

MINERALS
AND MINERAL PARAGENESES

A New Solid Solution with Garnet Structure: Berzeliite–Schäferite
Isomorphic Series from the Fumarole Exhalation
of the Tolbachik Volcano, Kamchatka

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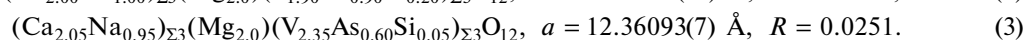
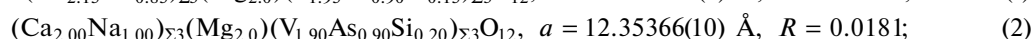
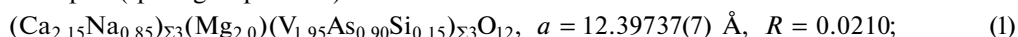
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Abstract—An extended isostructural solid solution (isomorphic series) between arsenate and vanadate of the garnet supergroup — berzeliite (NaCa₂)Mg₂(AsO₄)₃ and schäferite (NaCa₂)Mg₂(VO₄)₃ — was studied for the first time. The studied material is from sublimates of the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka. These minerals here form aggregates of yellow or orange transparent crystals (up to 1 mm in size). Anhydrite, forsterite, diopside, andradite, hayuin, potassium–sodium feldspars, hematite, magnesioferrite, spinel, barite, aphtitalite-like sulfates, minerals of the powellite–scheelite series, ludwigite, calcium chillerite, paraberzeliite, members of the series rhabdobarite–(V)–rhabdobarite–(W)–rhabdobarite–(Mo), apatite–swabite–pliniusite, tilasite–isokite, udinaite–arsenudinaite, and wagnerite–arsenovagnerite associate with the studied minerals. They were formed under the oxidizing conditions at temperatures not lower than 550°C. The composition of the tetrahedrally coordinated components in the schäferite–berzeliite isomorphic series in the Arsenatnaya fumarole continuously varies from (V_{2.54}As_{0.48}P_{0.04}Si_{0.01}) to (As_{2.77}V_{0.22}Si_{0.03}P_{0.01}). The $X_{Ca^{2+}} + Z_{Si^{4+}} = X_{Na^+} + Z^{5+}$ heterovalent isomorphism scheme plays a subordinate role. The crystal structures of three samples (space group *Ia*–*3d*) with different As : V ratios were studied:



The dimorphism of the garnet supergroup and alluodite group arsenates is discussed.

Keywords: schäferite, berzeliite, garnet supergroup, berzeliite group, arsenate, vanadate, solid solution with garnet structure, Arsenatnaya fumarole, Tolbachik volcano, Kamchatka.

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INTRODUCTION

Compounds with a garnet structure are widespread in nature and are quite numerous among synthetic materials. All of them are characterized by cubic space group *Ia*–*3d* or tetragonal group *I4*₁/*acd*. The crystal structure of garnets consists of isolated ZO₄ tetrahedra and YO₆ octahedra, linked by their vertices into a three-dimensional heteropolyhedral framework with cavities containing X cations in dodecahedral coordination. According to the nomenclature of the International Mineralogical Association, the general formula for the minerals of the garnet supergroup is written as {X₃}[Y₂](Z₃)O₁₂ (Grew et al., 2013).

Many garnet-structured vanadates have been synthesized. The dodecahedrally coordinated position X in them may be occupied by Li⁺, Na⁺, K⁺, Cu⁺, Ag⁺, Tl⁺, Ca²⁺, Mn²⁺, Sr²⁺, Cd²⁺, Pb²⁺, Y³⁺, Ln³⁺, and Bi³⁺ and octahedral position Y may be occupied by Li⁺, Na²⁺, Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Al³⁺, Sc³⁺, V³⁺, Cr³⁺, Fe³⁺, Ga³⁺, and In³⁺. Reviews of the crystal chemistry of vanadate garnets are given in (Schwarz, Schmidt, 1967; Mill and Ronniger, 1973; Neurgaonkar and Hummel, 1975; Iishi and Ikuta, 2005). Much less is known about synthetic arsenate garnets. Dodecahedral position X in synthetic arsenates with a garnet structure is occupied by Li⁺,

Na^+ , K^+ , and Ca^{2+} , while octahedral position Y is occupied by Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , and Cr^{3+} (Schwarz and Schmidt, 1972; d'Yvoire et al., 1986; Khorari et al., 1995, 1997; Kouass et al., 2006; Ouerfelli et al., 2008).

Among the minerals of the garnet supergroup, silicates ($Z = \text{Si}$) sharply predominate, both in species diversity and, especially, in mass, while representatives of other chemical classes in nature are very rare — these being oxides ($Z = \text{Al}$, Fe^{3+} , Fe^{2+} , Zn), hydroxides (hydrogarnets, in which the tetrahedron $\square(\text{OH})_4$ with a vacancy in the center is located in the position of the ZO_4 tetrahedron), arsenates ($Z = \text{As}^{5+}$), and vanadates ($Z = \text{V}^{5+}$). Note that, in the geological literature, the term “garnet” is traditionally used mainly in relation to silicates.

For arsenates and vanadates of the garnet supergroup, as well as many other anhydrous oxosalts with As^{5+} and V^{5+} , to form, as a rule, a combination of a high oxidative potential and rather high temperatures is necessary (Nagashima and Armbruster, 2012). Despite the wide variety of synthetic compounds, only two such vanadates are known in nature, schäferite $(\text{Ca}_2\text{Na})\text{Mg}_2(\text{VO}_4)_3$ and palenzonaite $(\text{Ca}_2\text{Na})\text{Mn}_2^{2+}(\text{VO}_4)_3$, and two arsenates represented by their arsenic analogs, berzeliite $(\text{Ca}_2\text{Na})\text{Mg}_2(\text{As}^{5+}\text{O}_4)_3$ and manganberzeliite $(\text{Ca}_2\text{Na})\text{Mn}_2^{2+}(\text{AsO}_4)_3$. These four minerals (they are all cubic, $Ia-3d$) now constitute the berzeliite group, which is considered a subdivision of the garnet supergroup (Grew et al., 2013).

Schäferite is known only in exhalation formations. It is found in insignificant amounts in sublimes of the paleofumaroles of the Pleistocene volcanoes Belberberg and Nikenicher Sattel, Eifel, Germany (Krause et al., 1999; Blass et al., 2009), and its synthetic analogue is found in metallurgical slags of old smelter of Lavriona, Greece (Kolitsch et al., 2014; Koshlyakova et al., 2017). Berzeliite, manganberzeliite, and palenzonaite are described in arsenic and/or vanadium enriched metamorphic and metasomatic iron–manganese ores. Berzeliite and the more common manganberzeliite are among the common minerals in the famous skarn deposits of the Filipstad ore region in Sweden — Longbahn, Jakobsberg, and Nordmark. Manganberzeliite occurs in the metamorphosed Zn–Mn ores of the Franklin deposit (New Jersey, United States). Manganberzeliite and, to a lesser extent, berzeliite and palenzonaite are widespread in a number of manganese deposits and occurrences in the Alps — in Italy (Gambateza, Valetta, Molinello, Cassagna, etc.), Switzerland (Fianel, Falotta, Parsettens, etc.) and Austria (Miskopf, Wunspitze, etc.) (Majzlan et al., 2014).

The value of unit cell parameter a , as well as the sizes and characteristics of polyhedra in minerals of the berzeliite group and their synthetic and synthetic

analogues, change rather weakly even with significant variations in composition. Thus, for manganberzeliite, parameter a varies in the range of 12.46–12.52 Å range; for berzeliite, 12.33–12.35 Å; for schäferite, 12.39–12.45 Å; and, for palenzonaite, 12.53–12.57 Å (Ito, 1968; Schwarz and Schmidt, 1971; Matsubara, 1975; Neurgaonkar and Hummel, 1975; Hawthorne, 1976; Basso, 1987; Krause et al., 1999; Nakatsuka et al., 2003; Barresi et al., 2005; Iishi and Ikuta, 2006; Piccoli et al., 2007; Nagashima and Armbruster, 2012; Koshlyakova et al., 2017). Nevertheless, despite the isostructurality and closeness of the cell sizes, no extended isomorphic series were discovered either between vanadate and arsenate minerals of the berzeliite group or in systems with their synthetic analogs. In the literature there are references to individual samples of intermediate composition for manganese members of the berzeliite group: for example, the occurrence of 15–20 mol % of the palenzonaite end member is noted for manganberzeliite from Jacobsberg, Sweden, and Verence, Italy (Holtstam, 2001; Barresi et al., 2005). Palenzonaite containing 40 mol % of manganberzeliite end member, described in the Fianel deposit in Switzerland (Nagashima and Armbruster, 2012). Before our work, no minerals with a composition intermediate between berzeliite and schäferite were described. Only an insignificant amount of vanadium (0.9 wt %) was noted in berzeliite from Montaldo, Italy (Piccoli et al., 2007).

We have discovered for the first time an extended solid solution series between berzeliite and schäferite. Minerals belonging to this series were found in the deposits of the active fumarole Arsenatnaya associated with the Tolbachik volcano in Kamchatka. We provided brief information on Tolbachik berzeliite and schäferite in (Koshlyakova et al., 2018; Pekov et al., 2018), while this paper is devoted to a detailed description of this new not only for natural, but also synthetic garnet isomorphic series and a description of crystal chemical characteristics of its members. It should be noted that minerals of the berzeliite group were not found on the territory of Russia before the finds at Tolbachik.

METHODS

The study of micromorphology and the relationship of minerals was carried out with scanning electron microscopy, and the quantitative determination of the chemical composition of the samples was done with the method of electron-probe microanalysis. These works were carried out in the Laboratory of Local Methods for the Study of Matter of the Geological Faculty of Moscow State University by means of JEOL JSM-6480LV and Superprobe JXA-8230 electron microscopes equipped with wave and energy-dispersive spectrometers. The analysis was carried out at an accelerating voltage of 20 kV and an electron-probe current of 10 nA/40 nA, the probe diameter was 2–3

μm , and the spectrum accumulation time was 100/120 s. The following standards were used: Na, Al—jadeite; K, P— KTiOPO_4 ; Mg, Si—olivine; Ca— CaSiO_3 ; Mn— MnTiO_3 ; Cu—Cu; Zn— ZnS ; Fe, S— FeS_2 ; Ti— TiO_2 ; V—V; and As—GaAs. The empirical formulas of the studied minerals are calculated for 12 O atoms. The iron impurity was taken to be trivalent in the calculation, since the conditions of mineral formation in the Arsenatnaya fumarole are sharply oxidizing and no minerals with Fe^{2+} were noted in its sediments (Pekov et al., 2018). An X-ray study of single crystals was performed on an XcaliburS diffractometer equipped with a CCD detector on a $\text{MoK}\alpha$ -radiation. The SHELX software package (Sheldrick, 2008) was used to interpret and refine the crystal structures.

Occurrence, Morphology and Physical Properties of the Minerals of Berzeliite—Schäferite Series in the Fumaroles of the Tolbachik Volcano

The studied samples were taken, except for one (see below), from the Arsenatnaya fumarole located at the Second cinder cone of the Northern Vent of the Great Tolbachik Fissure Eruption (NV GTFE) 1975–1976. (Big ..., 1984). Arsenatnaya fumarole is distinguished by a very wide mineral diversity and complexity of the chemical composition of the minerals, in which 52 arsenates and four vanadates were found, the species-forming cations of which are Cu^{2+} , Mg, Al, Fe^{3+} , Ti^{4+} , Zn, Ca, Na, and K. A detailed description of Arsenatnaya fumarole and its zoning is given in (Pekov et al., 2018; Shchipalkina et al., 2020a), and a more general review of the mineralogy of Tolbachik fumaroles is given in (Vergasova and Filatov, 2016; Pekov et al., 2020).

Fumaroles acting on the GTFE cones, including Arsenatnaya, are of oxidative type. The volcanic gas in them is mixed with heated atmospheric air (currently, the hot gas of the Second Cone fumaroles is approximately 99% air (Zelenski et al., 2011)). According to the measurements that we regularly performed in 2012–2018 using a chromel alumel thermocouple, the gas temperature in Arsenatnaya reaches 500°C (Pekov et al., 2018; Shchipalkina et al., 2020a). Sublimates formed in the middle and lower zones of this fumarole, where the temperature is 200 – 500°C , are represented by anhydrous oxosalts, oxides, and halides containing most of the elements of variable valence in the highest oxidation states.

Fumarole Arsenatnaya is a system of cavities between blocks of basalt slag altered to varying degrees by volcanic gas. The walls of cavities and cracks here, as well as the pores in the basalt itself, are encrusted with exhalatory minerals and are extraordinarily rich in some places. The strong temperature gradient and the associated changes in the gas composition are reflected in the mineral composition of the exhalations,

which significantly changes in the vertical section of the fumarole.

Berzeliite and schäferite were found only at the deepest and, accordingly, the hottest horizons of the Arsenatnaya fumarole, located at a depth of 3–4 m from the surface. In some areas of this rather extended (more than 5 m) zone, they are one of the main phases of thick (up to 10 cm thick) sublimate crusts and the main concentrators of V and As. All other vanadium-rich minerals known in this fumarole are also concentrated here. According to our estimates, the formation temperature of the mineral association is 550 – 700°C (Shchipalkina et al., 2020a, b). Minerals of the berzeliite—schäferite series form transparent crystals with a glassy luster. They are most often colored in yellow and orange colors of different shades. With an increase in the V : As ratio, the color intensity and the proportion of the red component generally increase. Low-vanadium samples of berzeliite often have a very pale yellowish color or are almost colorless, while the richest V schäferite is deep orange to bright orange or brick red. The BSE images show that crystals of berzeliite and schäferite often exhibit growth oscillatory or spotted zoning. Crystals of these minerals are often well faceted, and their sizes usually do not exceed 0.1 mm; in rare cases, they reach 1 mm. The main habit form is the {211} tetragontrioctahedron, faces of the {110} rhombododecahedron are sometimes present, and the {210} tetrahexahedron and the {100} cube faces are rare (Figs. 1a, 1b). Crystals are perfect and symmetrically developed, but distorted individuals elongated and/or flattened in arbitrary directions are observed more often. Skeletal crystals — edge or faceted and, sometimes, with a complexly sculptured surface, which reflects unsteady crystallization conditions in the fumarole system — are abundant. Crystals of the described minerals sometimes form compact or open-work intergrowths up to 0.5 cm in diameter, but the most common form of their precipitation is crusts about 0.1 mm thick, in some cases continuous, but usually intermittent. Berzeliite and schäferite in them form intergrowths with anhydrite and almost always overgrow it (Figs. 1c, 1d). The area of such crusts can reach hundreds of square centimeters. Interest is raised by the yellow or orange “garnet buds” that are often found there — spherical segregations up to 3 cm in diameter, separate or gathered in bunches. They have the appearance of massive spherulites formed by members of the berzeliite—schäferite series, but, in fact, these minerals form only a thin (usually no thicker than 0.5 mm) crystalline crust on their surface and are present in small amounts in their inner parts, while the buds’ main volume is composed of a cavernous aggregate of anhydrite (Figs. 1e, 1f).

Berzeliite and schäferite are associated with other high-temperature minerals that are common in the deep zones of the Arsenatnaya fumarole (Pekov et al., 2018; Shchipalkina et al., 2020a). The silicates in this association are represented by forsterite, diopside,

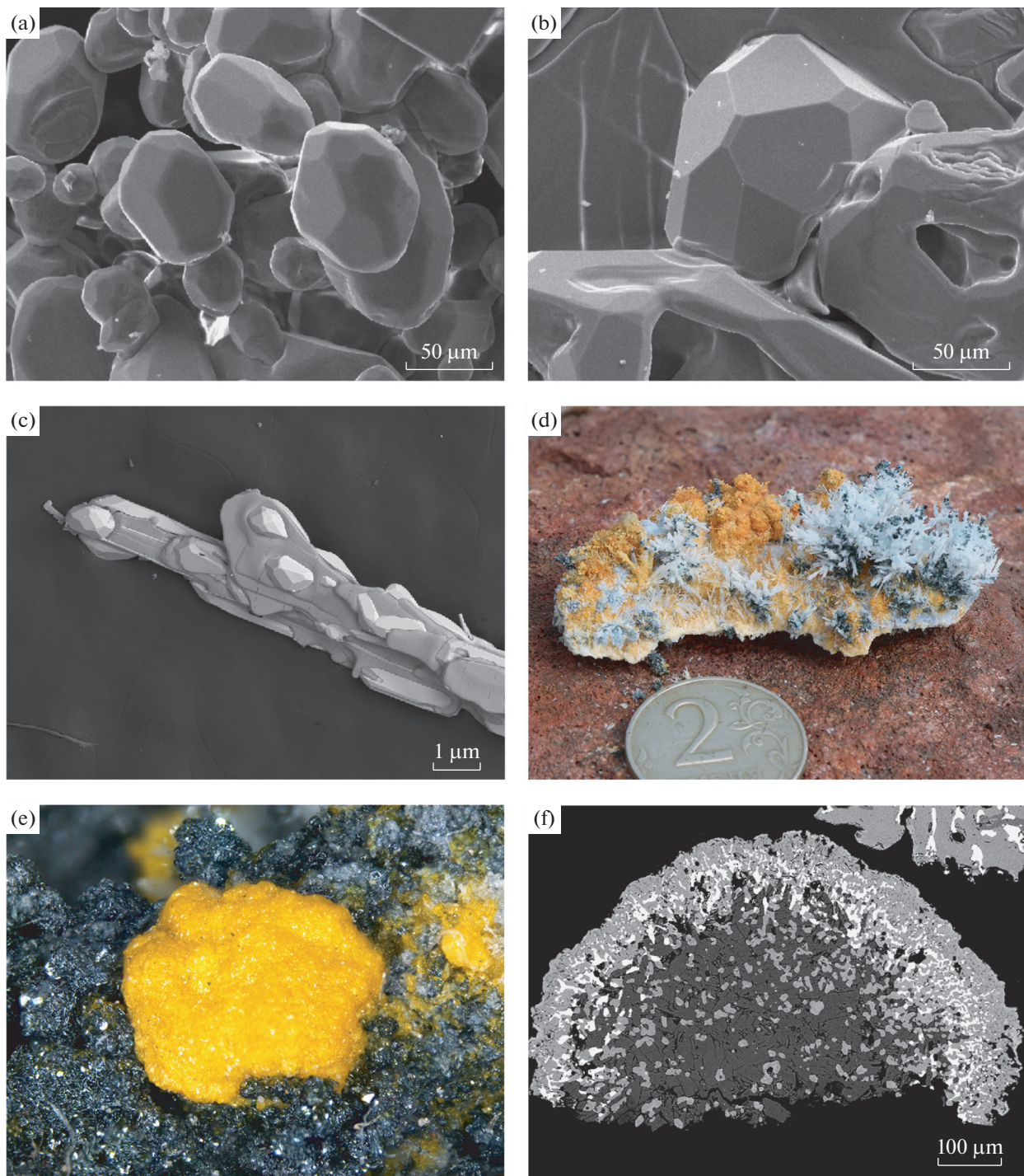


Fig. 1. Aggregates of berzeliite–schäferite-series garnets from exhalations of the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka. (a, b) Berzeliite, (c) vanadium-bearing berzeliite overgrowing anhydrite (secondary electron image), (d) orange openwork crusts of minerals of the berzeliite–schäferite-series overgrowing crust of white anhydrite and black hematite crystals with transparent acicular crystals of svabite (photo by D.A. Varlamov), (e) 2-mm bright yellow “garnet kidney” on crust of black hematite crystal crust, and (f) section of the “garnet kidney”: light gray outer zone, schäferite; white phase, baryte; dark gray phase, anhydrite. Backscattered electron image.

andradite, hauyne, and potassium–sodium feldspars, while the oxides are represented by hematite, magnetoferrite, and spinel. Anhydrite predominates in association with schäferite and berzeliite. Barite and members of the aphtalite group are also present. Borates are represented by minerals of the rhabdoborite group with the general formula $Mg_{12}M_{1/3}^{6+}[(BO_3)_{6-x}(PO_4)_xF_{2-x}]$, where $M = V^{5+}$, Mo^{6+} , W^{6+} , and $x < 1$ (Pekov et al., 2020), as well as ludwigite. Also, along with berzeliite and schäferite, there are minerals of the vellite–scheelite series. All arsenates, phosphates, and vanadates in this assemblage form extended solid solutions with substitutions in tetrahedral positions: ${}^TAs^{5+} \leftrightarrow {}^TV^{5+} \leftrightarrow {}^TP^{5+}$. These solid solutions are represented by minerals of the apatite supergroup (fluorapatite $Ca_5(PO_4)_3F$, swabite $Ca_5(AsO_4)_3F$, and pliniusite $Ca_5(VO_4)_3F$), tilasite groups (tilasite $CaMg(AsO_4)F$ and isokite $CaMg(AsO_4)F$), alluodite groups (calciummohillerite $NaCaMg_3(AsO_4)_3$ and $NaCa_2Mg_2(AsO_4)_3$), series udinaite $NaMg_4(VO_4)_3$ –arsenudinite $NaMg_4(AsO_4)_3$ and wagnerite $Mg_2(PO_4)F$ –arsenovagnerite $Mg_2(AsO_4)F$. It should be noted that arsenates with low contents of vanadium and, as a rule, phosphorus are in close association with berzeliite, while schäferite is mainly associated with varieties of these minerals enriched in vanadium and phosphorus, as well as with phosphates and vanadates.

Arsenic free schäferite was found in another location at Tolbachik—in one of the fumaroles on the First slag cone of the NV GTFE, adjacent to the Second cone from the south. This mineral grows here on basalt slag in the form of individual red-brown tetragontrioctahedral crystals, which are usually distorted and reach a size of 0.2 mm.

Chemical Composition

The crystal chemical formulas of minerals of the berzeliite–schäferite series are calculated for 12 atoms of oxygen; large cations Na and Ca are assigned to dodecahedral position X ; medium-sized Mg, Al, Mn, Fe, Cu, and Zn to octahedral Y ; and high-valence As, V, P, and Si to tetrahedral position Z . The results obtained for the X -, Y -, and Z -components of the sum are in good agreement with the garnet stoichiometry. The chemical composition of members of the berzeliite–schäferite series from Arsenatnaya fumarole (22 representative analyzes) is given in Table 1. The studied minerals belong to a continuous solid solution, in which the $V : As$ ratio turned out to be the only significantly varying value. It varies from ${}^Z(V_{2.5}As_{0.5})$ to ${}^Z(As_{2.8}V_{0.2})$ (Table 1, nos. 1 and 22). In addition to vanadium and arsenic, these minerals sometimes contain up to 0.2 apfu P and up to 0.35 apfu Si, the concentrations of which do not correlate with the $As : V$ ratio. The ratios of the components occupying tetrahedral position Z are shown in Fig. 2. This diagram, which is based on 230 analyzes of samples from the

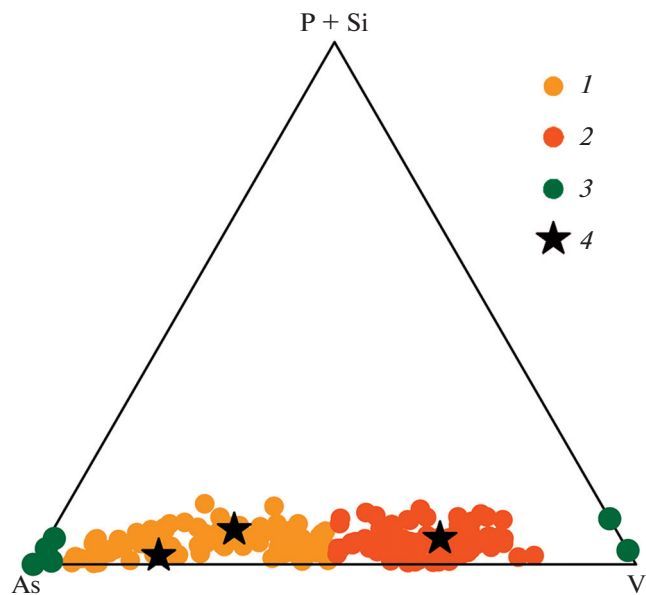


Fig. 2. Ratios of main tetrahedrally coordinated components in members of the berzeliite–schäferite solid-solution series: (1) berzeliite and (2) schäferite from the Arsenatnaya fumarole, Tolbachik (this study), (3) berzeliite and schäferite from other localities (see Table 2), and (4) structurally studied single crystals (this study, see Table 3).

Arsenatnaya fumarole, clearly demonstrates that the series of berzeliite–schäferite in nature is continuous. Mg sharply prevails among the medium-sized cations in the composition of schäferite and berzeliite. The content of minor elements (Al, Mn, Fe, Cu, and Zn) is always less than 0.1 apfu, and their total concentration does not exceed 0.2 apfu. Large X cations are represented in our samples only by Na and Ca. The $Na : Ca$ ratio, which in the ideal formula is 1 : 2, fluctuates somewhat and naturally changes in the direction of an increase in the calcium content with partial replacement of pentavalent vanadium and arsenic by silicon. The composition of large cations varies from $X\{Na_{1.0}Ca_{2.0}\}$ for practically siliceous varieties to $X\{Na_{0.7}Ca_{2.3}\}$ for a sample with a maximum Si content of 0.35 apfu (Table 1, no. 17). Schäferite from the First Cone of the NV GTFE (Table 2, no. 8) does not contain arsenic and is markedly enriched in iron and sodium. Its empirical formula is: $(Na_{1.48}Ca_{1.53})_{\Sigma 3.01}(Mg_{1.45}Fe_{0.44}^{3+}Ti_{0.05}Mn_{0.01})_{\Sigma 1.95}(V_{2.91}P_{0.08})_{\Sigma 2.99}O_{12}$.

Single-Crystal X-ray Data and X-ray Structure Analysis

Three crystals of the berzeliite–schäferite series with different $As : V$ ratios from Arsenatnaya fumarole were studied by single-crystal X-ray diffraction analysis (XRD). In all cases, a garnet-type structure and space group $Ia\bar{3}d$ were confirmed. The formulas derived for these crystals from the set of electron-probe data and X-ray diffraction data, as well as the rest of the crystallographic data and structure refine-

Table 1. Representative chemical analyses of schäferite–berzeliite solid-solution series minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka (wt %)

Component	1	2	3	4	5	6	7	8	9
	Schäferite								
Na ₂ O	6.13	5.36	5.12	5.88	5.51	5.73	5.73	5.35	5.08
MgO	16.20	14.67	14.20	15.41	16.07	15.30	15.41	15.68	14.84
CaO	21.67	22.63	23.02	21.03	22.50	22.00	21.95	22.04	22.37
MnO	0.13	0.79	1.47	0.15	0.33	0.23	0.16		0.34
CuO		0.33	0.73			0.06	0.03		0.12
ZnO		0.01				0.01	0.01		0.01
Fe ₂ O ₃		0.25	0.47			0.09	0.06		0.15
SiO ₂	0.11	0.69	1.30	0.09	0.71	0.47	0.38	0.95	1.52
TiO ₂		0.04	0.15						
P ₂ O ₅	0.55	0.85	0.55	0.69	1.22	1.52	1.55	2.02	0.19
V ₂ O ₅	<i>43.93</i>	40.12	38.58	35.83	34.65	33.45	31.62	29.44	27.46
As ₂ O ₅	<i>10.83</i>	13.33	14.23	19.25	18.81	21.24	24.50	24.53	28.08
SO ₃	0.06	0.08	0.04	0.08	0.04	0.07	0.19		0.03
Sum	99.61	99.15	99.86	98.41	99.84	100.17	101.59	100.01	100.19
Formula coefficients (O = 12)									
Na	1.01	0.89	0.86	1.00	0.92	0.95	0.95	0.89	0.86
Mg	2.04	1.88	1.82	2.00	2.06	1.96	1.95	2.02	1.94
Ca	1.97	2.08	2.12	1.97	2.07	2.03	2.00	2.04	2.10
Mn	0.01	0.06	0.11	0.01	0.02	0.02	0.01		0.03
Cu		0.02	0.05			–	–		0.01
Fe		0.02	0.03			0.01	–		0.01
Si	0.01	0.06	0.11	0.01	0.06	0.04	0.03	0.08	0.13
Ti		–	0.01						
P	0.04	0.06	0.04	0.05	0.09	0.11	0.11	0.15	0.01
V	<i>2.46</i>	2.28	2.19	2.06	1.97	1.90	1.78	1.68	1.59
As	<i>0.48</i>	0.60	0.64	0.88	0.85	0.95	1.09	1.11	1.28
S	–	–	–	0.01	–	–	0.01		–
ΣX	2.98	2.97	2.98	2.97	2.97	2.98	2.95	2.93	2.96
ΣY	2.05	1.98	2.02	2.01	2.07	1.99	1.96	2.02	1.99
ΣZ	2.99	3.00	2.98	3.02	2.97	3.00	3.02	3.02	3.01

Table 1. (Contd.)

Componen	10	11	12	13	14	15	16	17	18	19	20	21	22
	Berzeliite												
Na ₂ O	5.70	4.86	5.49	5.47	5.45	5.48	4.82	<i>3.94</i>	5.41	5.21	5.18	5.31	5.45
MgO	14.44	15.21	14.81	15.07	14.75	15.12	14.97	14.36	14.44	14.58	14.23	14.15	14.20
CaO	20.82	22.71	20.77	21.40	21.05	20.80	21.63	<i>23.11</i>	20.50	21.02	20.63	20.36	19.80
MnO	0.09	0.22	0.23	0.21	0.29	0.22	0.15	0.26	0.42	0.29	0.44	0.43	0.39
CuO	0.07	0.08	0.34	0.11	0.03					0.01	0.05	0.02	0.01
ZnO		0.01					0.02			0.02			0.01
Fe ₂ O ₃	0.03	0.24	0.08	0.06	0.12		0.18	0.44		0.24	0.16	0.17	0.20
SiO ₂	0.07	1.97	0.38	0.77	0.75	0.52	1.74	<i>3.79</i>	0.58	1.17	0.85	0.68	0.29
TiO ₂		0.02	0.01	0.04			0.10	0.18		0.03		0.05	
P ₂ O ₅	0.23	0.23	0.25	0.10	0.93	1.93	0.25	0.02	0.02	0.32	0.10	0.12	0.10
V ₂ O ₅	24.79	23.41	21.19	20.03	15.89	15.05	12.76	11.29	9.22	9.18	6.00	5.34	<i>3.64</i>
As ₂ O ₅	32.71	31.57	34.51	36.33	40.81	38.91	43.28	41.35	48.26	48.08	53.20	53.58	<i>57.32</i>
SO ₃	0.10	0.03	0.35	0.04	0.04	0.02	0.10		0.01	0.13		0.02	0.02
Sum	99.05	100.56	98.41	99.63	100.11	98.05	100.00	98.74	98.86	100.28	100.84	100.23	101.43
Formula coefficients (O = 12)													
Na	0.99	0.83	0.96	0.95	0.95	0.97	0.85	<i>0.70</i>	0.98	0.92	0.93	0.96	0.98
Mg	1.92	1.99	2.00	2.02	1.98	2.06	2.02	1.97	2.01	1.99	1.95	1.96	1.95
Ca	1.99	2.14	2.02	2.06	2.03	2.04	2.10	<i>2.28</i>	2.05	2.06	2.04	2.03	1.96
Mn	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.03	0.02	0.03	0.03	0.03
Cu	–	0.01	0.02	0.01	–								
Fe	–	0.02	0.01	–	0.01		0.01	0.03		0.02	0.01	0.01	0.01
Si	0.01	0.17	0.03	0.07	0.07	0.05	0.16	<i>0.35</i>	0.05	0.11	0.08	0.06	0.03
Ti		–	–	–			0.01	0.01		–		–	
P	0.02	0.02	0.02	0.01	0.07	0.15	0.02		–	0.03	0.01	0.01	0.01
V	1.47	1.36	1.27	1.19	0.94	0.91	0.76	0.68	0.57	0.55	0.37	0.33	<i>0.22</i>
As	1.53	1.45	1.64	1.71	1.92	1.86	2.05	1.98	2.35	2.30	2.56	2.60	<i>2.77</i>
S	0.01	–	0.02	–	–	–	0.01		–	0.01		–	–
ΣX	2.99	2.97	2.98	3.01	2.98	3.01	2.95	2.93	3.03	2.98	2.97	2.99	2.94
ΣY	1.94	2.04	2.05	2.05	2.01	2.08	2.05	2.09	2.04	2.03	1.99	2.00	1.99
ΣZ	3.04	3.00	2.98	2.98	3.00	2.97	3.00	2.99	2.98	3.00	3.02	3.00	3.03

Analyzes are ordered by increasing As⁵⁺ content. Compositions of the structurally studied crystals are highlighted in bold: (1) no. 5, crystal; (2), no. 15, crystal; and (3) no. 18, crystal. The minimum and maximum recorded contents of the components are marked in bold italics. Empty cells correspond to concentrations below the detection limit. Dashes indicate contents of <0.01 apfu ΣX = Na + Ca; ΣY = Mg + Mn + Cu + Zn + Fe³⁺ + Ti; ΣZ = As + V + P + Si + S.

ment parameters, are given in Table. 3. The atomic positions and bond valence sums are given in Table. 4. Selected interatomic distances are listed in Table 5.

The dimensions of the cubic unit cell were determined from a schäferite single crystal from the First Cone of the NVGTFE: *a* = 12.413 (6) Å, *V* = 1913 (2) Å³.

DISCUSSION

In the exhalations of Arsenatnaya fumarole, a continuous series of isostructural solid solutions between berzeliite and schäferite of the following compositions are observed:

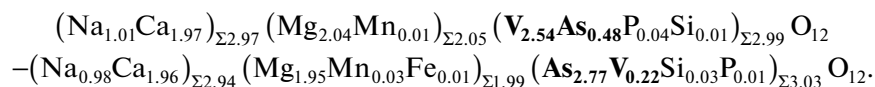


Table 2. Chemical composition of berzeliite and schäferite from other localities (wt %)

Component	1	2	3	4	5	6	7	8
	Berzeliite					Schäferite		
Na ₂ O	4.82	5.50	4.56	4.70	5.23	4.52	9.16	9.08
K ₂ O	0.01	0.01	0.08					
MgO	11.69	12.26	13.60	9.30	11.90	16.46	8.54	11.60
MnO	3.51	1.24	2.83	9.59	3.80	0.37	0.14	0.18
CaO	20.63	19.43	19.27	18.76	19.45	23.44	16.28	16.97
FeO	0.06	1.52		0.03		0.08		
NiO	0.03	0.03					5.28	
ZnO							0.56	
PbO	0.05	0.02	0.35	0.19				
Al ₂ O ₃							0.08	0.13
Fe ₂ O ₃							6.94	6.89
SiO ₂	0.73	0.17	0.66	0.57		0.12	0.15	
TiO ₂	0.03	0.10					0.25	0.87
P ₂ O ₅	0.25	0.05	1.23	1.48		0.23	3.47	1.11
V ₂ O ₅	0.33	1.32	0.23	0.09		53.95	48.79	52.48
As ₂ O ₅	57.40	57.73	56.72	54.92	59.62	0.10		
H ₂ O ⁺			0.37	0.24				
H ₂ O ⁻			0.34	0.12				
Total	99.54	99.38	100.24	100.01	100.00	99.27	99.74*	99.31
Formula coefficients (O = 12)								
Na	0.90	1.02	0.84	0.89	1.00	0.73	1.52	1.48
K	—	—	0.01					
Mg	1.68	1.75	1.94	1.35	1.70	2.04	1.09	1.45
Mn	0.29	0.10	0.23	0.79	0.30	0.03	0.01	0.01
Ca	2.13	2.00	1.97	1.96	2.00	2.09	1.49	1.53
Fe ²⁺								
Ni								
Zn								
Pb								
Al	—	0.12						
Fe ³⁺								
Si	0.07	0.02	0.06	0.06		0.01	0.01	
Ti	—	0.01					0.02	0.05
P	0.02	—	0.09	0.12		0.02	0.25	0.08
V	0.02	0.08	0.03	—		2.96	2.75	2.91
As	2.89	2.89	2.82	2.79	3.00	—		

1, Longbahn, Sweden (Nagashima and Ambruster, 2012); 2, Montaldo, Italy (Nagashima and Ambruster, 2012); 3, 4, Longban (*Handbook ...*, 1990); 5, Longbang (Hawthorne, 1976); 6, Eifel, Germany (Krause et al., 1999); 7, Lavrion, Greece (Koshlyakova et al., 2017); 8, First cone of NV GTFE, Tolbachik volcano, Kamchatka (our data).

* The sum of the analysis also includes (wt %) 0.06 CuO and 0.04 SO₃.

The main variable value in this series is the As : V ratio; the main substitution scheme is ${}^Z\text{As}^{5+} \leftrightarrow {}^Z\text{V}^{5+}$. A subordinate, but still significant role is played by the heterovalent isomorphism scheme ${}^X\text{Ca}^{2+} + {}^Z\text{Si}^{4+} = {}^X\text{Na}^+ + {}^Z\text{V}^{5+}$. The maximum content of silicon and, accordingly, excess in comparison with the ideal formula of calcium is 0.3 apfu. The Y octahedral site is almost completely occupied by Mg (Table 1).

Before our work on isomorphism in natural berzeliite and schäferite, it was known that the Y position in berzeliite can contain significant amounts of Mn^{2+} and, probably, berzeliite forms a continuous series of isostructural solid solutions with manganberzeliite. According to the small number of chemical analyses of berzeliite published in the literature (Table 2), the maximum manganese content is 0.8 apfu (Table 2, No. 4) (*Handbook ...*, 1990). In the schäferite, significant substitutions in the Y position were described for samples from old metallurgical slags of Lavrion (Greece). There, the technogenic analogue of schäferite participates in the formation of a continuous system of solid solutions with the ${}^Y\text{Mg} \leftrightarrow {}^Y\text{Fe}^{3+} \leftrightarrow {}^Y\text{Ni}$ isomorphism, and Ni- and Fe-dominant representatives of this system were also found. The ratio of Na and Ca, occupying the same position X in these vanadates, is determined only by the requirements of the electroneutrality of the formula and, accordingly, changes under heterovalent isomorphism. Among the schäferite-like vanadates from Lavrion, samples with ${}^X\text{Na}$ prevailing over ${}^X\text{Ca}$ are also known, since the entry of ferric iron occurs in them according to the scheme ${}^X\text{Ca}^{2+} + {}^Y\text{Mg}^{2+} \leftrightarrow {}^X\text{Na}^+ + {}^Y\text{Fe}^{3+}$ (Table 2, no. 7; Koshlyakova et al., 2017). The same substitution was observed in schäferite from the exhalations of the First Cone of the GTFE, which has the formula $(\text{Na}_{1.48}\text{Ca}_{1.53})_{\Sigma 3.01}(\text{Mg}_{1.45}\text{Fe}_{0.44}\text{Ti}_{0.05}\text{Mn}_{0.01})_{\Sigma 1.95}(\text{V}_{2.91}\text{P}_{0.08})_{\Sigma 2.99}\text{O}_{12}$ (Table 1, 2, no. 8).

In the exhalations of Arsenatnaya fumarole, significant isomorphism in tetrahedral positions is characteristic of all arsenates, phosphates, and vanadates in a high-temperature (550–700°C) association with berzeliite and schäferite: all of them (minerals of the apatite supergroup, tilasite, alluorite, udinaite, and wagnerite) form solid solutions with broad isomorphic substitutions ${}^T\text{As}^{5+} \leftrightarrow {}^T\text{V}^{5+} \leftrightarrow {}^T\text{P}^{5+}$. Interestingly, of large- and medium-sized species-forming cations, only Mg, Na, and/or Ca are recorded and isomorphism in positions other than tetrahedral is practically not manifested.

The crystal structures of the three studied members of the schäferite–berzeliite isomorphic series are the same. In the series of crystals with the occupation of the tetrahedral position (1) ${}^Z(\text{V}_{1.95}\text{As}_{0.90}\text{Si}_{0.15})_{\Sigma 3}$, (2) ${}^Z(\text{As}_{1.90}\text{V}_{0.90}\text{P}_{0.20})_{\Sigma 3}$, and (3) ${}^Z(\text{As}_{2.35}\text{V}_{0.60}\text{Si}_{0.05})_{\Sigma 3}$, parameter a varies from 12.35 to 12.40 Å, the Z–O distance varies from 1.696 to 1.709 Å, and the X–O and Y–O distances remain practically constant (Table 5).

Small variations in these characteristics can be explained by the closeness of the radii of pentavalent vanadium and arsenic (0.355 and 0.335 Å, respectively; Shannon, 1976) and the absence of significant substitutions, which would involve cations of different sizes. The parameters of the cubic cell and the sizes of oxygen polyhedra in the studied crystals are close to the characteristics of berzeliite and schäferite given in the literature. At the same time, the cell sizes are expected to exceed values typical for most silicate garnets ($a = 11.5\text{--}12.5$ Å; Hawthorne, 1976; Krause et al., 1999; Nagashima and Armbruster, 2012; Novak and Gibbs, 1971; etc.), first of all, by replacing Si^{4+} with somewhat larger As^{5+} or V^{5+} .

In addition to berzeliite, the exhalations of Arsenatnaya fumarole contain its dimorph with an alluodite structure — paraberzeliite. Arsenates of the alluodite structural type are the most abundant arsenic minerals in the exhalations of this fumarole, where they are represented by ten mineral species. The monoclinic structure of the alluodite type is characterized by the space group $C2/c$, the general formula of the minerals of this group is written as $A(1)A(2)M(1)M(2)_2(\text{TO}_4)_3$, where $A = \text{Na, K, Ca, Mn, Cu}^{2+}, \text{OH}^-, \text{H}_2\text{O}$, and vacancy; $M = \text{Li, Na, Ca, Mg, Mn, Cu}^{2+}, \text{Zn, Al, Fe}^{2+}, \text{and Fe}^{3+}$; and $T = \text{As}^{5+}$ and P^{5+} (Hatert, 2019). The “garnet – representative of the structural type of alluodite” dimorphism for compounds with the formula $\text{NaCa}_2\text{M}_2^{2+}(\text{AsO}_4)_3$ has not only been noted in nature (Ercit, 1993; Pekov et al., 2018), but also studied experimentally (Khorari et al., 1995, 1997). According to experimental data, impurities of different-sized cations have a significant effect on the preferred crystallization under the same conditions of one or another structural type. Replacement of Na and Ca by cations or vacancies that differ greatly from them in size leads to the stabilization of the alluodite structure relative to the garnet structure (Khorari et al., 1995, 1997). The authors of the cited works explain this by the fact that, in an alluodite-type structure, the corresponding impurities can be distributed between three positions $A(2)$, $A(1)$, and $M(1)$, which differ in size and coordination, whereas they jointly occupy a single dodecahedral position X in arsenates with a garnet structure. Similar patterns are observed for natural samples; for example, the alluodite-like mineral karyinite $\text{NaCa}_2\text{Mn}_2(\text{AsO}_4)_3$, which is often associated with its polymorph manganberzeliite in metamorphosed manganese ores, differs from it in the content of a significant impurity of lead (Ercit, 1993). In Arsenatnaya fumarole exhalations, paraberzeliite is associated with berzeliite, but it is much less widespread and differs from berzeliite in crystallochemically by the presence of vacancies and K impurity (up to 0.25 and 0.1 apfu, respectively), replacement of calcium with magnesium (up to 0.4 apfu),

Table 3. Chemical composition, crystal data, data-collection information, and structure-refinement details for (1) schäferite and (2, 3) berzeliite from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka

Sample	1	2	3
Formula	{Ca _{2.15} Na _{0.85} } _{Σ3} [Mg _{2.00}] (V _{1.95} As _{0.90} Si _{0.15}) _{Σ3} O ₁₂	{Ca _{2.0} Na _{1.0} } _{Σ3} [Mg _{2.00}] (As _{1.90} V _{0.90} P _{0.20}) _{Σ3} O ₁₂	{Ca _{2.05} Na _{0.95} } _{Σ3} [Mg _{2.00}] (As _{2.35} V _{0.60} Si _{0.05}) _{Σ3} O ₁₂
Formula weight	517.31	538.16	552.65
Crystal system, sp. group, Z		Cubic, <i>Ia</i> – <i>3d</i> , 8	
<i>a</i> , Å	12.39737(7)	12.35366(10)	12.36093(10)
<i>V</i> , Å ³	1905.41(3)	1885.33(5)	1888.66(5)
<i>F</i> (000)	1992	2059	2108
μ , mm ⁻¹	6.435	8.952	10.220
Diffractometer		Xcalibur S CCD	
Temperature, K		293(2)	
Radiation		MoK α , $\lambda = 0.71073$ Å	
θ (°)	4.026–34.880	4.041–34.819	4.038–34.796
<i>h</i> , <i>k</i> , <i>l</i>		–19 \leftrightarrow 19, –19 \leftrightarrow 19, –19	
Number of measured [<i>I</i> > 2 σ (<i>I</i>)] independent, and observed reflections	21955, 352, 337	21328, 346, 334	22201, 348, 336
R _{int}	0.0392	0.0387	0.0466
Structure solution		Direct methods	
Refinement		<i>F</i> ²	
Extinction coefficient	0.00100(13)	0.00062(9)	0.00054(7)
<i>R</i> 1 and <i>wR</i> 2 for <i>I</i> > 2 σ (<i>I</i>)	0.0210, 0.0543	0.0181, 0.0466	0.0251, 0.0489
<i>R</i> 1 and <i>wR</i> 2 for complete data	0.0242, 0.0554	0.0199, 0.0470	0.0266, 0.0492
Number of refined parameters	20	18	18
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$, e Å ⁻³	0.319, –0.483	0.343, –0.253	0.373, –0.351
GoF	1.380	1.425	1.485
Weighing scheme		(1): $w = 1/[\sigma^2(F_0^2) + (0.0177P)^2 + 3.5452P]$, (2): $w = 1/[\sigma^2(F_0^2) + (0.0143P)^2 + 3.0993P]$, (3): $w = 1/[\sigma^2(F_0^2) + (0.0099P)^2 + 7.4010P]$, where $P = ([\max(0 \text{ or } F_0^2)] + 2F_c^2)/3$	

Table 4. Coordinates and equivalent displacement parameters (*U*_{eq}, in Å²) of atoms and bond-valence sums for (1) schäferite and (2, 3) berzeliite from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka

		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	BVS
(1)	<i>X</i>	0.125	0	0.25	0.01173(16)	1.76
	<i>Y</i>	0	0	0	0.0086(2)	2.04
	<i>Z</i>	0.375	0	0.25	0.00626(13)	4.85
	<i>O</i>	0.03863(8)	0.05112(8)	0.65555(8)	0.0107(2)	1.99
(2)	<i>X</i>	0.125	0	0.25	0.01155(15)	1.76
	<i>Y</i>	0	0	0	0.0103(2)	2.05
	<i>Z</i>	0.375	0	0.25	0.00708(12)	4.87
	<i>O</i>	0.03880(8)	0.05092(8)	0.65605(8)	0.0110(2)	1.94
(3)	<i>X</i>	0.125	0	0.25	0.01111(18)	1.78
	<i>Y</i>	0	0	0	0.0084(3)	2.04
	<i>Z</i>	0.375	0	0.25	0.00613(13)	4.88
	<i>O</i>	0.03861(11)	0.05092(11)	0.65612(11)	0.0091(3)	2.01

Table 5. Selected interatomic distances (Å) in the crystal structures of schäferite (1) and berzeliite (2) and (3) from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka

	X–O	$\langle X-O \rangle$	Y–O	Z–O
1	2.4265(10) × 6 2.5400(10) × 6	2.483	2.0856(10) × 6	1.7086(10) × 4
2	2.4160(10) × 6 2.5349(10) × 6	2.476	2.0837(10) × 6	1.6961(10) × 4
3	2.4152(14) × 6 2.5359(14) × 6	2.476	2.0852(13) × 6	1.6980(14) × 4

and by finding perceptible impurities of Mn, Fe³⁺, and Cu (up to 0.5, 0.5, and 0.1 apfu) and the absence of V⁵⁺.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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