НОВЫЕ МИНЕРАЛЫ

PHILOXENITE, $(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$, A NEW MINERAL FROM FUMAROLE EXHALATIONS OF THE TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

© 2020 г. I. V. Pekov[1, *], A. A. Agakhanov[2], N. V. Zubkova[1], D. I. Belakovskiy[2], M. F. Vigasina[1], S. N. Britvin[3, 4], A. G. Turchkova[1], and E. G. Sidorov[5]

[1]*Faculty of Geology, Moscow State University, Vorobievy Gory, Moscow, 119991 Russia*

[2]*Fersman Mineralogical Museum RAS, Leninsky pr., 18-2, Moscow, 119071 Russia*

[3]*Institute of Earth Sciences, Saint Petersburg State University, University emb., 7/9, Saint Petersburg, 199034 Russia*

[4]*Kola Science Center RAS, Fersman st., 14, Apatity, 184200 Russia*

[5]*Institute of Volcanology and Seismology, Far Eastern Branch RAS, Piip Boulevard, 9, Petropavlovsk-Kamchatsky, 683006 Russia*

**e-mail: igorpekov@mail.ru*

Received May 18, 2020; Revised May 18, 2020; Accepted June 17, 2020

A new mineral philoxenite $(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$ is found in sublimates of the Yadovitaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with euchlorine, langbeinite, hematite, tenorite, piypite, alumoklyuchevskite, dolerophanite, vergasovaite, cupromolybdite, ziesite, and yaroshevskite. Philoxenite forms isolated oblique-angled, pseudotrigonal or polygonal tabular crystals up to 0.3 × 0.6 mm. The mineral is transparent, colourless to very pale yellowish with a vitreous lustre. Philoxenite is brittle. Cleavage was not observed, the fracture is uneven. D_{calc} = 3.03 g cm^{-3}. Philoxenite is optically biaxial (–), α = 1.562(2), β = 1.572(2), γ = 1.580(2), $2V_{meas}$ = 85(5)° (λ = 589 nm). The Raman spectrum is given. The chemical composition (wt %, electron-microprobe data) is: Na_2O 4.67, K_2O 13.34, Rb_2O 0.13, CaO 2.84, PbO 4.54, MgO 6.37, MnO 0.20, CuO 5.40, ZnO 1.48, Al_2O_3 3.40, Fe_2O_3 3.29, SO_3 54.62, total 100.28. The empirical formula calculated on the basis of 32 O *apfu* is $(K_{3.30}Na_{1.76}Ca_{0.59}Pb_{0.24}Rb_{0.02})_{\Sigma 5.91}(Mg_{1.84}Cu_{0.79}Al_{0.78}Fe^{3+}_{0.48}Zn_{0.21}Mn_{0.03})_{\Sigma 4.13}S_{7.96}O_{32}$. Philoxenite is triclinic, space group *P*-1, *a* = 8.8410(3), *b* = 8.9971(3), *c* = 16.1861(5) Å, α = = 91.927(3), β = 94.516(3), γ = 90.118(3)°, *V* = 1282.77(7) Å^3, and *Z* = 2. The strongest reflections of the X-ray powder pattern [*d*,Å(*I*)(*hkl*)] are: 5.70(18)(111); 4.030(24)(004); 3.146(100)(–220); 3.136(72)(220); 2.965(36)(–1–15), 2.912(35)(–115), 2.834(36)(0–32, 1–15), and 2.784(42)(115, 032). The crystal structure of philoxenite is unique. It is based on a novel-type microporous heteropolyhedral framework built by SO_4 tetrahedra and MO_6 octahedra (*M* = Mg, Cu^{2+}, Zn, Fe^{3+} and Al). The name philoxenite is derived from the ancient Greek words φίλος, *a friend*, and ξένος, *a guest*, in allusion to the complex cationic composition of the mineral and the presence of significant amounts of admixtures at nine of eleven independent cationic positions in its crystal structure.

Keywords: philoxenite, new mineral, sulfate, fumarole, Tolbachik volcano, Kamchatka

DOI: 10.31857/S086960552004005X

INTRODUCTION

Tolbachik volcano at Kamchatka is an outstanding geological object in different aspects. One of them is the mineralogy of the fumarolic formation: at present day, Tolbachik can rightfully be called *the object number 1 in the world* in diversity, originality and knowledge degree of minerals formed in oxidizing-type fumaroles. Almost 350 minerals are reliably known in fumarole systems at Tolbachik and majority of them are of exhalation origin; more than 120 new mineral species have been discovered in Tolbachik fumaroles (Pekov et al., 2020). Sulfates are the most numerous minerals in Tolbachik fumaroles: sixty valid mineral species belonging to this chemical class are known here in high-temperature assemblages. Sulfates are the main constituents in sublimates of the majority of Tolbachik fumaroles. Among the most abundant sulfate minerals there are langbeinite, anhydrite, aphthitalite-group members, euchlorine and some others.

This article is devoted to a new sulfate mineral philoxenite (Cyrillic: филоксенит) $(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$ from fumarolic exhalations of Tolbachik. So complicated crystal chemistry, reflected even in the simplified formula, caused the choice of the name for this mineral species: it is derived from the ancient Greek words φίλος, *a friend*, and ξένος, *a guest*, in allusion to the complex cationic composition of the mineral and the presence of significant amounts of admixtures at nine of eleven independent cationic positions in its crystal structure.

The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2015–108). The type specimen (part of holotype) is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow with the catalogue number 95283.

OCCURRENCE AND GENERAL APPEARANCE

Philoxenite originates from the Yadovitaya ('Poisonous') fumarole located at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption 1975–1976 (NB GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41' N 160°14' E, 1200 m asl). The Second scoria cone of the NB GTFE is a monogenetic volcano about 300 m high and 0.1 km^3 in volume formed in 1975 (Fedotov, Markhinin, 1983). Many active fumaroles occur at this scoria cone even at present day, after more than forty years after the eruption.

Yadovitaya is one of the famous Tolbachik fumaroles, especially in the mineralogical aspect being, in particular, the type locality of twenty-seven (!) valid mineral species. It remains active and hot from 1975 and has been characterized in several papers. The most detailed data were reported by L.P. Vergasova and S.K. Filatov (2016). The gases of the Yadovitaya fumarole are escaping through a cave about 1.5 m wide and 2 m deep with the walls covered by thick incrustations of different sublimate minerals, mainly sulfates. Euchlorine, piypite, langbeinite or metathénardite are prevailing in the different parts of the cave. Arsenate crusts with lammerite as the main component occur in some areas.

Philoxenite is one of the rarest minerals in Yadovitaya: only several crystals are found. All these crystals are present in the single specimen collected by us in July 2015 from the moderately hot zone of the fumarole. The temperature measured using chromel-alumel thermocouple in this zone during collecting was *ca* 250°C. We think that philoxenite was deposited directly from gaseous phase as volcanic sublimate or was formed as a result of the interaction between fumarolic gases and host basalt scoria (probable source of low-volatile Mg, Ca and Al) at temperatures not less than 250–300 °C.

Philoxenite forms isolated well-shaped tabular crystals up to 0.6 mm across and up to 0.3 mm thick. The crystals are oblique-angled, pseudotrigonal or polygonal. They occur in cavities within euchlorine crusts (Fig. 1) overgrowing basalt scoria altered by fumarolic gases. Other

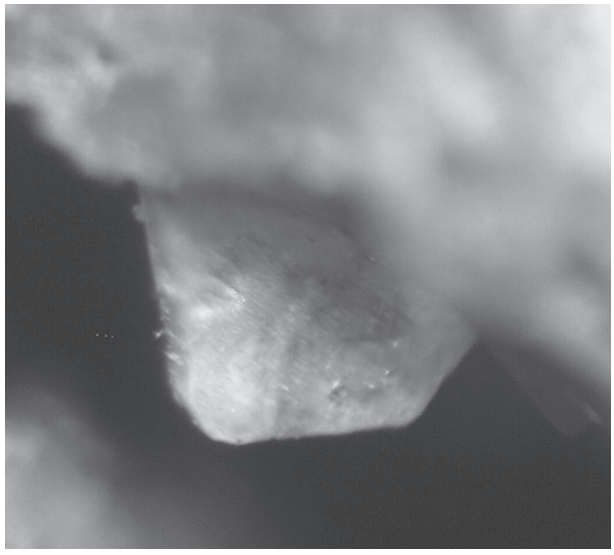

Fig. 1. Tabular crystal of philoxenite on euchlorine. FOV width: 0.7 mm. Photo: I.V. Pekov and A.V. Kasatkin.
Рис. 1. Таблитчатый кристалл филоксенита на эвхлорине. Ширина поля снимка 0.7 мм. Фотография: И.В. Пеков и А.В. Касаткин.

associated minerals are langbeinite, hematite, tenorite, piypite, alumoklyuchevskite, dolerophanite, vergasovaite, cupromolybdite, ziesite, and yaroshevskite.

PHYSICAL PROPERTIES AND OPTICAL DATA

Philoxenite is colourless to very pale yellowish, transparent, with a vitreous lustre and a white streak. The mineral is non-fluorescent in ultraviolet rays. Philoxenite is brittle with uneven fracture and Mohs' hardness of *ca* 3. No cleavage or parting was observed. Density was not measured because of paucity of material; the density calculated using the empirical formula and unit-cell volume obtained from single-crystal data is 3.027 g cm^{-3}.

In plane-polarized transmitted light, philoxenite is colourless and non-pleochroic. It is optically biaxial (–), $\alpha = 1.562(2)$, $\beta = 1.572(2)$, $\gamma = 1.580(2)$ (589 nm), $2V_{meas} = 85(5)°$ and $2V_{calc} = 83°$. Dispersion of optical axes is very strong, $r > v$.

RAMAN SPECTROSCOPY

The Raman spectrum of philoxenite (Fig. 2*a*) was recorded using an EnSpectr R532 spectrometer with an Ar+ laser (532 nm) at room temperature. The output power of the laser beam was about 20 mW. The spectrum was processed using the EnSpectr expert mode program in the range from 100 to 4000 cm^{-1} with the use of a holographic diffraction grating with 1800 lines cm^{-1} and a resolution equal to 6 cm^{-1}. The diameter of the focal spot on the sample was about 10 μm. Raman spectrum was acquired on a polycrystalline (powdered) sample.

The bands in the Raman spectrum of philoxenite and their assignments, according to K. Nakamoto (1986), are (cm^{-1}, s – strong band): 1240, 1185, 1135, 1123 [$F_2(\nu_3)$-type stretching vibrations of SO_4^{2-}], 1043s, 1036s [$A_1(\nu_1)$ symmetric stretching vibrations of SO_4^{2-}], 662, 622, 614 [$F_2(\nu_4)$ bending vibrations of SO_4^{2-}], 490 and 452 [$E(\nu_2)$ bending vibrations of SO_4^{2-}].

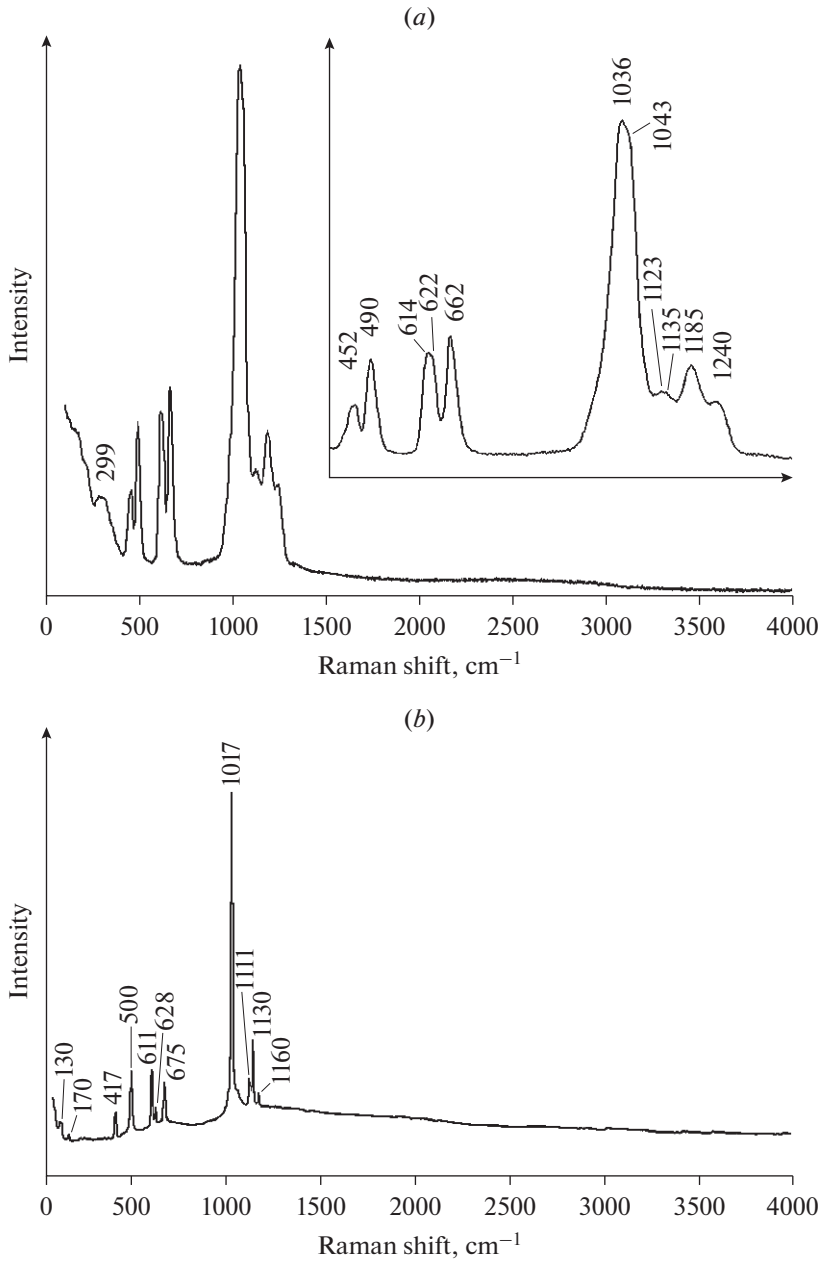

Fig. 2. Raman spectra of philoxenite (*a*, with enlarged low-frequency region) and langbeinite (*b*), both from the Yadovitaya fumarole, Tolbachik volcano, Kamchatka, Russia.

Рис. 2. КР-спектры филоксенита (*a*, с увеличенным фрагментом, показывающим низкочастотную область) и лангбейнита (*b*). Оба образца происходят из фумаролы Ядовитой, вулкан Толбачик, Камчатка.

Table 1. Comparative data for philoxenite and langbeinite
Таблица 1. Сравнительная характеристика филоксенита и лангбейнита

Mineral	Philoxenite	Langbeinite*
Formula	$(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$	$K_2Mg_2(SO_4)_3$
Crystal system	Triclinic	Cubic
Space group	$P\text{-}1$	$P2_13$
a, Å	8.8410(3)	9.92
b, Å	8.9971(3)	
c, Å	16.1861(5)	
α, °	91.927(3)	
β, °	94.516(3)	
γ, °	90.118(3)	
V, Å^3	1282.77(7)	976
Z	2	4
Strong lines of the powder X-ray diffraction pattern: d, Å – I, %	5.70 – 18 4.030 – 24 3.146 – 100 3.136 – 72 2.965 – 36 2.912 – 35 2.834 – 36 2.784 – 42	4.05 – 25 3.137 – 100 2.992 – 16 2.753 – 16 2.651 – 35 2.405 – 12 1.946 – 10 1.609 – 12
Optical data	Biaxial (–), $\alpha = 1.562$, $\beta = 1.572$, $\gamma = 1.580$, $2V_{meas} = 80°$	Isotropic, $n = 1.533$–1.535
Density, g·cm^{-3}	3.03 (calc)	2.77–2.83
Source	this work	Mereiter, 1979; Anthony et al., 2003

* Unit-cell and powder X-ray diffraction data are given for the synthetic analogue of langbeinite (JCPDS-ICDD 19-974).

The absence of bands with frequencies higher than 1250 cm^{-1} indicates the absence of groups with O–H, C–H, C–O, N–H and N–O bonds in philoxenite.

The Raman spectrum of the cubic ($P2_13$) sulfate langbeinite $K_2Mg_2(SO_4)_3$ remotely related to philoxenite, recorded under the same conditions, is shown in Fig. 2*b*. It has some common features with the spectrum of philoxenite, however, the latter contains more bands, including distinct splitting of the strongest band near 1040 cm^{-1}, definitely due to lower symmetry of philoxenite and the presence of eleven differently occupied sites of metal cations in its crystal structure (see below) whereas the structure of langbeinite contains four such sites (Mereiter, 1979).

CHEMICAL DATA

The chemical composition of philoxenite was determined using a Jeol 733 electron microprobe instrument operated in WDS mode with an accelerating voltage of 20 kV, a beam current of 20 nA, and a beam diameter of 3 μm. The chemical composition (average of five spot analyses) is given in Table 2. Contents of other elements with atomic numbers higher than that of carbon are below detection limits.

The empirical formula calculated on the basis of 32 O atoms per formula unit is $K_{3.30}Na_{1.76}Ca_{0.59}Pb_{0.24}Rb_{0.02}Mg_{1.84}Cu_{0.79}Al_{0.78}Fe^{3+}_{0.48}Zn_{0.21}Mn_{0.03}S_{7.96}O_{32}$. It can be also written in the following form, with large A cations and medium-sized M cations grouped taking into consideration the structure data (see below): $^{A}(K_{3.30}Na_{1.76}Ca_{0.59}Pb_{0.24}Rb_{0.02})_{\Sigma 5.91}{}^{M}(Mg_{1.84}Cu_{0.79}Al_{0.78}Fe^{3+}_{0.48}Zn_{0.21}Mn_{0.03})_{\Sigma 4.13}S_{7.96}O_{32}$.

Table 2. Chemical composition (wt %) of philoxenite
Таблица 2. Химический состав (мас. %) филоксенита

Constituent	Mean	Range	Standard deviation	Probe standard
Na_2O	4.67	4.06–5.19	0.42	Albite
K_2O	13.34	13.21–13.50	0.12	Microcline
Rb_2O	0.13	0.00–0.35	0.13	$Rb_2Nb_4O_{11}$
CaO	2.84	2.71–2.99	0.11	Wollastonite
PbO	4.54	4.30–4.97	0.27	$PbTiO_3$
MgO	6.37	5.87–6.65	0.33	Chromite
MnO	0.20	0.00–0.42	0.19	Mn
CuO	5.40	5.13–5.62	0.18	Cu
ZnO	1.48	1.38–1.60	0.10	ZnS
Al_2O_3	3.40	3.15–3.79	0.25	Al_2O_3
Fe_2O_3*	3.29	2.94–3.80	0.37	Magnetite
SO_3	54.62	53.85–54.95	0.47	ZnS
Total	100.28			

* Fe is considered as Fe^{3+} based on the structure data and taking into consideration the extremely oxidizing conditions of mineral deposition in the Yadovitaya fumarole: all other iron minerals, known here, contain only Fe^{3+}.

The Gladstone-Dale compatibility index $[1 - (K_p/K_c)]$ value (Mandarino, 1981) for philoxenite is –0.003, *superior.*

At room temperature philoxenite hydrolyses (becomes dull and soft in half an hour) in H_2O and further slowly dissolves.

X-RAY CRYSTALLOGRAPHY, CRYSTAL STUCTURE DATA AND SIMPLIFIED FORMULA

Powder X-ray diffraction (XRD) data of philoxenite (Table 3) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector (r = 127.4 mm) using Debye-Scherrer geometry, Co$K\alpha$ radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA and an exposure time of 10 min. Angular resolution of the detector is 0.045 2Θ (pixel size 0.1 mm). The data were integrated using the software package osc2tab (Britvin et al., 2017). The powder XRD diagram of philoxenite is unique and can be used as good diagnostic tool for the mineral. Parameters of the triclinic unit cell calculated from powder data are: a = 8.84(4), b = 9.00(2), c = 16.20(3) Å, α = 91.94(3), β = = 94.51(2), γ = 90.08(3)°, V = 1284(1) Å^3, and Z = 2.

Single-crystal XRD studies were carried out using an Xcalibur S CCD diffractometer (Mo-$K\alpha$ radiation). Philoxenite is triclinic, space group P-1. The unit-cell parameters obtained from single-crystal XRD data are given in Table 1.

The crystal structure of philoxenite was solved by direct methods based on single-crystal XRD data and refined to R = 0.0567 on the basis of 5367 independent reflections with $I > 2\sigma(I)$. The crystal structure of the new mineral is unique. It is characterized and discussed in separate paper (Zubkova et al., 2020) and here we report only major structural features of philoxenite.

Table 3. Powder X-ray diffraction data of philoxenite
Таблица 3. Результаты расчета порошковой рентгенограммы филоксенита

I_{obs}	d_{obs}, Å	I_{calc}*	d_{calc}, Å **	*h k l*
3	8.01	2, 2	8.063, 8.004	002, −101
1	7.49	1.5	7.489	101
9	5.99	8	6.016	−1−11
4	5.93	5	5.942	−111
12	5.79	11	5.811	1−11
18	**5.70**	22	5.700	111
1	4.254	1	4.255	−1−13
1	4.148	0.5, 0.5	4.168, 4.159	201, −113
24	**4.030**	19, 1	4.032, 4.027	004, 1−13
6	3.981	6	3.985	0−22
8	3.872	8	3.871	022
4	3.815	4	3.822	121
8	3.740	9	3.745	202
11	3.475	14	3.481	2−12
15	3.433	18	3.433	212
3	3.308	5	3.314	−1−23
4	3.231	2, 0.5	3.276, 3.225	114, 005
9	3.205	11	3.207	1−23
100	**3.146**	100	3.155	−220
72	**3.136**	75, 3	3.140, 3.129	220, −2−21
12	3.107	13	3.111	123
2	3.050	1, 0.5	3.053, 3.037	0−24, 221
36	**2.965**	2, 54	2.971, 2.967	−222, −1−15
35	**2.912**	41, 4	2.911, 2.909	−115, −214
36	**2.834**	10, 1, 31, 3	2.841, 2.836, 2.835, 2.834	0−32, 1−24, 1−15, 130
42	**2.784**	3, 7, 4, 24, 11	2.789, 2.788, 2.786, 2.780, 2.779	310, −3−11, −311, 115, 032
3	2.710	1, 3, 0.5	2.709, 2.708, 2.706	311, 214, −205
11	2.668	15	2.668	−303
5	2.565	2, 4	2.568, 2.567	−1−33, −3−13
5	2.550	1, 3	2.552, 2.549	016, −313
4	2.521	3, 3	2.525, 2.519	−224, 1−33
4	2.509	0.5, 0.5, 2	2.510, 2.507, 2.505	205, 1−25, −133
2	2.476	1, 1	2.484, 2.473	−230, 230
4	2.451	1, 0.5, 3	2.457, 2.454, 2.449	−3−21, 320, 133
5	2.417	5, 0.5, 0.5	2.419, 2.418, 2.414	3−21, 3−13, −2−32
4	2.395	2, 1	2.396, 2.393	321, 313
1	2.286	1.5	2.285	−216
3	2.188	2, 1	2.187, 2.184	107, −315
2	2.167	1, 2	2.169, 2.165	2−16, 225
5	2.140	1, 2, 4	2.142, 2.139, 2.139	1−17, 1−35, 216
3	2.128	5	2.127	−2−26

Table 3. (Contd.)

I_{obs}	d_{obs}, Å	I_{calc}*	d_{calc}, Å **	*h k l*
4	2.077	6, 3, 2	2.080, 2.077, 2.071	−226, 3−31, 135
7	2.055	1, 5, 7	2.055, 2.055, 2.055	−1−27, 331, −1−43
4	2.034	6, 0.5, 1	2.036, 2.034, 2.030	4−12, −2−35, 1−43
12	2.016	7, 2, 7	2.016, 2.014, 2.011	008, 2−26, −143
4	1.993	4	1.993	1−27
6	1.957	4, 3	1.958, 1.957	−4−14, −4−22
7	1.948	2, 4, 1, 0.5, 6	1.950, 1.948, 1.945, 1.945, 1.941	−422, −414, 2−17, 4−13, 127
1	1.901	1, 2	1.902, 1.900	1−18, 333
1	1.862	1	1.861	−2−18
2	1.840	1, 0.5	1.840, 1.840	4−14, 3−34
6	1.824	2, 12	1.826, 1.824	414, −3−35
7	1.790	1, 12	1.792, 1.789	2−44, −335
6	1.758	2, 5, 0.5	1.761, 1.757, 1.756	−1−19, 1−51, 341
5	1.741	1.5, 4	1.746, 1.741	244, 151
5	1.738	1, 1, 5, 2	1.739, 1.736, 1.736, 1.735	−119, 218, 3−35, −511
2	1.717	2	1.716	424
2	1.706	1.5, 3	1.709, 1.703	5−11, 511
3	1.699	1, 3	1.696, 1.695	046, 335
1	1.646	0.5, 1.5, 1	1.647, 1.644, 1.644	038, 3−27, −5−21
1	1.622	1, 0.5	1.623, 1.621	425, −2−38
2	1.615	0.5, 0.5, 1, 1	1.615, 1.615, 1.613, 1.612	5−13, −3−37, 327, −246
1	1.603	1.5	1.603	2−46
8	1.578	1, 1, 1, 11	1.579, 1.578, 1.578, 1.577	522, 0.1.10, −238, −440
5	1.571	1, 4, 1	1.573, 1.570, 1.570	−515, 440, −3−19
4	1.557	0.5, 1, 2, 1, 4, 1	1.558, 1.555, 1.555, 1.555, 1.555, 1.554	−442, 246, −1−39, −319, −2.0.10, 4−26
5	1.535	1, 4, 2, 1, 1, 2	1.536, 1.535, 1.534, 1.533, 1.533, 1.532	−155, 0.−2.10, −3−51, 1.1.10, −4−18, −351
2	1.523	1, 1.5, 1	1.523, 1.522, 1.521	−531, −5−31, −418
2	1.515	0.5, 2, 0.5	1.516, 1.514, 1.514	530, −436, −5−25
2	1.505	0.5, 1, 2	1.504, 1.502, 1.502	−4−44, −525, 0.2.10
2	1.484	1, 1	1.485, 1.483	−444, −2.−2.10
2	1.480	0.5, 3	1.479, 1.477	309, 2.0.10
2	1.467	0.5, 3	1.470, 1.466	−161, −602
1	1.433	1	1.433	1−63
2	1.420	0.5, 0.5, 1, 0.5	1.421, 1.418, 1.418, 1.418	−260, −2−61, −3−39, 2−56
2	1.406	1, 1, 1, 1	1.407, 1.406, 1.405, 1.405	163, 612, −4−46, −535
1	1.393	1	1.393	−5−27

* For the calculated pattern, only reflections with intensities ≥0.5 are given; ** for the unit-cell parameters calculated from single-crystal data. The strongest reflections are marked in boldtype.

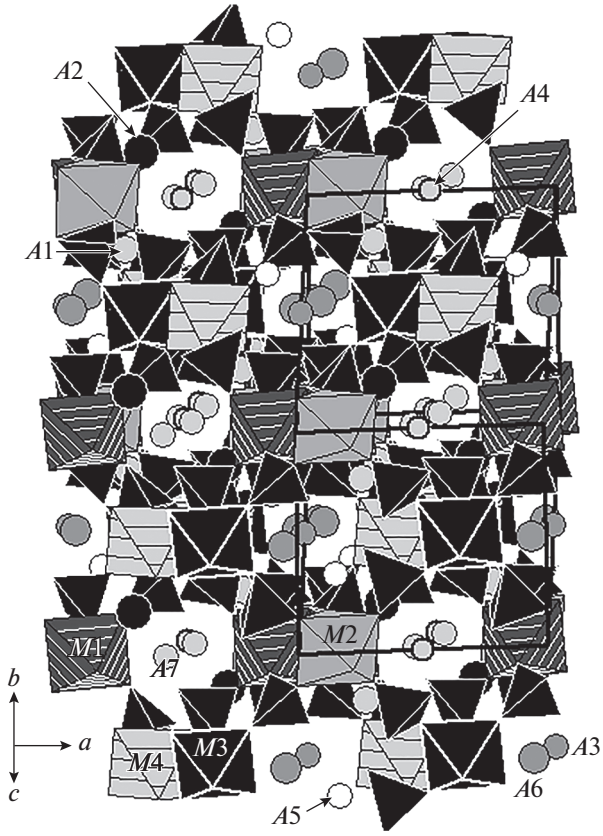

Fig. 3. The crystal structure of philoxenite. The unit cell is outlined.

Рис. 3. Кристаллическая структура филоксенита. Показана элементарная ячейка.

The crystal structure of this mineral (Fig. 3) contains eleven crystallographically nonequivalent positions of metal cations *Me*: seven *A* sites of large cations (K, Na, Ca and Pb^{2+}) and four octahedrally coordinated *M* sites of medium-sized cations (Mg, Cu^{2+}, Zn, Fe^{3+} and Al). Isolated MO_6 octahedra are connected *via* isolated from each other SO_4 tetrahedra forming a novel-type of a heteropolyhedral (tetrahedral-octahedral) three-dimensional framework. This framework is interrupted: one oxygen vertex of each SO_4 tetrahedron is not shared with MO_6 octahedron. Large *A* cations are located in the tunnels of this microporous *M*–S–O framework.

The structural formula of philoxenite is ($Z = 1$):

$$^{A(2,6)}(K_{0.90}Na_{0.07}Pb_{0.03})_4\,^{A(5)}(K_{0.69}Na_{0.28}Pb_{0.03})_2\,^{A(7)}(K_{0.85}Pb_{0.15})_2\,^{A(1)}(Na_{0.61}Ca_{0.39})_2$$
$$^{A(3)}(Na_{0.72}Ca_{0.28})\,^{A(4)}(Na_{0.81}Ca_{0.19})\,^{M(2)}\left(Mg_{0.60}Cu^{2+}_{0.40}\right)_2\,^{M(1)}\left(Mg_{0.56}Cu^{2+}_{0.44}\right)_2$$
$$^{M(4)}(Mg_{0.43}Al_{0.35}Zn_{0.22})_2\,^{M(3)}\left(Fe^{3+}_{0.42}Al_{0.40}Mg_{0.18}\right)_2(SO_4)_{16}.$$

We prefer to present the content of the *M*(3) site in the simplified formula of the mineral as $(Fe^{3+}_{0.5}Al_{0.5})$ but not as (Fe^{3+},Al) because the contents of Fe and Al in this site are almost equal

and, therefore, even slight their variations in chemical analyses result insignificant prevailing of Fe or Al in *M*(3). This could not be, in our mind, a reason of the formal division of philoxenite to two separate mineral species, with Fe > Al and with Al > Fe in the *M*(3) site. In this approach we are guided by the rule formulated in the IMA report devoted to solid solutions in mineral nomenclature: "*if the known composition embrace to 50% mark, but do not appear to extend to either end member, only one name should apply to the compositional range. However, the compositional range should be taken into account; if it is very small, then only one name should be given, but if it is large, consideration may be given to two names*" (Nickel, 1992). In philoxenite, the compositional range is very small and embraces the 50% mark between Al- and Fe-dominant compositions of the content the *M*(3) site.

Complicated scheme of cation substitutions, including heterovalent ones, prevents to write a correct charge-balanced formula idealized to only species-defining (*i.e.*, prevailing in different structure positions) chemical constituents. The simplified formula considering all the above-discussed data is $(K,Na,Pb)_4(Na, Ca)_2(Mg, Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$.

Philoxenite demonstrates rare example of a natural sulfate with the microporous heteropolyhedral three-dimensional framework, even interrupted one.

Philoxenite is remotely related to langbeinite $K_2Mg_2(SO_4)_3$. The general motifs of arrangement of *Me* cations in these minerals are similar (Zubkova et al., 2020) that results in some common features in their powder X-ray diffraction patterns (in part of strong reflections) and Raman spectra (Table 1; Fig. 2). However, philoxenite and langbeinite, occurring in the same mineral association in the Yadovitaya fumarole, significantly differ in majority of essential characteristics (Table 1).

ACKNOWLEDGEMENTS

This study was supported by the Russian Science Foundation, grant no. 19-17-00050. The technical support by the SPbSU X-Ray Diffraction Resource Center (in part of powder XRD study of philoxenite) is acknowledged.

REFERENCES

Anthony J.W., Bideaux R.A., Bladh K.W., Nichols, M.C. Handbook of Mineralogy. Vol. Borates, Carbonates, Sulfates. Mineral Data Publishing: Tucson, **2003**. 813 p.

Britvin S.N., Dolivo-Dobrovolsky D.V., Krzhizhanovskaya M.G. Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zapiski RMO* (*Proc. Russian Miner. Soc.*). **2017**. Pt. 146. N 3. P. 104–107 (*in Russian*).

Fedotov S.A., Markhinin Y.K., eds. The Great Tolbachik Fissure Eruption. Cambridge University Press, New York, **1983**. 341 p.

Mandarino J.A. The Gladstone–Dale relationship: Part IV. The compatibility concept and its application. *Canad. Miner.* **1981**. Vol. 19. P. 441–450.

Mereiter K. Refinement of the crystal structure of langbeinite, $K_2Mg_2(SO_4)_3$. *Neues Jahrb. Miner, Monatshefte*. **1979**. P. 182–188.

Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley & Sons: New York, **1986**. 484 p.

Nickel E.H. Solid solutions in mineral nomenclature. Canad. Miner. **1992**. Vol. 30. P. 231–234.

Pekov I.V., Agakhanov A.A., Zubkova N.V., Koshlyakova N.N., Shchipalkina N.V., Sandalov F.D., Yapaskurt V.O., Turchkova A.G., Sidorov E.G. Oxidizing-type fumaroles of the Tolbachik volcano, a mineralogical and geochemical unique. *Russian Geol. Geophys.* **2020**. Vol. 61. N 5–6. P. 675–688.

Vergasova L.P., Filatov S.K. A study of volcanogenic exhalation mineralization. *J. Volcan. Seismol.* **2016**. Vol. 10. N 2. P. 71–85.

Zubkova N.V., Pekov I.V., Agakhanov A.A., Pushcharovsky D.Yu. A novel-type microporous heteropolyhedral framework in crystal structure of the natural sulfate philoxenite. *Crystallogr. Rep.* **2020** (in press).

ФИЛОКСЕНИТ $(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$ – НОВЫЙ МИНЕРАЛ ИЗ ФУМАРОЛЬНЫХ ЭКСГАЛЯЦИЙ ВУЛКАНА ТОЛБАЧИК (КАМЧАТКА, РОССИЯ)

д. чл. И. В. Пеков[a, *], А. А. Агаханов[b], Н. В. Зубкова[a], д. чл. Д. И. Белаковский[b], М. Ф. Вигасина[a], д. чл. С. Н. Бритвин[c, d], д. чл. А. Г. Турчкова[a], д. чл. Е. Г. Сидоров[e]

[a] *Московский государственный университет, геологический факультет, Воробьевы горы, Москва, 119991 Россия*

[b] *Минералогический музей им. А.Е. Ферсмана, Ленинский пр., 18-2, Москва, 119071 Россия*

[c] *Институт наук о Земле, Санкт-Петербургский государственный университет, Университетская наб., 7/9, Санкт-Петербург, 199034 Россия*

[d] *Кольский научный центр РАН, ул. Ферсмана, 14, Апатиты, 184209 Россия*

[e] *Институт вулканологии и сейсмологии ДВО РАН, бул. Пийпа, 9, Петропавловск-Камчатский, 683000 Россия*

**e-mail: igorpekov@mail.ru*

Поступила в редакцию 18.05.2020 г.
После доработки 18.05.2020 г.
Принято к печати 17.06.2020 г.

Новый минерал филоксенит $(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$ найден в возгонах фумаролы Ядовитой на Втором шлаковом конусе Северного прорыва Большого трещинного Толбачинского извержения (вулкан Толбачик, Камчатка, Россия). С ним ассоциируют эвхлорин, лангбейнит, гематит, тенорит, пийпит, алюмоключевскит, долерофанит, вергасоваит, купромолибдит, цизит и ярошевскит. Филоксенит образует отдельные косоугольные таблитчатые кристаллы до 0.3 × 0.6 мм, псевдотригональные или полигональные. Новый минерал прозрачный, бесцветный или бледно-желтоватый, со стеклянным блеском. Филоксенит хрупкий, без спайности, излом неровный. $D_{выч}$ = 3.03 г/см^3. Минерал оптически двуосный (–), n_p = 1.562(2), n_m = 1.572(2), n_g = 1.580(2), $2V_{изм}$ = = 85(5)° (λ = 589 нм). Приведен КР-спектр. Химический состав (мас. %, электронно-зондовые данные): Na_2O 4.67, K_2O 13.34, Rb_2O 0.13, CaO 2.84, PbO 4.54, MgO 6.37, MnO 0.20, CuO 5.40, ZnO 1.48, Al_2O_3 3.40, Fe_2O_3 3.29, SO_3 54.62, сумма 100.28. Эмпирическая формула, рассчитанная на 32 атома O, такова: $(K_{3.30}Na_{1.76}Ca_{0.59}Pb_{0.24}Rb_{0.02})_{\Sigma 5.91}(Mg_{1.84}Cu_{0.79}Al_{0.78}Fe^{3+}_{0.48}Zn_{0.21}Mn_{0.03})_{\Sigma 4.13}S_{7.96}O_{32}$. Филоксенит триклинный, пространственная группа *P*-1, *a* = 8.8410(3), *b* = 8.9971(3), *c* = 16.1861(5) Å, α = 91.927(3), β = = 94.516(3), γ = 90.118(3)°, *V* = 1282.77(7) Å^3, *Z* = 2. Главные линии порошковой рентгенограммы [(*d*,Å(*I*)(*hkl*)]: 5.70(18)(111); 4.030(24)(004); 3.146(100)(–220); 3.136(72)(220); 2.965(36)(–1–15), 2.912(35)(–115), 2.834(36)(0–32, 1–15), 2.784(42)(115, 032). Кристаллическая структура филоксенита уникальна. В ее основе лежит микропористый гетерополиэдрический каркас нового типа, образованный тетраэдрами SO_4 и октаэдрами MO_6, где *M* = Mg, Cu^{2+}, Zn, Fe^{3+}, Al. Название минерала образовано от древнегреческих слов φίλος – *друг*, и ξένος – *гость*, и отражает сложный химический состав минерала и тот факт, что существенные количества элементов-примесей входят в девять из одиннадцати независимых катионных позиций в его кристаллической структуре.

Ключевые слова: филоксенит, новый минерал, сульфат, фумарола, вулкан Толбачик, Камчатка

СПИСОК ЛИТЕРАТУРЫ

Бритвин С.Н., Доливо-Добровольский Д.В., Кржижановская М.Г. Программный пакет для обработки рентгеновских порошковых данных, полученных с цилиндрического детектора дифрактометра Rigaku RAXIS Rapid II // Записки РМО. **2017.** Ч. 146. Вып. 3. С. 104–107.

Вергасова Л.П., Филатов С.К. Опыт изучения вулканогенно-эксгаляционной минерализации // Вулканология и сейсмология. **2016**. № 2. С. 3–17.

Зубкова Н.В., Пеков И.В., Агаханов А.А., Пущаровский Д.Ю. Микропористый гетерополиэдрический каркас нового типа в кристаллической структуре природного сульфата филоксенита // Кристаллография. **2020**. Т. 65 (в печати).

Пеков И.В., Агаханов А.А., Зубкова Н.В., Кошлякова Н.Н., Щипалкина Н.В., Сандалов Ф.Д., Япаскурт В.О., Турчкова А.Г., Сидоров Е.Г. Фумарольные системы окислительного типа на вулкане Толбачик – минералогический и геохимический уникум // Геология и геофизика. **2020**. № 5–6. С. 826–843.