

Vasilseverginite, $\text{Cu}_9\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2$, a new fumarolic mineral with a hybrid structure containing novel anion-centered tetrahedral structural units

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ABSTRACT

The new mineral vasilseverginite, ideally $\text{Cu}_9\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2$, was found in the Arsenatnaya fumarole at the second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with tenorite, lammerite, stranskiite, lammerite- β , langbeinite, dolerophanite, sanidine, hematite, and gahnite. Vasilseverginite occurs as prismatic crystals up to $0.02 \times 0.02 \times 0.06 \text{ mm}^3$ combined in groups or interrupted crusts up to $1 \times 2 \text{ cm}^2$ in area and up to 0.1 mm thick. It is transparent, bright green, with vitreous luster. D_{calc} is $4.41 \text{ g}\cdot\text{cm}^{-3}$. Vasilseverginite is optically biaxial (–), α 1.816(5), β 1.870(5), γ 1.897(5), estimated $2V$ is $30(15)^\circ$. Chemical composition (wt%, electron-microprobe) is: CuO 64.03, ZnO 0.79, Fe_2O_3 0.25, P_2O_5 0.05, As_2O_5 20.83, SO_3 14.92, total 100.87. The empirical formula calculated on $\text{O} = 20 \text{ apfu}$ is $(\text{Cu}_{8.78}\text{Zn}_{0.11}\text{Fe}_{0.03}^{3+})_{\Sigma 8.92}\text{As}_{1.98}\text{P}_{0.01}\text{S}_{2.03}\text{O}_{20}$. Vasilseverginite is monoclinic, $P2_1/n$, $a = 8.1131(4)$, $b = 9.9182(4)$, $c = 11.0225(5) \text{ \AA}$, $\beta = 110.855(2)^\circ$, $V = 828.84(6) \text{ \AA}^3$, and $Z = 2$. The strongest reflections in the powder XRD pattern [$d, \text{\AA}(hkl)$] are: $7.13(41)(10\bar{1})$, $5.99(70)(110, 11\bar{1})$, $5.260(100)(101)$, $4.642(46)(111)$, $3.140(31)(03\bar{1})$, $2.821(35)(02\bar{3})$, $2.784(38)(13\bar{2}, 03\bar{2})$, $2.597(35)(20\bar{4})$, and $2.556(50)(23\bar{1}, 212)$. The crystal structure, solved using single-crystal X-ray diffraction data, $R_1 = 0.025$, is based upon complex $[\text{O}_4\text{Cu}_9]^{10+}$ layers parallel to $(\bar{1}01)$ that are composed of edge- and corner-sharing (OCu_4) tetrahedra. The topology is unprecedented in inorganic structural chemistry. The crystal structure can be considered a hybrid of the structures of popovite $\text{Cu}_5\text{O}_2(\text{AsO}_4)_2$ and dolerophanite $\text{Cu}_2\text{O}(\text{SO}_4)$ according to the scheme $\text{Cu}_9\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2 = \text{Cu}_5\text{O}_2(\text{AsO}_4)_2 + 2\text{Cu}_2\text{O}(\text{SO}_4)$. The chemical hybridization does not result in a significant increase in chemical complexity of vasilseverginite compared to the sum of those of popovite and dolerophanite, whereas the structural hybridization leads to the doubling of structural information per unit cell. The mineral is named in memory of the outstanding Russian mineralogist, geologist, and chemist Vasilii Mikhailovich Severgin (1765–1826).

Keywords: Vasilseverginite, new mineral, copper arsenate sulfate, popovite, dolerophanite, crystal structure, oxo-centered tetrahedra, structural complexity, hybridization of mineral species, fumarole sublimate, Tolbachik volcano

INTRODUCTION

From the viewpoint of geochemical and environmental importance, sulfates and arsenates attract considerable attention, due to their existence in a wide range of geo- and cosmochemical environments. The ordered combination of arsenate and sulfate anions in the same mineral is rare; there are only 20 minerals known that contain both sulfate and arsenate as species-defining components. Among the 20, only two phases are H-free.

Natural H-bearing (with OH^- or/and H_2O) arsenate-sulfates usually have a low-temperature, supergene origin and occur mainly in the oxidation zones of ore deposits. Among the members of the beudantite group, a subdivision of the alunite supergroup, only beudantite, $\text{PbFe}_3^{3+}(\text{AsO}_4)(\text{SO}_4)_2(\text{OH})_6$, is a relatively common mineral, whereas other four species are

rare, namely gallobeudantite, $\text{PbGa}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$, hidalgoite, $\text{PbAl}_3(\text{AsO}_4)(\text{SO}_4)_2(\text{OH})_6$, kemmlitzite, $\text{SrAl}_3(\text{AsO}_4)(\text{SO}_4)_2(\text{OH})_6$, and weilerite, $\text{BaAl}_3(\text{AsO}_4)(\text{SO}_4)_2(\text{OH})_6$. In the crystal structures of some of these minerals, sulfate and arsenate anions are disordered, whereas others demonstrate ordered distribution of S^{6+} and As^{5+} over tetrahedral sites (Bayliss et al. 2010). The known hydrous Fe arsenate-sulfates are bukovskýite, $\text{Fe}_3^{3+}(\text{AsO}_4)(\text{SO}_4)(\text{OH})\cdot 9\text{H}_2\text{O}$ (Majzlan et al. 2012), sarmientite, $\text{Fe}_3^{3+}(\text{AsO}_4)(\text{SO}_4)(\text{OH})\cdot 5\text{H}_2\text{O}$ (Colombo et al. 2014), hilarionite, $\text{Fe}_2^{3+}(\text{AsO}_4)(\text{SO}_4)(\text{OH})\cdot 6\text{H}_2\text{O}$ (Pekov et al. 2014), and zýkaite, $\text{Fe}_4^{3+}(\text{AsO}_4)_3(\text{SO}_4)(\text{OH})\cdot 15\text{H}_2\text{O}$ (Čech et al. 1978). Bukovskýite and sarmientite are As,S-ordered minerals, whereas the crystal structures of hilarionite and zýkaite are unknown. For mallesitigite, $\text{Pb}_3\text{Sb}(\text{SO}_4)(\text{AsO}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$ (Sima 1998), the disordered distribution of As and S is likely, by analogy with other fleischerite-group members. In the crystal structure of juansilvaite, $\text{Na}_5\text{Al}_3[\text{AsO}_3(\text{OH})]_4[\text{AsO}_2(\text{OH})_2]_2(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$, sulfate groups

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and acid arsenate groups of two types demonstrate ordering (Kampf et al. 2017). Seven H-bearing arsenate-sulfates contain species-defining Cu^{2+} . Arsentsumebite, $\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{SO}_4)(\text{OH})$, a member of the brackebuschite group, has partially ordered distribution of As and S (Zubkova et al. 2002), which also occurs in the sulfate-bearing variety of thometzekite, a tsumcorite-group mineral with the idealized formula $\text{PbCu}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Krause et al. 1998). As-S ordering was reported for chalcophyllite, $\text{Cu}_{18}\text{Al}_2(\text{AsO}_4)_4(\text{SO}_4)_3(\text{OH})_{24} \cdot 36\text{H}_2\text{O}$ (Sabelli 1980), tangdanite, $\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{SO}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_2\text{O}$ (Ma et al. 2014), claraite, $(\text{Cu},\text{Zn})_{15}(\text{CO}_3)_4(\text{AsO}_4)_2(\text{SO}_4)(\text{OH})_{14} \cdot 7\text{H}_2\text{O}$ (Biagioni and Orlandi 2017), and leogangite, $\text{Cu}_{10}(\text{AsO}_4)_4(\text{SO}_4)(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ (Lengauer et al. 2004), and suggested for parnaute $\text{Cu}_9(\text{AsO}_4)_2(\text{SO}_4)(\text{OH})_{10} \cdot 7\text{H}_2\text{O}$ (Mills et al. 2013). The crystal structure of barrotite, $\text{Cu}_9\text{Al}(\text{HSiO}_4)_2[(\text{SO}_4)(\text{HAsO}_4)_{0.5}](\text{OH})_{12} \cdot 8\text{H}_2\text{O}$ (Sarp et al. 2014), is still unknown.

The H-free arsenates-sulfates are much rarer and are represented by nishanbaevite, ideally $\text{KAl}_2\text{O}(\text{AsO}_4)(\text{SO}_4)$ (Pekov et al. 2019) and vasilseverginite, $\text{Cu}_9\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2$, the mineral described herein. Both minerals demonstrate an ordered distribution of AsO_4 and SO_4 tetrahedral groups and contain additional oxygen atoms O_{ad} , not bonded to As^{5+} or S^{6+} . Both minerals are unique to the active, oxidizing-type Arsenatnaya fumarole at the Tolbachik volcano (Kamchatka, Russia), in which they were formed as volcanic sublimates under temperatures higher than 350–400 °C, like other arsenates described from this locality (Pekov et al. 2018a, 2018b).

The new mineral vasilseverginite (Cyrillic: вasilseverгинит) is named in memory of the outstanding Russian mineralogist, geologist, and chemist Vasilii Mikhailovich Severgin (1765–1826), Academician of the Russian Academy of Sciences. He wrote the first books on geology and mineralogy in Russia (Severgin 1791, 1798, 1807), created the first chemical nomenclature in Russian, and compiled the first Russian chemical dictionary. Acad. Severgin was one of the founders of the Russian Mineralogical Society in 1817.

Both the new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No. 2015-083). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, under the catalog number 95280.

ANALYTICAL METHODS

The chemical data for vasilseverginite were obtained using a JEOL JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer, with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 3 μm beam diameter. The reference materials used are given in Table 1. Contents of other elements with atomic numbers higher than that of carbon are below detection limits.

The Raman spectrum of vasilseverginite was recorded using an EnSpectr R532 spectrometer with a green laser (532 nm) at room temperature. The laser beam output power was about 7 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 of 6 cm^{-1} . The diameter of the focal spot on the sample was about 10 μm . The Raman spectrum was acquired on a polycrystalline sample.

Powder X-ray diffraction (XRD) study of the new mineral was carried out using a Rigaku RAXIS Rapid II single-crystal diffractometer equipped with a curved image plate detector (Debye-Scherrer geometry, $r = 127.4\text{ mm}$) and $\text{CoK}\alpha$ radiation source (rotating anode, 40 kV, 15 mA), with Rigaku VariMax microfocus mirror

TABLE 1. Chemical composition (wt%) of vasilseverginite

Constituent	Mean	Range	Standard deviation	Reference material
CuO	64.03	63.53–64.52	0.44	CuFeS_2
ZnO	0.79	0.09–1.30	0.61	ZnS
Fe_2O_3^a	0.25	0.00–0.60	0.25	FeS
P_2O_5	0.05	0.00–0.14	0.05	GaP
As_2O_5	20.83	20.13–21.48	0.56	FeAsS
SO_3	14.92	13.14–15.83	1.03	SrSO_4
Total	100.87			

^a Fe is considered as trivalent, owing to the extremely oxidizing conditions in the Arsenatnaya fumarole (Pekov et al. 2018a).

optics. Imaging plate-to-profile data conversion was performed using osc2xrd software (Britvin et al. 2017).

A single-crystal X-ray data set was collected by means of a Bruker Kappa APEX DUO diffractometer equipped with a microfocus $\text{MoK}\alpha$ radiation source. A full Ewald sphere of reciprocal space was collected at a frame sweep of 1° to $2\theta = 56^\circ$. Data collection and refinement of unit-cell parameters were carried out using Bruker APEX2 software (Bruker 2003). Data processing and integration routines were performed by means of a Rigaku Oxford Diffraction CrysAlisPro software. The crystal structure was solved by the intrinsic phasing method implemented in a SHELXT-2018 program (Sheldrick 2015) and refined to $R_1 = 0.025$ on the basis of 1428 unique observed [$I > 2\sigma(I)$] reflections, using SHELXT-2015 software incorporated into Olex2 graphical user interface (Dolomanov et al. 2009). A complete set of crystallographic data can be retrieved from the CIF file attached as the Online Material¹.

The chemical and structural complexity parameters have been calculated using the procedure outlined by Krivovichev et al. (2018a, 2018b). The chemical complexity was evaluated by the amounts of chemical Shannon information per atom ($^{\text{chem}}I_G$) and per formula unit, fu ($^{\text{chem}}I_{G,\text{total}}$), whereas the structural complexity was measured as the amounts of structural Shannon information per atom ($^{\text{str}}I_G$) and per unit cell ($^{\text{str}}I_{G,\text{total}}$).

RESULTS AND DISCUSSION

Occurrence and mineral association

The Arsenatnaya fumarole is situated at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–1976. This scoria cone, a monogenetic volcano about 300 m high and $\sim 0.1\text{ km}^3$ in volume formed in 1975 (Fedotov and Markhinin 1983), is located 18 km South of the Ploskiy Tolbachik volcano in the central part of Kamchatka Peninsula, Far-Eastern Region, Russia ($55^\circ 41' \text{N}$ $160^\circ 14' \text{E}$, 1200 m asl). The fumarolic activity at this scoria cone remains strong: in 2012–2018, we observed here numerous gas vents with temperatures up to 490 °C.

The specimens containing vasilseverginite were collected in July 2013 from the intermediate zone of the Arsenatnaya fumarole (Pekov et al. 2018a) located at a depth of 1–1.5 m from the day surface. The temperatures, measured during sampling by means of a chromel-alumel thermocouple in the pockets from which these specimens originate, were 360–380 °C. We believe that vasilseverginite was deposited directly from the gaseous phase as a volcanic sublimate at temperatures higher than 380 °C.

On the holotype specimen, vasilseverginite occurs in intimate association with tenorite, lammerite, lammerite- β , stranskiite, langbeinite, dolerophanite, hematite, As-bearing sandinite, and Cu-bearing gahnite. On other specimens, the new mineral is associated also with johillerite, urusovite, ericlauxmanite, kozyrevskite, popovite, tilasite, svabite, bradaczekite, apthitalite, metathénardite, belomarinaite, krashennikovite, anhydrite, euchlorine, wulfite, alumoklyuchevskite, cryptochalcite, fluoborite, sylvite, and halite. The associated minerals are listed in order of the decrease of abundance.

General appearance, physical properties, and optical data

Vasilseverginite occurs as well-formed prismatic crystals up to $0.02 \times 0.02 \times 0.06 \text{ mm}^3$, with complex oblique terminations (Fig. 1). The crystal forms were not determined. Vasilseverginite crystals are combined in groups or interrupted, typically open-work incrustations (Figs. 1 and 2) up to $1 \times 2 \text{ cm}^2$ in area and up to 0.1 mm thick, usually overgrowing basalt scoria (Fig. 2a) or crystalline crusts of tenorite (Fig. 2b).

Vasilseverginite is transparent, bright green, in some cases with a distinct golden hue. The streak is light green. The luster is vitreous. The mineral is brittle, cleavage or parting was not observed, and the fracture is uneven. The density and Mohs hardness were not measured because crystals of vasilseverginite are too small and aggregates are open work. The density calculated using the empirical formula is 4.409 g/cm^3 .

Under the microscope, in plane-polarized transmitted light vasilseverginite is weakly pleochroic: X = yellowish-green, Y and Z = emerald green. It is optically biaxial (–), $\alpha = 1.816(5)$, $\beta = 1.870(5)$, $\gamma = 1.897(5)$ (589 nm), the estimated $2V$ value is $30(15)^\circ$ and $2V_{\text{calc}} = 69^\circ$. Such difference between measured and calculated $2V$ values is probably caused by the low quality of crystals, which is also reflected in the relatively high estimated

errors ± 0.005 for all three refractive indices. Dispersion of optical axes is weak, $r > v$.

Chemical composition

The chemical composition of the holotype specimen of vasilseverginite (in wt%, mean results for five spot analyses) are given in Table 1. The empirical formula calculated on the basis of 20 O atoms per formula unit is $(\text{Cu}_{8.78}\text{Zn}_{0.11}\text{Fe}_{0.03}^{3+})_{\Sigma 8.92}\text{As}_{1.98}\text{P}_{0.01}\text{S}_{2.03}\text{O}_{20}$. The idealized formula is $\text{Cu}_9\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2$, which requires CuO 64.74, As_2O_5 20.78, SO_3 14.48, total 100 wt%.

Raman spectroscopy

The Raman spectrum of vasilseverginite is shown in Figure 3. The Raman mode assignments, in accordance with Nakamoto (1986), are as follows. Bands with maxima at 1204, 1103, and 1075 cm^{-1} correspond to antisymmetric $\text{S}^{6+}\text{-O}$ stretching vibra-

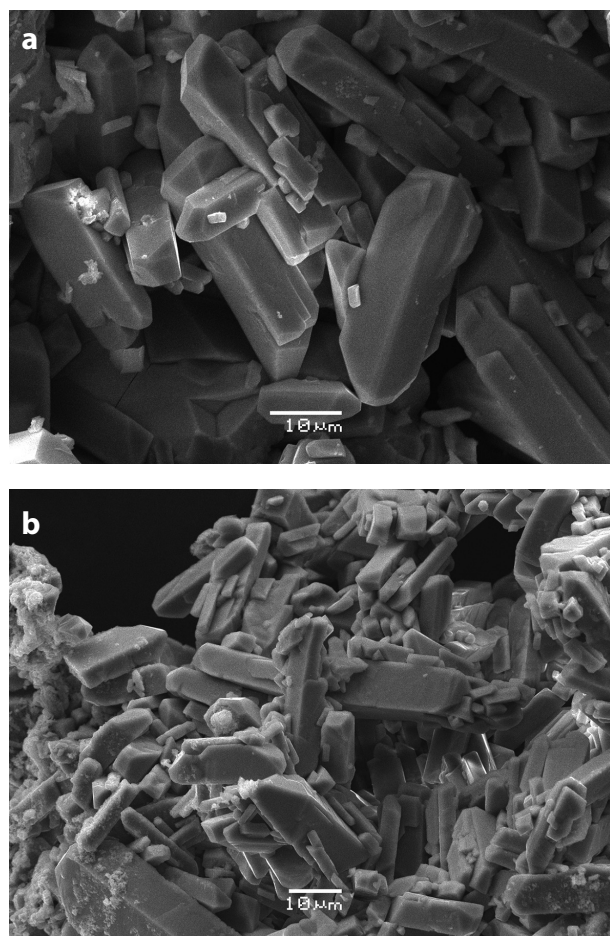


FIGURE 1. SEM (SE) images of typical crystal group (a) and crystal crust (b) of vasilseverginite.

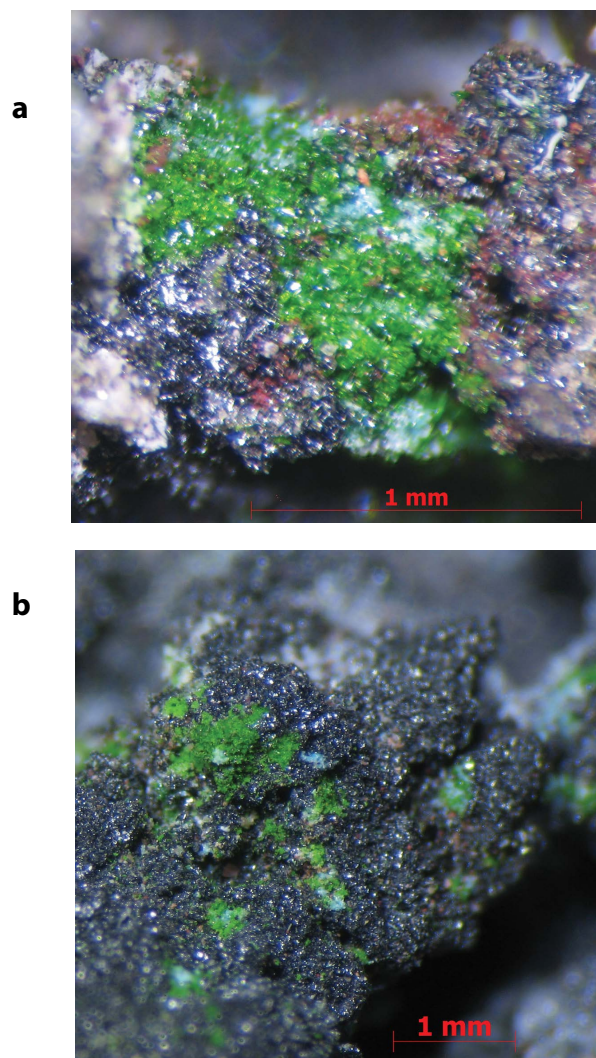


FIGURE 2. Bright green aggregates of vasilseverginite on basalt scoria with iron-black tenorite and white sanidine (a) and on iron-black tenorite crystal crust with light blue stranskiite (b). Photo: I.V. Pekov and A.V. Kasatkin. (Color online.)

tions, whereas those at 1007 and 982 cm^{-1} correspond to symmetric stretching vibrations of $(\text{SO}_4)^{2-}$ groups. The strongest single band at 846 cm^{-1} corresponds to As^{5+} -O stretching vibrations of $(\text{AsO}_4)^{3-}$ groups. The bands in the region 650–570 cm^{-1} correspond to S^{6+} -O bending vibrations. The strong band at 558 cm^{-1} could be assigned to Cu^{2+} -O stretching mode corresponding to short Cu-O distances, about 1.9–2.0 Å (Table 2). Bands with frequencies lower than 400 cm^{-1} probably correspond to As^{5+} -O bending vibrations, Cu^{2+} -O stretching vibrations corresponding to long Cu-O distances, about 2.3–2.4 Å (Table 2), and lattice modes. The absence of bands with Raman shifts higher than 1250 cm^{-1} indicates the absence of H-, C-, and N-bearing groups in vasilseverginite.

Powder X-ray diffraction

Powder XRD data of vasilseverginite are reported in Table 3. The powder XRD pattern of the new mineral is unique and can be used as a good diagnostic tool. Parameters of the monoclinic unit

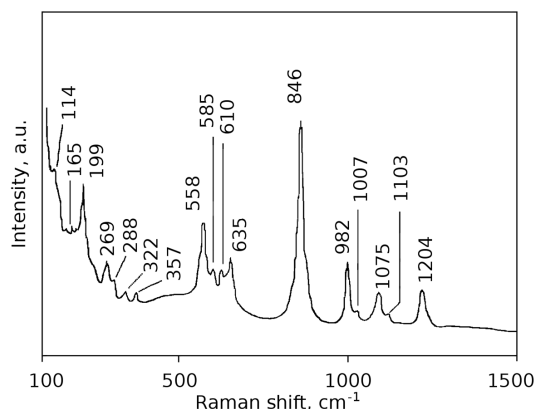


FIGURE 3. Raman spectrum of vasilseverginite (only region with Raman bands is shown).

TABLE 2. Selected bond lengths (Å) for vasilseverginite

Bond	Distance	Bond	Distance
Cu1-O1	2.039(3)	S-O1	1.490(3)
Cu1-O4	2.295(3)	S-O2	1.501(3)
Cu1-O8	1.986(3)	S-O3	1.504(3)
Cu1-O9	1.982(3)	S-O4	1.453(3)
Cu1-O10	1.941(3)	<S-O>	1.487
<Cu1-O>	2.049	As-O5	1.708(3)
Cu2-O3	2.071(3)	As-O6	1.702(3)
Cu2-O5	1.971(3)	As-O7	1.685(3)
Cu2-O6	1.975(3)	As-O8	1.668(3)
Cu2-O9	1.901(3)	<As-O>	1.691
Cu2-O4	2.440(3)		
<Cu2-O>	2.072	O9-Cu1	1.982(3)
Cu3-O5	1.936(3)	O9-Cu2	1.901(3)
Cu3-O6	2.027(3)	O9-Cu3	2.034(3)
Cu3-O9	2.034(3)	O9-Cu4	1.994(3)
Cu3-O10	1.886(3)	<O9-Cu>	1.978
Cu3-O4	2.530(3)		
Cu3-O8	2.641(3)	O10-Cu1	1.941(3)
<Cu3-O>	2.083	O10-Cu3	1.886(3)
Cu4-O2	1.965(3)	O10-Cu4	1.900(3)
Cu4-O3	2.390(3)	O10-Cu5	1.914(3)
Cu4-O7	2.035(3)	<O10-Cu>	1.910
Cu4-O9	1.994(3)		
Cu4-O10	1.900(3)		
<Cu4-O>	2.096		
Cu5-O1 × 2	2.390(3)		
Cu5-O7 × 2	2.031(3)		
Cu5-O10 × 2	1.914(3)		
<Cu5-O>	2.112		

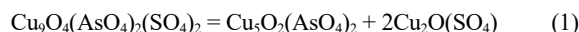
cell calculated from powder data are: $a = 8.113(4)$, $b = 9.918(2)$, $c = 10.992(6)$ Å, $\beta = 110.90(4)^\circ$, and $V = 826.2(8)$ Å³.

Crystal structure

The crystal structure of vasilseverginite demonstrates a new structure type that has no analogs among minerals and synthetic inorganic materials. It contains five symmetrically independent Cu sites coordinated either by five (Cu1, Cu2, Cu4) or six (Cu3, Cu5) O atoms. The Cu^{2+} coordination polyhedra are strongly distorted due to the Jahn-Teller effect (Fig. 4). The description of the crystal structure of vasilseverginite in terms of cation coordination polyhedra is very difficult because of the very complex system of linkage involving the distorted Cu square pyramids and octahedra (Fig. 5a). In contrast, the description in terms of anion-centered (OCu_4) tetrahedra (Krivovichev et al. 2013) formed by additional O_{ad} atoms (not bonded to As or S) is very straightforward (Figs. 5b and 6). The O9 and O10 atoms are not bonded to As or S and are coordinated tetrahedrally by four Cu atoms each, thus forming (OCu_4) oxo-centered tetrahedra. The structure is based upon complex $[\text{O}_4\text{Cu}_9]^{10+}$ layers composed of edge- and corner-sharing (OCu_4) tetrahedra (Figs. 6c and 6d). The layers are parallel to $(\bar{1}01)$. The (SO_4) tetrahedra are located inside the layers, whereas the (AsO_4) tetrahedra provide their linkage in the third dimension (Fig. 6a). It is worthy to note that the topology of the $[\text{O}_4\text{Cu}_9]^{10+}$ layers is novel and unprecedented among known minerals and synthetic compounds.

Hybrid character of the structure and chemical and structural complexity

In terms of chemistry, vasilseverginite has the composition intermediate between popovite, $\text{Cu}_5\text{O}_2(\text{AsO}_4)_2$ (Pekov et al. 2015), and dolerophanite, $\text{Cu}_2\text{O}(\text{SO}_4)$ (Scacchi 1873; Effenberger 1985):



Both dolerophanite and popovite have been found in the Tolbachik fumaroles, and both contain structural units composed from

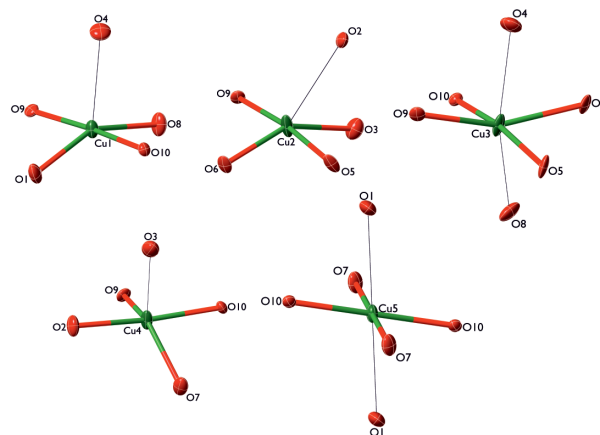


FIGURE 4. Coordination polyhedra of Cu^{2+} cations in the crystal structure of vasilseverginite. Legend: Cu atoms = green; O atoms = red. Displacement ellipsoids are drawn at 75% probability level. Cu-O bonds longer than 2.078 Å are shown as thin gray lines. (Color online.)

TABLE 3. Powder X-ray diffraction data (*d* in angstroms) for vasilseverginite

<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{calc} ^a	<i>d</i> _{calc} ^b	<i>hkl</i>
19	7.50	13	7.515	10 $\bar{1}$
41	7.13	40	7.144	01 $\bar{1}$
70	5.99	31, 44	6.023, 5.990	110, 11 $\bar{1}$
100	5.260	100	5.275	101
46	4.642	41	4.657	111
21	4.560	20	4.571	01 $\bar{2}$
2	4.465	2	4.468	02 $\bar{1}$
16	4.134	8, 6	4.150, 4.139	120, 12 $\bar{1}$
18	3.780	19	3.791	200
5	3.651	3	3.655	10 $\bar{3}$
14	3.565	14, 1	3.572, 3.541	02 $\bar{2}$, 210
7	3.502	7	3.514	21 $\bar{2}$
28	3.451	25	3.461	11 $\bar{2}$
12	3.238	12	3.244	01 $\bar{3}$
31	3.140	29, 4	3.148, 3.140	03 $\bar{1}$, 22 $\bar{1}$
11	3.049	4	3.051	21 $\bar{1}$
15	3.021	13, 3, 2, 1	3.030, 3.026, 3.017, 3.012	130, 131, 21 $\bar{3}$, 220
18	2.959	20	2.962	12 $\bar{2}$
35	2.821	23	2.823	02 $\bar{3}$
38	2.784	36, 25	2.791, 2.782	132, 03 $\bar{2}$
27	2.668	41, 2, 1	2.675, 2.669, 2.655	113, 22 $\bar{3}$, 114
18	2.630	30	2.637	20 $\bar{2}$
35	2.597	68, 3	2.604, 2.592	204, 31 $\bar{1}$
17	2.588	14	2.584	31 $\bar{2}$
50	2.556	92, 11	2.563, 2.549	23 $\bar{1}$, 21 $\bar{2}$
3	2.498	11, 1	2.505, 2.493	30 $\bar{3}$, 014
3	2.475	2, 1	2.482, 2.479	23 $\bar{2}$, 040
6	2.438	5, 7	2.449, 2.429	310, 31 $\bar{3}$
5	2.420	2	2.424	12 $\bar{3}$
18	2.374	32, 14	2.381, 2.362	03 $\bar{3}$, 32 $\bar{1}$
15	2.353	12, 5	2.355, 3.355	32 $\bar{2}$, 14 $\bar{1}$
4	2.282	2	2.285	024
8	2.239	12, 1	2.244, 2.239	141, 14 $\bar{2}$
4	2.207	6	2.217	31 $\bar{1}$
9	2.188	10, 10	2.196, 2.192	105, 314
3	2.150	7, 5	2.157, 2.144	114, 11 $\bar{5}$
5	2.132	8	2.135	21 $\bar{3}$
2	2.108	1	2.112	21 $\bar{5}$
9	2.067	8, 2	2.070, 2.067	24 $\bar{2}$, 321
5	2.047	2, 1	2.052, 2.046	14 $\bar{3}$, 234
7	2.022	7, 1, 1	2.028, 2.019, 2.017	40 $\bar{2}$, 124, 01 $\bar{5}$

<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{calc} ^a	<i>d</i> _{calc} ^b	<i>hkl</i>
6	2.003	6, 4, 2	2.010, 2.008, 2.001	04 $\bar{3}$, 330, 223
3	1.973	5, 3	1.979, 1.964	30 $\bar{5}$, 312
2	1.956	1, 1, 1	1.961, 1.956, 1.952	241, 41 $\bar{1}$, 243
3	1.936	5	1.940	31 $\bar{5}$
3	1.914	7	1.918	15 $\bar{1}$
2	1.897	2	1.902	02 $\bar{5}$
3	1.870	1, 4	1.874, 1.862	331, 410
12	1.853	19, 3, 1, 2, 1	1.858, 1.857, 1.851, 1.851, 1.850	322, 151, 05 $\bar{2}$, 42 $\bar{1}$, 143
3	1.832	1, 3	1.838, 1.830	32 $\bar{5}$, 105
3	1.825	1, 2	1.824, 1.822	233, 341
5	1.804	4, 4	1.809, 1.806	235, 242
7	1.784	6	1.786	044
3	1.759	7, 2	1.762, 1.758	343, 250
5	1.713	1, 6	1.717, 1.717	125, 006
3	1.696	2, 6	1.698, 1.692	335, 016
4	1.671	2	1.676	341
5	1.651	10	1.653	060
2	1.628	3, 2, 1	1.632, 1.629, 1.622	061, 245, 02 $\bar{6}$
2	1.610	2	1.612	234
3	1.593	3	1.595	51 $\bar{3}$
6	1.569	8, 1	1.571, 1.570	054, 44 $\bar{2}$
8	1.553	11, 4, 3, 1, 2	1.559, 1.555, 1.555, 1.554, 1.552	342, 353, 514, 217, 333
5	1.545	7	1.546	345
12	1.534	13, 14, 1, 6	1.537, 1.537, 1.536, 1.533	435, 336, 523, 117
7	1.494	11	1.495	351
4	1.486	5, 2	1.487, 1.487	126, 354
3	1.464	5	1.465	263
3	1.432	6, 1	1.434, 1.432	343, 235
7	1.417	7, 2, 6	1.421, 1.417, 1.414	237, 164, 511
5	1.410	3, 1	1.411, 1.408	027, 361
6	1.397	1, 3, 2, 1, 8	1.401, 1.401, 1.399, 1.396, 1.396	355, 262, 516, 423, 264
3	1.376	3, 1, 2	1.378, 1.378, 1.375	530, 208, 305
2	1.357	3, 3	1.359, 1.356	526, 542
2	1.353	2	1.354	543
3	1.341	4, 1, 1, 2, 1	1.345, 1.344, 1.344, 1.343, 1.339	155, 037, 256, 60 $\bar{2}$, 118
2	1.323	4, 1, 2, 1	1.326, 1.324, 1.323, 1.321	614, 164, 172, 165
2	1.315	3, 1	1.316, 1.313	507, 265
1	1.297	2	1.298	056
1	1.294	3	1.293	273
2	1.287	3, 2	1.289, 1.285	065, 545

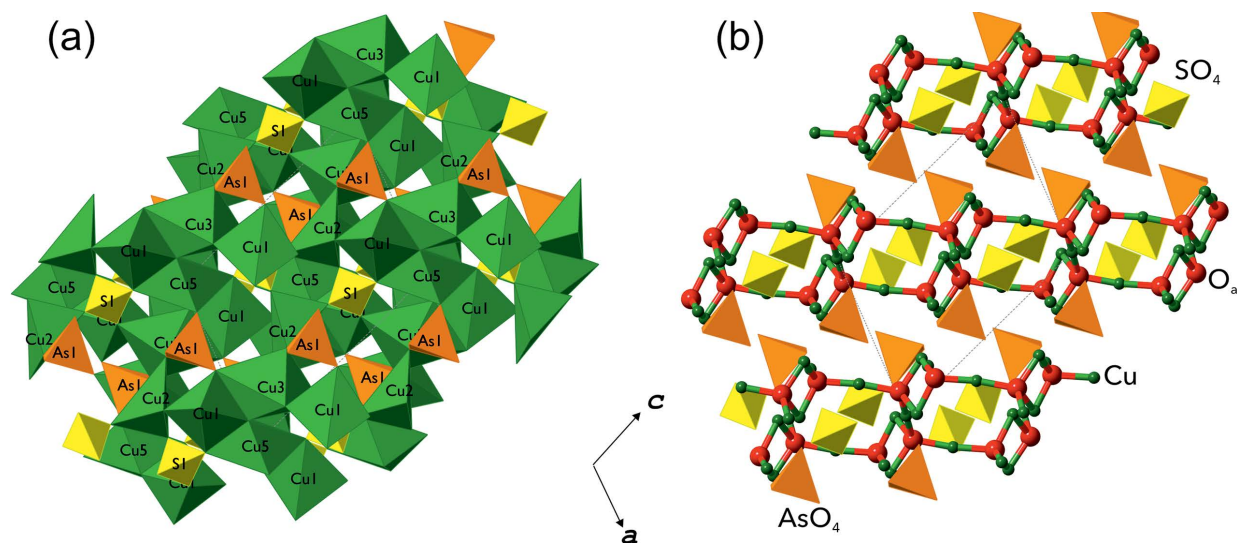
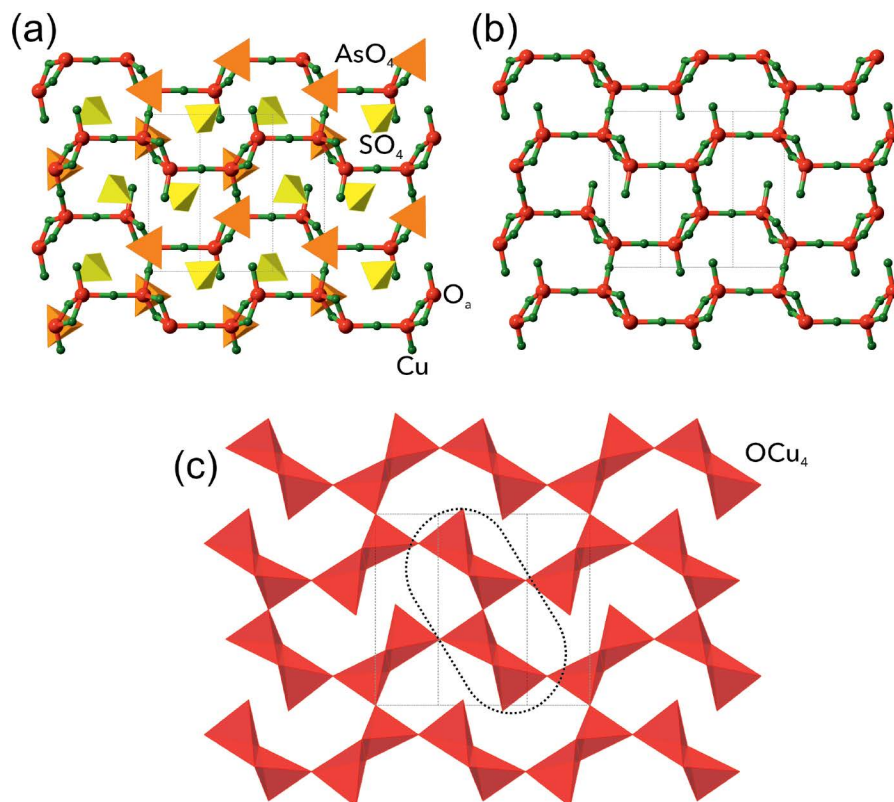
^a For the calculated pattern, only reflections with intensities ≥ 1 are given.^b Based on the unit-cell parameters calculated from single-crystal data. The strongest observed reflections are marked in bold type.**FIGURE 5.** Crystal structure of vasilseverginite shown with cation-centered coordination polyhedra (a) and as a combination of $(\text{SO}_4)^{2-}$ and $(\text{AsO}_4)^{3-}$ tetrahedra and $[\text{O}_4\text{Cu}_6]^{10+}$ double layers consisting of edge- and corner-sharing (OCu_4) tetrahedra (b). (Color online.)

FIGURE 6. The $[\text{O}_4\text{Cu}_9]^{10+}$ double layer in the crystal structure of vasilseverginite surrounded by $(\text{SO}_4)^{2-}$ and $(\text{AsO}_4)^{3-}$ tetrahedra (a) and the same layer shown as ball-and-stick (b) and polyhedral (c) representations. The dotted line in c outlines the contour of the tetramer of edge- and corner-sharing tetrahedra. (Color online.)



edge- and corner-sharing (OCu_4) tetrahedra (Pekov et al. 2018b). However, the topologies and dimensionalities of the units are different. In dolerophanite, the (OCu_4) tetrahedra form sheets (Fig. 7a), whereas the crystal structure of popovite contains chains of alternating corner- and edge-linkage of (OCu_4) tetrahedra (Fig. 7b). In the dolerophanite sheet, all Cu atoms are bridging between adjacent (OCu_4) tetrahedra, either by sharing edges (the $\text{Cu}_{\text{br}[e]}$ atoms) or corners (the $\text{Cu}_{\text{br}[c]}$ atoms). In contrast, the $[\text{O}_2\text{Cu}_5]$ chain in popovite, along with the $\text{Cu}_{\text{br}[e]}$ and $\text{Cu}_{\text{br}[c]}$ atoms, contains also terminal Cu_t atoms that do not participate in the formation of the oxo-centered structural unit. The $\text{Cu}_{\text{br}[e]}:\text{Cu}_{\text{br}[c]}:\text{Cu}_t$ ratios in dolerophanite and popovite are equal to 1:1:0 and 2:1:2, respectively. The same ratio for vasilseverginite is equal to 4:3:2, which can easily be obtained as a sum of 2:2:0 (double dolerophanite ratio) and 2:1:2 (popovite ratio). Indeed, the topologies of the oxo-centered structural units in dolerophanite, popovite, and vasilseverginite can be considered as based upon the same fundamental building block (FBB) consisting of four (OCu_4) tetrahedra sharing edges and corners (Figs. 6c and 7). These blocks are polymerized into infinite chains in popovite and into sheets in dolerophanite. The polymerization of the FBBs in vasilseverginite represents an intermediate case with the presence of terminal Cu_t atoms, but the resulting topology is two-dimensional.

Therefore, the crystal structure of vasilseverginite can be considered as a hybrid of the crystal structures of dolerophanite and popovite. The structural and chemical complexity parameters for the three minerals estimated using information-based measures (Krivovichev 2012, 2013, 2014; Krivovichev et al. 2018a, 2018b) are given in Table 4. In both chemical and structural terms, the sequence of minerals in the order of decreasing complexity is vasilseverginite > popovite > dolerophanite. It is of interest that

the chemical complexity of vasilseverginite (Vs) approximately corresponds to the sum of those of popovite (Po) and dolerophanite (Do), i.e., is described by the Equation 1 ($\text{Vs} = \text{Po} + 2\text{Do}$):

$$^{\text{chem}}I(\text{Vs}) = 47.498 \approx ^{\text{chem}}I_{G,\text{total}}(\text{Po}) + 2 \times ^{\text{chem}}I_{G,\text{total}}(\text{Do}) = 42.867,$$

where $^{\text{chem}}I_{G,\text{total}}$ is the total amount of chemical Shannon information measured in bit per formula unit.

In contrast, the total structural complexity of Vs is approximately doubled compared to the sum of complexities of Po and Do:

$$^{\text{str}}I_{G,\text{total}}(\text{Vs}) = 268.930 \approx 2 \times [^{\text{str}}I_{G,\text{total}}(\text{Po}) + 2 \times ^{\text{str}}I_{G,\text{total}}(\text{Do})] = 282.974,$$

where $^{\text{str}}I_{G,\text{total}}$ is the total amount of structural Shannon information measured in bit per reduced unit cell.

Thus, the chemical hybridization of popovite and dolerophanite does not result in a significant increase in chemical complexity (the sum of their chemical information amounts is approximately equal to that of vasilseverginite), whereas the structural hybridization leads to the doubling of structural information per unit cell (the structural information of vasilseverginite

TABLE 4. Information-based chemical and structural complexity parameters for dolerophanite, popovite, and vasilseverginite

Mineral	Formula	Space group	Chemical complexity			Structural complexity		
			$^{\text{chem}}v$	$^{\text{chem}}I_G$	$^{\text{chem}}I_{G,\text{Total}}$	$^{\text{str}}v$	$^{\text{str}}I_G$	$^{\text{str}}I_{G,\text{Total}}$
Dolerophanite	$\text{Cu}_2\text{O}(\text{SO}_4)$	$C2/m$	8	1.299	10.392	16	2.750	44.000
Popovite	$\text{Cu}_2\text{O}_2(\text{AsO}_4)_2$	$P\bar{1}$	17	1.299	22.083	17	3.146	53.487
Vasilseverginite	$\text{Cu}_3\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2$	$P2_1/n$	33	1.439	47.498	66	4.075	268.930

Note: v in atoms per cell; I_G in bit per atom; $I_{G,\text{Total}}$ in bit per formula (chem) or per cell (str).

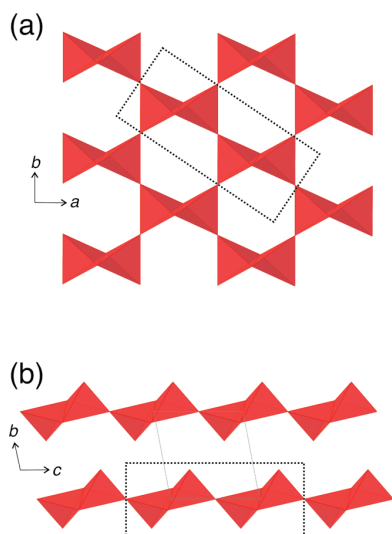


FIGURE 7. The $[\text{O}_2\text{Cu}_4]^{4+}$ sheet in dolerophanite (a) and the arrangement of the $[\text{O}_2\text{Cu}_5]^{6+}$ chains in popovite (b). The dotted lines outline the contours of the tetramers of edge- and corner-sharing tetrahedra. (Color online.)

is doubled compared to the sum of structural information amounts of popovite and dolerophanite).

IMPLICATIONS

It has recently been mentioned that one of the aspects that a new mineral discovery may provide is an insight into crystal chemistry or the structures of natural and synthetic phases (Barton 2019). The discovery of vasilseverginite brings a new insight into the modularity of structures with anion-centered tetrahedral units based upon (OCu_4) tetrahedra. Vasilseverginite is both a chemical and a structural hybrid of popovite and dolerophanite, and the hybridization results in the formation of a new structure type with a novel layer topology. The Cu compounds with oxo-centered clusters, either polymerized or forming polyoxocuprate clusters (Kondinski and Monakhov 2017), attract much attention in condensed matter physics and materials chemistry, due to their interesting magnetic properties (Volkova and Marinin 2018; Botana et al. 2018; Badrtdinov et al. 2018; Winiarski et al. 2019), and new mineralogical discoveries may provide important insights into pathways of the preparation of novel synthetic compounds (Britvin et al. 2020; Siidra et al. 2020). The concept of hybridization of mineral species developed in this work may bring new ideas for the preparation of novel structural architectures on the border of stability fields of chemically and structurally simpler compounds.

The discovery of vasilseverginite also provides further indirect evidence for the existence of polynuclear oxo-centered copper clusters in the gaseous phase (Kovrugin et al. 2015), which may serve as a means of transport for Cu by volcanic gases in fumaroles, thus enhancing the mobility of metals in volcanic environments.

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