

Belomarinaite $\text{KNa}(\text{SO}_4)$: A new sulphate from 2012–2013 Tolbachik Fissure eruption, Kamchatka Peninsula, Russia

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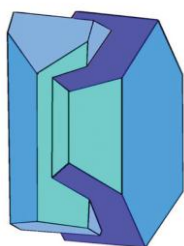
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Abstract

Belomarinaite, ideally KNaSO_4 , is a new sulphate mineral discovered in the Toludskoe lava field formed during Tolbachik Fissure eruption in 2012–2013. The mineral occurs as arborescent aggregates of tabular crystals ($1 \times 0.3 \times 0.1 \text{ mm}^3$) comprising hematite impurities. The average size of the aggregates is 0.5–0.7 mm. The empirical formula is $(\text{K}_{0.95}\text{Na}_{0.92}\text{Cu}_{0.04})\text{S}_{1.01}\text{O}_4$. The crystal structure of belomarinaite was determined using single-crystal X-ray diffraction data: space group $P3m1$, $a = 5.6072(3)$, $c = 7.1781(4) \text{ \AA}$, $V = 195.45(2) \text{ \AA}^3$, $Z = 2$, $R_1 = 2.6\%$. In the crystal structure of belomarinaite, there are six cation sites: the $^{[4]}\text{S}(1,2)$ sites are occupied by S, the $^{[6]}\text{Na}$ and $^{[12]}\text{K}$ sites are occupied by Na and K, respectively, giving $\text{Na}_{0.5}\text{K}_{0.5}$ apfu and the $^{[10]}\text{M1}$ and $^{[10]}\text{M2}$ sites are occupied by $\text{Na}_{0.80}\text{K}_{0.20}$ and $\text{K}_{0.80}\text{Na}_{0.20}$ apfu, respectively. The crystal structure is a framework of SO_4 tetrahedra, Na octahedra and K, M1 and M2 polyhedra. Belomarinaite is isostructural with the synthetic compound KNaSO_4 . In belomarinaite, Na and K are disordered over M1 and M2 sites; in its synthetic analogue, Na and K are ordered over M1 and M2 sites,



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respectively. Its Mohs' hardness is 2–3. The mineral is uniaxial (+), $\omega = 1.485(3)$, $\varepsilon = 1.488(3)$ ($\lambda = 589$ nm). The strongest lines of the X-ray powder diffraction pattern (d , Å (I , %) (hkl)) are: 4.022 (31) (101); 3.591 (26) (002); 2.884 (74) (102); 2.800 (100) (110); 2.391 (16) (003); 2.296 (8) 201; 2.008 (38) (022); and 1.634 (10) (212). The mineral was named in honour of Russian volcanologist Marina Gennadievna Belousova (b. 1960) for her significant contributions to the monitoring of the Tolbachik Fissure eruption.

Keywords: New mineral, Belomarinaite, Sulphate, Crystal structure, Fumarole minerals, Kamchatka peninsula

Introduction

In this work, the occurrence, crystal structure and properties of belomarinaite, a new mineral from Tolbachik Volcano, are reported.

In the system Na_2SO_4 – K_2SO_4 , eight phases have been described: $\text{K}_3\text{Na}(\text{SO}_4)_2$ ($P-3m1$), KNaSO_4 ($P3m1$), α - K_2SO_4 ($P6_3/mmc$), β - K_2SO_4 ($Pm\bar{c}n$), Na_2SO_4 ($Fddd$), Na_2SO_4 ($Cmcm$), Na_2SO_4 ($P6_3/mmc$) and Na_2SO_4 ($Pbnm$). But only five of them have been discovered as minerals: aphtitalite ($\text{K}_3\text{Na}(\text{SO}_4)_2$), thenardite (Na_2SO_4) ($Fddd$), metathenardite (Na_2SO_4) ($P6_3/mmc$), arcanite (K_2SO_4) ($Pm\bar{c}n$) and now belomarinaite (KNaSO_4). Moreover, metathenardite and belomarinaite were discovered in the last two years. Crystal chemistry of aphtitalite and related structures was reviewed by Moore (1973, 1976, 1981), Eysel (1973), Egorov-Tismenko et al. (1984) and Hawthorne et al. (2000).

Belomarinaite was discovered on the Toludskoe lava field which was formed during Tolbachik Fissure eruption in 2012–2013 (latitude $55^\circ 45' 1.32''$, longitude $160^\circ 19' 40.74''$, altitude 1480 m). The specimen was found in a skylight of a lava tube which emanated volcanic gases of temperature equals to 1024°C (Fig. 1). According to our unpublished HTXRD data, belomarinaite exists in the temperature range 20– 460°C .

Belomarinaite has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal 2017-69a). The

mineral was named in honour of Russian volcanologist Marina Gennadievna Belousova (b. 1960) (Institute of Volcanology and Seismology, Russian Academy of Sciences, Petropavlovsk–Kamchatskiy, Russia) for her significant contributions to the monitoring of the Tolbachik Fissure eruption. The type material is deposited in the Mineralogical Museum of Saint Petersburg State University (catalogue number 1/19678).

Experimental methods and results

General appearance and physical properties

Belomarinaite occurs as arborescent aggregates of tabular crystals up to $1 \times 0.3 \times 0.1 \text{ mm}^3$ (Fig. 2). Average linear size of the aggregates is 0.5–0.7 mm. Colour is pale blue to green. Streak is white. It has a vitreous lustre. No cleavage is observed in the arborescent aggregates. Fracture is irregular to uneven. Parting is not observed. The Mohs' hardness is 2–3. Calculated density based on empirical formula and single-crystal unit cell parameters is 2.687 g/cm^3 .

The mineral is optically uniaxial, positive, $\omega = 1.485(3)$, $\varepsilon = 1.488(3)$ ($\lambda = 589 \text{ nm}$). No dispersion is observed. It does not exhibit pleochroism. The Gladstone–Dale compatibility index (Mandarino, 1981) based on empirical formula and unit cell parameters from powder XRD data is calculated as $1 - (K_p/K_C) = 0.007$ (superior).

Chemical composition

58 analyses were carried out using a TESCAN 'Vega3' electron microprobe equipped with an Oxford Instruments X-Max 50 silicon drift EDS system, operated at 20 kV and 0.730 nA, and a beam size of 0.22 μm . Analytical results are given in Table 1. Processing was performed using AZtec software and X-MAX-80 mm^2 detector (Institute of Volcanology and Seismology, Petropavlovsk–Kamchatsky, Russia). The empirical formula based on 4 O *apfu* is $(\text{K}_{0.95}\text{Na}_{0.92}\text{Cu}_{0.04})_{\Sigma 1.91}\text{S}_{1.01}\text{O}_4$. The ideal formula is KNaSO_4 , which requires Na_2O 19.60, K_2O 29.78 and SO_3 50.62 wt%.

TABLE 1. Chemical composition of belomarinaite.

Constituent	Mean	Range	Stand. Dev.	Probe Standard
Na ₂ O	18.14	16.51–20.60	0.87	Sanidine
K ₂ O	28.68	27.27–30.59	0.93	Sanidine
SO ₃	51.46	49.97–52.47	0.48	FeS ₂
CuO	2.29	0.60–3.29	0.56	CuFeS ₂
Total	100.57		0.88	

Powder X-ray diffraction data

Powder X-ray diffraction data were collected using a Rigaku MiniFlex II diffractometer (CuK α radiation; $R = 150$ mm). According to this data, belomarinaite is trigonal, with the space group $P3m1$ and the unit cell parameters $a = 5.607(1)$, $c = 7.178(1)$ Å, $V = 195.25(6)$ Å³ and $Z = 2$.

The experimental and calculated powder-diffraction patterns are given in Table 2. The diagnostic lines are (d , Å (I , %) (hkl)): 4.022 (31) (101); 3.591 (26) (002); 2.884 (74) (102); 2.800 (100) (110); 2.391 (16) (003); 2.296 (8) 201; 2.008 (38) (022); and 1.634 (10) (212).

TABLE 2. Powder X-ray diffraction data of belomarinaite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}	hkl
5	4.858	7	4.856	010
31	4.022	13, 27	4.022, 4.022	011, 101
26	3.591	16	3.589	002
74	2.884	15, 56	2.886, 2.886	012, 102
100	2.800	100	2.803	110
5	2.609	5	2.611	111
6	2.426	5	2.428	020
16	2.391	11	2.392	003
8	2.296	7	2.300	201
2	2.144	2	2.146	103
38	2.008	40	2.011	022
2	1.820	4	1.820	113
4	1.794	5	1.794	004
10	1.634	12	1.634	212
8	1.618	11	1.618	030
6	1.512	9	1.511	114
3	1.443	3	1.443	204
6	1.401	10	1.401	220
1	1.376	2	1.376	105
2	1.259	5	1.260	132

Single-crystal X-ray diffraction data

Single-crystal X-ray diffraction data were collected using a Bruker Kappa APEX DUO diffractometer equipped with an image plate using MoK α radiation. A hemisphere of three-dimensional data was collected using a frame width of 0.5° in ω , with 50 s used to acquire each frame. The data were corrected for Lorentz, polarisation and background effects using Bruker programs APEX and XPREP. A semi-empirical absorption-correction based on the intensities of equivalent reflections was applied in the SADABS program.

The crystal structure of belomarinaite was solved by charge flipping and refined on the basis of 713 unique observed reflections using Jana 2006 program suite (Petricek *et al.* 2006) (Table 3). Atomic coordinates, atomic anisotropic displacement parameters and selected bond distances are given in Tables 4–6. The crystal structure of belomarinaite and coordination polyhedra of alkali cations are given in Figures 3–4.

Discussion

Crystal structure of belomarinaite

Belomarinaite is isostructural with the synthetic compound KNaSO₄ [space group $P3m1$, $a = 5.6066(7)$, $c = 7.177(1)$ Å, $Z = 2$, $R_1 = 4.2\%$] (Okada and Ossaka, 1980). In the crystal structure of belomarinaite, there are six cation sites: the ^[4]S(1,2) sites occupied by S, the ^[6]Na and ^[12]K sites and the ^[10]M1 and ^[10]M2 sites. The S1–O and S2–O distances are 1.378–1.446 and 1.458–1.485 Å, respectively. The Baur (1974) distortion index in belomarinaite for the S1O₄ is 0.018 and 0.007 for the S2O₄, thus distortions of the SO₄ tetrahedra are relatively high. The K and Na sites are occupied by one alkali atom, K and Na, respectively, with a standard deviation of ± 0.02 – 0.03 . The Na atom is octahedrally coordinated by six O atoms with Na–O = 2.332–2.355 Å (Table 6). The K–O distances vary from 2.842 to 3.254 Å (average 3.06 Å). The M2–O distances vary from 2.388 to 3.150 Å (average distance is 2.87 Å) and the M1–O distances vary from 2.588 to 3.050 Å (average distance is 2.86 Å). The crystal structure refinement performed

in the current work let us to conclude that the M1 site is occupied at 78% by Na and at 22% by K atoms, $\text{Na}_{0.78}\text{K}_{0.22}$, *i.e.* $\text{Na}_{0.39}\text{K}_{0.11}$ apfu and the M2 site is occupied at 78% by K and at 22% by Na atoms, $\text{K}_{0.78}\text{Na}_{0.22}$, *i.e.* $\text{K}_{0.39}\text{Na}_{0.11}$ apfu (Table 4). The M2 and M1 polyhedra share common faces of $2.4 \times 3.4 \text{ \AA}^2$. The size of these faces is suitable for atomic migration and for K–Na order–disorder processes as well (Fig. 4). The crystal structure is a framework of SO_4 tetrahedra, Na octahedra and K, M1 and M2 polyhedra. The apices of neighbouring SO_4 tetrahedra point in opposite directions along the *c*-axis.

Okada and Ossaka (1980) showed that the K and Na atoms are ordered at the M2 and M1 sites. We conclude that (1) belomarinaite is isostructural with its synthetic analogue KNaSO_4 and (2) in belomarinaite, Na and K are disordered over M1 and M2 sites; in its synthetic analogue, Na and K are ordered over M1 and M2 sites, respectively.

Belomarinaite is also structurally related to aphthitalite, möhnite, bubnovaite, hanksite and metatenardite (Table 7).

TABLE 3. Crystal data, data collection information and structure refinement details for belomarinaite.

Chemical formula	KNaSO_4
M_r	158.1
Crystal system, space group	Trigonal, $P3m1$
Temperature (K)	293
a, c (\AA)	5.6072 (3), 7.1781 (4)
V (\AA^3)	195.45 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.87
Crystal size (mm)	0.10×0.07×0.08
Diffractometer	Bruker Kappa APEX DUO
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	2069, 713, 664
R_{int}	0.012
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.851
$R[F^2 > 3\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.033, 1.95
No. of reflections	713
No. of parameters	38
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.28, −0.34

TABLE 4. Atomic coordinates, equivalent isotropic displacement parameters (\AA^2) and structural occupancy factor of belomarinaite.

	x	y	z	U_{eq}	Occ. (<1)
Na	0	0	0.5165 (12)	0.0233 (5)	
$M1(\text{Na/K})$	0.666667	0.333333	0.6981 (3)	0.0199 (9)	0.78/0.22
$M2(\text{K/Na})$	0.333333	0.666667	0.3183 (2)	0.0303 (8)	0.78/0.22
K	0	0	0.0124 (5)	0.0368 (4)	
S1	0.666667	0.333333	0.2505 (3)	0.0213 (6)	
S2	0.333333	0.666667	0.7787 (3)	0.0145 (5)	
O1	0.666667	0.333333	0.0586 (14)	0.071 (4)	
O2	0.333333	0.666667	0.9856 (12)	0.0378 (18)	
O3	0.1913 (6)	-0.1913 (6)	0.7128 (11)	0.058 (3)	
O4	0.8070 (5)	-0.8070 (5)	0.3180 (11)	0.055 (2)	

TABLE 5. Anisotropic atomic displacement parameters (\AA^2) of belomarinaite.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0174 (5)	0.0174 (5)	0.035 (1)	0.0087 (2)	0	0
$M1$	0.0145 (9)	0.0145 (9)	0.031 (2)	0.0072 (4)	0	0
$M2$	0.0325 (8)	0.0325 (8)	0.026 (2)	0.0162 (4)	0	0
K	0.0450 (5)	0.0450 (5)	0.0204 (7)	0.0225 (2)	0	0
S1	0.0173 (7)	0.0173 (7)	0.029 (1)	0.0086 (3)	0	0
S2	0.0151 (6)	0.0151 (6)	0.0134 (9)	0.0075 (3)	0	0
O1	0.099 (5)	0.099 (5)	0.016 (3)	0.049 (3)	0	0
O2	0.045 (2)	0.045 (2)	0.023 (3)	0.023 (1)	0	0
O3	0.078 (3)	0.078 (3)	0.050 (3)	0.063 (3)	-0.005 (1)	0.005 (1)
O4	0.049 (2)	0.049 (2)	0.081 (4)	0.036 (2)	-0.019 (1)	0.019 (1)

TABLE 6. Selected interatomic distances (\AA) in the structure of belomarinaite.

Bond	Distance	Bond	Distance
K		$M1(\text{Na}_{0.78}\text{K}_{0.22})$	
K—O3	$2.842(7) \times 3$	M1—O1	2.588(10)
K—O4	$2.885(7) \times 3$	M1—O3	$2.816(4) \times 6$
K—O1	$3.243(2) \times 3$	M1—O4	$3.050(8) \times 3$
K—O2	$3.254(2) \times 3$	<M1—O>	2.863
<K—O>	3.056	$M2(\text{K}_{0.78}\text{Na}_{0.22})$	
Na		M2—O2	2.388(7)
Na—O3	$2.332(8) \times 3$	M2—O4	$2.815(2) \times 6$
Na—O4	$2.355(8) \times 3$	M2—O3	$3.150(5) \times 3$
<Na—O>	2.344	<M2—O>	2.873
S1—O1	1.378(10)	S2—O2	1.485(8)
S1—O4	$1.446(4) \times 3$	S2—O3	$1.458(5) \times 3$
<S1—O>	1.429	<S2—O>	1.465

TABLE 7. Crystallographic data for belomarinaite and related minerals (based on Gorelova *et al.* 2016).

Mineral	Chemical formula	Sp. gr.	<i>a</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³	Reference
Belomarinaite	KNaSO ₄	<i>P3m1</i>	5.604(1)	7.178(2)	195.24(7)	This work
	KNaSO ₄ (Synthetic)	<i>P3m1</i>	5.607(1)	7.177(1)	195.4(1)	Okada & Osaka, 1980
Aphthitalite	K ₃ Na(SO ₄) ₂	<i>P-3m1</i>	5.680(1)	7.309(3)	204.2(1)	Okada & Osaka, 1980
Möhnite	(NH ₄)K ₂ Na(SO ₄) ₂	<i>P-3m1</i>	5.7402(3)	7.435(1)	212.16(1)	Chukanov <i>et al.</i> 2015
Metathenardite	Na ₂ SO ₄	<i>P6₃/mmc</i>	5.347 (1)	7.088 (2)	175.48(7)	Pekov <i>et al.</i> 2016
	α -K ₂ SO ₄ (at 800 °C)	<i>P6₃/mmc</i>	5.947(2)	8.375(3)	256.5(1)	Miyake <i>et al.</i> 1980
Bubnovaite	K ₂ Na ₈ Ca(SO ₄) ₆	<i>P31c</i>	10.804(3)	22.011(6)	2225(2)	Gorelova <i>et al.</i> 2016
Hanksite	Na ₂₂ K(SO ₄) ₉ (CO ₃) ₂ Cl	<i>P6₃/m</i>	10.490(1)	21.240(1)	2024(1)	Kato & Saalfeld, 1972

The inheritance of the cation polyhedra during the cooling of the high-temperature solid solutions

The bond lengths in the Na-dominant ^[10]M1 polyhedron ($\langle \text{M1-O} \rangle = 2.83 \text{ Å}$) are too large for Na compared to the mean value of 2.34 Å (International Tables., 2006). To understand the nature of this phenomenon, let us consider similar examples in BaNaMe(BO₃)₂ (*Me* = Sc, Y) borates describe in (Volkov *et al.*, 2012). According to the data (International Tables, 2006), the mean $\langle \text{Ba-O} \rangle$ and $\langle \text{Na-O} \rangle$ bond lengths are 2.738 and 2.336 Å, respectively. At high temperatures, these cations (Ba²⁺ and Na⁺) are disordered over the same cation sites. Further, upon the cooling, the Ba and Na atoms become ordered at 775°C (Sc) and 375°C (Y), respectively. Moreover, a cation ordering leads to a slight rearrangement of the BaO₉ ($\langle \text{Ba-O} \rangle = 2.796 \text{ Å}$ (Sc) and 2.822 Å (Y)) and NaO₉ ($\langle \text{Na-O} \rangle = 2.873 \text{ Å}$ (Sc) and 2.867 Å (Y)) coordination polyhedra (Fig. 4). In the NaO₆ polyhedra (Fig. 4, solid lines), the bonds are also

large, 2.642 and 2.714 Å. The BaO₉ and NaO₉ polyhedra are linked between each other by shared faces of 3.4×3.4 Å².

These examples can be used to the investigation of the mineral inheritance occurred in the belomarinaite crystal structure upon cooling. The mineral was found in a skylight of a lava tube at about 1000 °C. High-temperature polymorphs of K₂SO₄, K₃Na(SO₄)₂, KNaSO₄, Na₂SO₄ are isotypic and crystallise in the *P*6₃/*mmc* space group (Fishmeister, 1962). At room temperature, K₃Na(SO₄)₂ and KNaSO₄ are structurally similar to their high-temperature polymorphs (Gorelova et al., 2016). Also in the crystal structure of room- and high-temperature polymorphs the K and Na coordination polyhedra are similar. In the crystal structure of belomarinaite the K atoms form regular coordination polyhedra with mean bond lengths equal to 2.87 and 3.06 Å, while the Na atoms form one regular coordination polyhedron with bond lengths equal to 2.332 – 2.355 Å and one unusual, M1O₁₀, in which M–O chemical bonds are much longer (2.588 – 3.050 Å). The K and Na atoms are ordered over two [10]-coordinated *M*1 and *M*2 sites upon cooling due to its difference in ionic radii. One can suggest that the longer Na–O bonds of the unusual NaO₁₀ polyhedron are inherited from the high-temperature polymorph KNaSO₄ (*P*6₃/*mmc*).

Conclusions

As a result of the investigation of the chemical composition, crystal structure and physical properties of samples from Tolbachik Volcano (Kamchatka Peninsula), a new mineral belomarinaite, ideally KNaSO₄, was discovered. The consideration of crystal structure lets one to conclude that belomarinaite is an example of the phase, which forms in the crystallisation system in accordance with Ostwald's rule (Ostwald, 1897; Krivovichev et al. 2016). As a result of high-temperature exhalation processes, structural fragments of phases crystallised first are structurally similar to the atomic and molecular structure of volcanic gases, which produce these phases.

The K and Na atoms are ordered in the crystal structure of belomarinaite. These atoms are disordered over two sites in the crystal structure of high-temperature KNaSO_4 which crystallises in the $P6_3/mmc$ space group (Fishmeister, 1962). The differences between the atoms ionic radii increase with the temperature decrease. According to this, the M1O_{10} coordination polyhedron with the very long Na–O bonds in the crystal structure of belomarinaite are inherited from the high-temperature polymorph of KNaSO_4 . At the early stages of the cooling process, the solid solutions, which contain the small cations in its chemical composition, can be crystallised as the phases, which contain inherited polyhedra with relatively long bond lengths.

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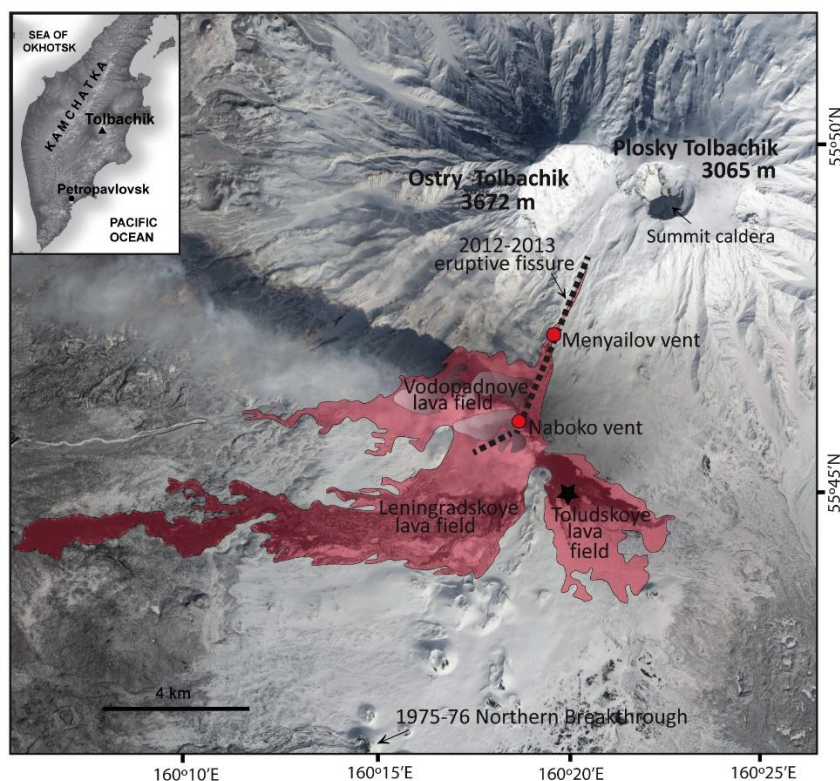
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Figure captions

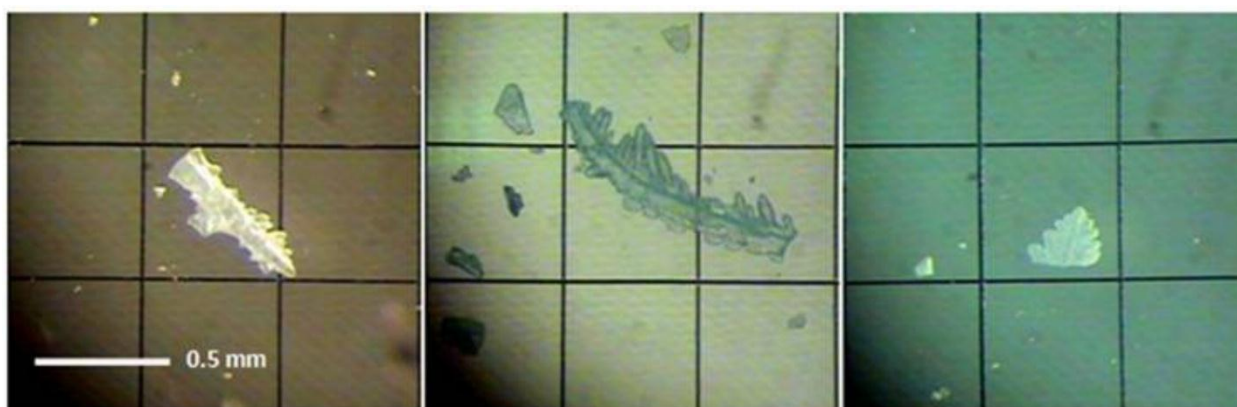


a

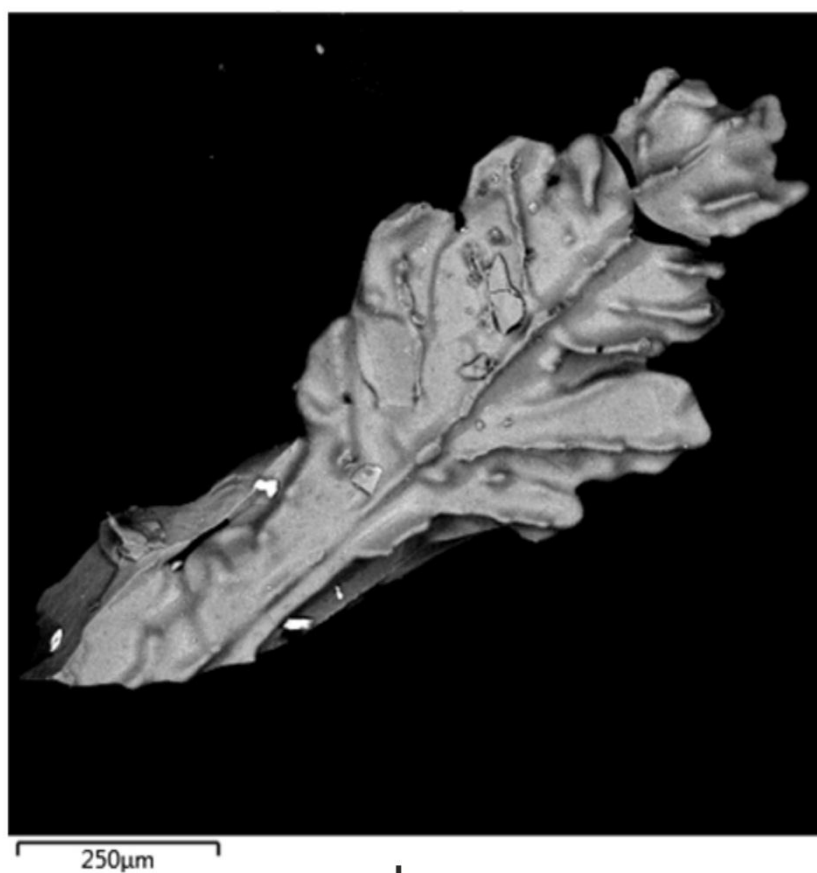


b

FIG. 1. a – Photo of the lava fields of the 2012-2013 Tolbachik eruption showing the place of finding of belomarinaite mineral (Toludskoye lava field) (Belousov *et al.* 2015, with modifications by A. B. Belousov), b – The skylight of a lava tube where the belomarinaite mineral was found (greenish-yellow deposit on a roof of a tube). Photo by M.G. Belousova.



a



b

FIG. 2. a – Optical images of belomarinaite, b – Electron microscope image of arborescent aggregate of belomarinaite.

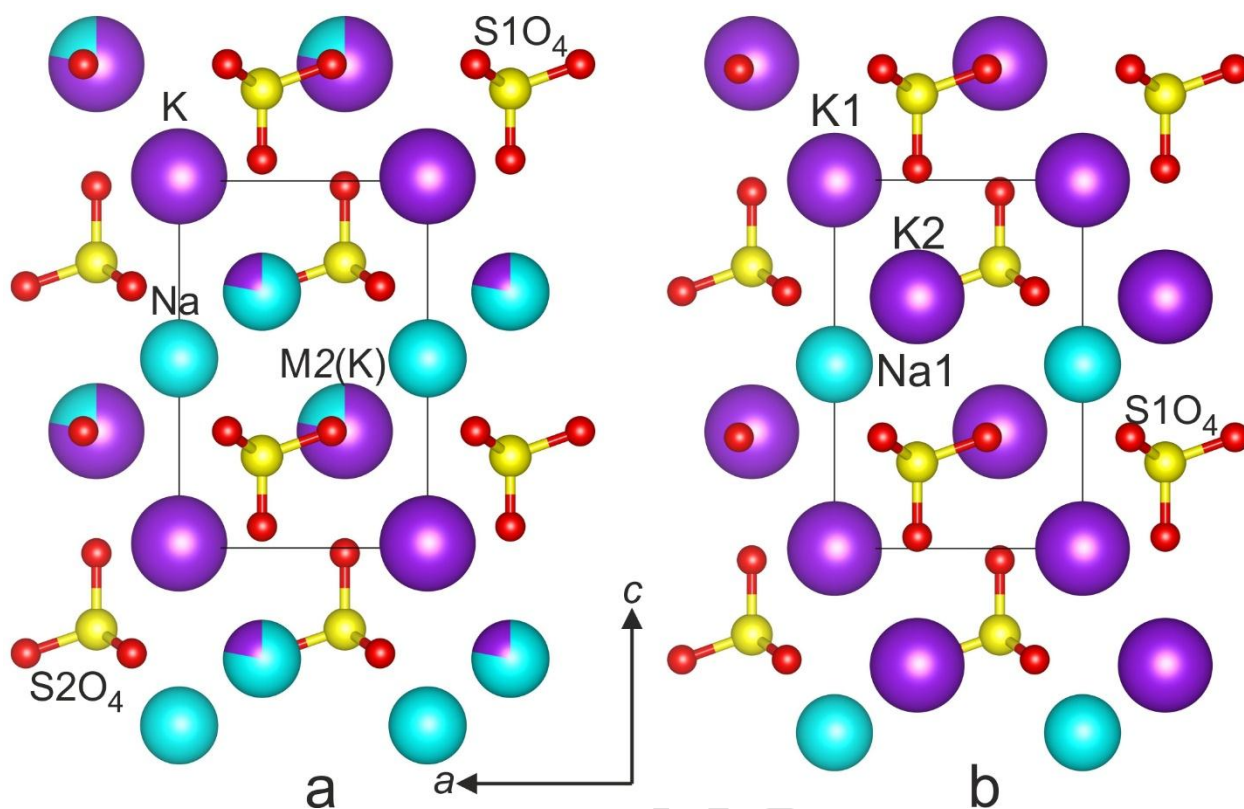


FIG. 3. Crystal structure of belomarinaite (a) and aphthitalite (b)

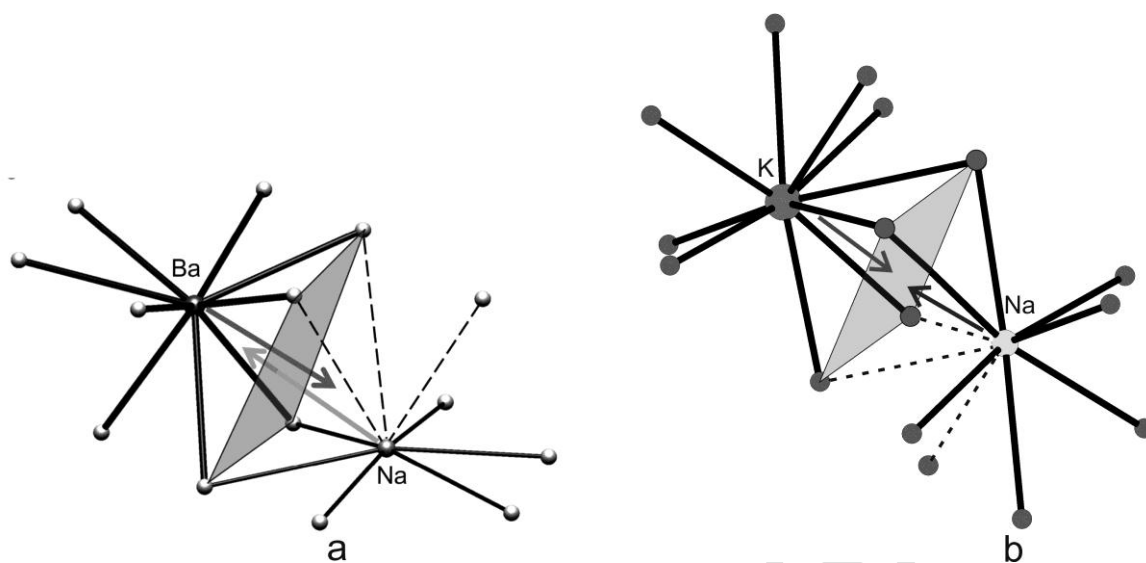


FIG. 4. The linkage of the inherited polyhedra: a – BaO₉ and NaO₉ polyhedra in the BaNaMe(BO₃)₂ (Me = Sc, Y) crystal structures (Volkov, Filatov et al., 2012), b – Na₂O₁₀ and K₂O₁₀ polyhedra in the belomarinaite crystal structure (this work). Solid lines mark normal Na polyhedra.