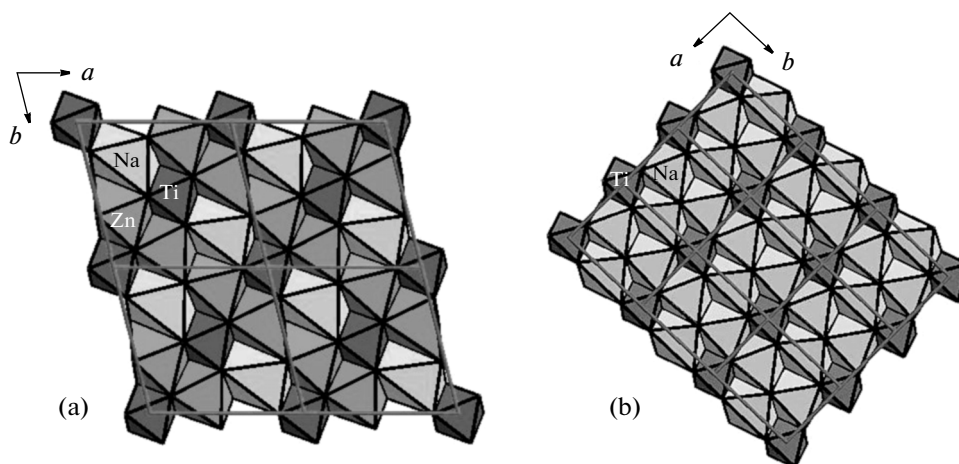


Fig. 5. O-layers in the structures of (a) zvyaginite (our data) and (b) epistolite (drawn from data of Sokolova and Hawthorne (2004). Unit cells are shown.

ions derived from dissolved sphalerite, which is very abundant in this zone of pegmatite: $\text{Na}_4\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_2(\text{OH},\text{F})_2(\text{H}_2\text{O})_4 + \text{Zn}^{2+} + \text{H}^+ + x\text{H}_2\text{O} \rightarrow \text{NaZnNb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}(\text{OH},\text{F})_3(\text{H}_2\text{O})_{4+x} + 3\text{Na}^+$. The direct replacement of vuonnemite with zvyaginite cannot be ruled out if the former remained unaltered up to the stage of extensive dissolution of

sphalerite: $\text{Na}_5\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_3(\text{F}_x\text{OH}_{1-x}) \cdot 2\text{Na}_3\text{PO}_4 + \text{Zn}^{2+} + 2\text{H}^+ + (4x + x)\text{H}_2\text{O} \rightarrow \text{NaZnNb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}(\text{OH}_{3-x}\text{F}_x)_{\Sigma 3}(\text{H}_2\text{O})_{4+x} + 10\text{Na}^+ + 2(\text{PO}_4)^{3-}$ (both schemes of reactions are simplified). However, the two-stage process involving an intermediate phase of epistolite is more likely: in some samples, we observe the assemblage of fresh sphalerite

Table 5. Bond order calculations for zvyaginite

	Nb(1)*	Nb(2)	Ti(1)	Ti(2)	Zn(1)*	Zn(2)*	Na(1)*	Na(2)*	Na(3)*	Si(1)	Si(2)	Si(3)	Si(4)	S
O(1)		0.87						0.03		1.10				2.00
O(2)	0.79								0.08			1.04		1.91
O(3)				0.68 $\times 2\downarrow$		0.17	0.06			0.98				1.89
O(4)		0.86						0.04				1.10		2.00
O(5)				0.65 $\times 2\downarrow$	0.14		0.06				0.98			1.83
O(6)	0.94					0.26	0.03							1.30
						0.03	0.04							
O(7)	0.69								0.08	1.16				1.93
O(8)								0.05	0.05			1.02	1.03	2.15
O(9)			0.61 $\times 2\downarrow$			0.17	0.06						1.02	1.86
O(10)	0.90							0.07			1.10			2.07
O(11)				0.68 $\times 2\downarrow$	0.09	0.15		0.09						1.01
O(12)			0.71 $\times 2\downarrow$		0.10	0.15			0.11					1.07
O(13)			0.64 $\times 2\downarrow$		0.18		0.06					1.01		1.89
O(14)	0.88							0.08					1.07	2.03
O(15)		0.91							0.05				0.96	1.92
O(16)		0.92							0.04		0.98			1.94
O(17)								0.04	0.03	0.98	0.98			2.03
O(18)		1.11			0.15		0.18							1.59
					0.15									
O(19)	0.31													0.31
O(20)		0.34												0.34
O(21)								0.30						0.30
O(22)									0.30					0.30
Σ	4.51*	5.01	3.92	4.02	0.81*	0.93*	0.49*	0.70*	0.74*	4.22	4.04	4.17	4.08	

* Calculated taking into account site occupancies (see Table 3). Parameters are taken from Brese and O'Keeffe (1991).

Table 6. Comparative data for zvyaginite, epistolite, vigrishinite, and murmanite

Mineral	Zvyaginite	Epistolite	Vigrishinite	Murmanite*
Formula	$\text{NaZnNb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}(\text{OH}, \text{F})_3 \cdot (\text{H}_2\text{O})_{4+x}$ ($x < 1$)	$\text{Na}_4\text{Nb}_2\text{Ti}[\text{Si}_2\text{O}_7]_2\text{O}_2(\text{OH}, \text{F})_2 \cdot (\text{H}_2\text{O})_4$	$\text{Zn}_2\text{Ti}_{4-x}\text{Si}_x\text{O}_7\text{I}_2(\text{OH}, \text{H}_2\text{O})_8$ ($x < 1$)	$\text{Na}_4\text{Ti}_4[\text{Si}_2\text{O}_7]_2\text{O}_4(\text{H}_2\text{O})_4$
Symmetry	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$ or $P1$
H-layer	$\text{Nb}_2(\square, \text{Na})_2\text{O}(\text{OH})\text{Si}_4\text{O}_{14}$	$\text{Nb}_2(\text{Na}, \square)_2\text{O}_2\text{Si}_4\text{O}_{14}$	$(\text{Ti}, \square)_2\text{Zn}(\text{OH}, \text{H}_2\text{O}, \square)_8\text{Si}_4\text{O}_{14}$	$\text{Ti}_2\text{Na}_2\text{O}_2\text{Si}_4\text{O}_{14}$
O-layer	$\text{Ti}(\text{Zn}, \square)_2(\square, \text{Na})(\text{OH}, \text{F})_2$	$\text{Ti}(\text{Na}, \square)_3(\text{OH}, \text{F})_2$	$(\text{Ti}, \square)_2(\text{OH}, \text{H}_2\text{O})$	$\text{Ti}_2\text{Na}_2\text{O}_2$
Interlayer space	$(\text{H}_2\text{O})_{4+x}$	$(\text{H}_2\text{O})_4$	$\text{Zn}(\text{H}_2\text{O})_{1-x}$	$(\text{H}_2\text{O})_4$
$a, \text{\AA}$	8.975	5.460	8.743	5.387
$b, \text{\AA}$	8.979	7.170	8.698	7.079
$c, \text{\AA}$	12.135	12.041	11.581	11.74
$\alpha, ^\circ$	74.328	103.63	91.54	93.80
$\beta, ^\circ$	80.651	96.01	98.29	97.93
$\gamma, ^\circ$	73.959	89.98	105.65	90.00
$V, \text{\AA}^3$	900.8	455.4	837	441.7
Z	2	1	2	1
Strongest reflections in the X-ray powder pattern ($d, \text{\AA} - I$)	11.72–100 5.83–40 5.28–53 4.289–86 2.916–57 2.862–72	12.00–80 5.902–70 4.322–100 2.990–90 2.869–90 1.790–70	11.7–67 8.27–50 6.94–43 5.73–54 4.17–65 2.861–100	11.56–90 5.81–90 4.22–100 3.762–60 2.867–100
Density, g/cm ³	2.88	2.65–2.89	3.03	2.76–2.84
α	1.626	1.610	1.755	1.682–1.735
β	1.714	1.650–1.720	1.82	1.765–1.770
γ	1.740	1.682–1.770	1.835	1.807–1.839
Optical sign, $2V$ (meas.)	(–)45°	(–)60–80°	(–)45°	(–)57–64°
Reference	This study	Antony et al., 1995; Sokolova, Hawthorne, 2004	Pekov et al., (2012)	Khalilov (1989); Nemeth et al., 2005; Camara et al., 2008

* The crystal structure of murmanite was also resolved in the unit cell corresponding to the unit cells of vigrishinite and zvyaginite: $a = 8.700$, $b = 8.728$, $c = 11.688$ Å, $\alpha = 94.31^\circ$, $\beta = 98.62^\circ$, $\gamma = 105.62^\circ$, $V = 830$ Å³, $Z = 2$ (Rastsvetaeva and Andrianov, 1986).

with Zn-free epistolite. The similar formation mechanism of vigrishinite from lomonosovite/murmanite was previously discussed in detail (Pekov et al., 2012).

Zvyaginite contains Zn cations in the *O*-layer, core of the *HOH* block, in contrast to vigrishinite, where most Zn is concentrated in the outer *H* layers and residually occurs in the space between *HOH*-blocks along with H_2O molecules (Fig. 6). Vigrishinite and zvyaginite, being not only cognate but also intimately associated minerals, which are formed simultaneously as a result of the same natural process, nevertheless show significant crystal chemical differences, which follow essential differences between their precursors, murmanite and epistolite.

The individual features of the bond order in their structures are probably the crucial factor. For example, in the *O*-layer of murmanite $[\text{Ti}_2\text{Na}_2\text{O}_2]$, anions O^{2-} are valence-saturated mainly with Ti^{4+} and change of univalent cation Na for divalent Zn results in local excess of positive charge. In the *O*-layer of epistolite $[\text{Ti}(\text{Na},\square)_3(\text{OH},\text{F})_2]$, the content of Ti is twice as low and thus favors the substitution of Na^+ for Zn^{2+} . At the same time, Nb^{5+} occurs in the *H*-layer of epistolite, while Ti^{4+} occurs in murmanite, probably preventing substitution of Na for higher charge cations in the first case. Windows in the outer *H*-layers of the *HOH*-blocks (Fig. 4b) facilitate access of Zn^{2+} cations to the core *O*-layer of *HOH*-block in epistolite by exchange.

The cation-exchange mechanism of the formation of zvyaginite and vigrishinite is supported by our ion-exchange experiments with epistolite and murmanite. Both minerals easily exchange Na^+ for Zn^{2+} in aqueous solutions under mild conditions ($<100^\circ\text{C}$). Up to 13.0 (Lykova et al., 2013) and 12.9 wt % ZnO were found in the cation-replaced murmanite and epistolite, respectively. Thus, it cannot be ruled out that epistolite and murmanite are transformed into zvyaginite and vigrishinite, respectively, even under supergene conditions.

The dissolved sphalerite is the evident source of Zn for zvyaginite and vigrishinite. In the decomposition of the great amount of sphalerite that is observed in Pegmatite no. 71 and some other pegmatites of the Lovozero pluton, the local enrichment of hydrothermal systems in Zn could be significant. A series of low-temperature aqueous zinc silicates was found within the leached cavities of sphalerite or close to them (at distance up to 1–3 cm) in many hydrothermally altered pegmatites of this pluton. Zn–Al smectites are the most common; zincsilite is less frequent (Semenov, 1972; Pekov, 2000); the members of the labuntsovite group, kuzmenkoite–Zn, organovite–Zn, alsakharovite–Zn, lepkhenelmite–Zn are rather common (Chukanov et al., 2003). It is supposed that these minerals immediately crystallized from the late-stage hydrothermal solutions enriched in Zn. In contrast to them, the ion-exchange mechanism of enrichment in Zn of heterophyllosilicates of the epistolite group is

the most probable. This is consistent with the experimentally established fact (Lykova et al., 2013a, 2013b) that unlike zeolites and other microporous silicates with the framework structures, which the most actively adsorb alkali and alkali-earth cations, natural heterophyllosilicates of the epistolite group are distinguished by high exchange capacity in regard to chalcophile elements, particularly Ag and Zn.

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