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Vasilseverginite, $Cu_9O_4(AsO_4)_2(SO_4)_2$, 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 $Cu_9O_4(AsO_4)_2(SO_4)_2$, 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 × 0.02 × 0.06 mm^3 combined in groups or interrupted crusts up to 1 × 2 cm^2 in area and up to 0.1 mm thick. It is transparent, bright green, with vitreous luster. D_{calc} is 4.41 g·cm^{-3}. Vasilseverginite is optically biaxial (–), α 1.816(5), β 1.870(5), γ 1.897(5), estimated $2V$ is 30(15)°. 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 O = 20 apfu is $(Cu_{8.78}Zn_{0.11}Fe^{3+}_{0.03})_{\Sigma 8.92}As_{1.98}P_{0.01}S_{2.03}O_{20}$. Vasilseverginite is monoclinic, $P2_1/n$, a = 8.1131(4), b = 9.9182(4), c = 11.0225(5) Å, β = 110.855(2)°, V = 828.84(6) Å^3, and Z = 2. The strongest reflections in the powder XRD pattern [d,Å(I)(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 $[O_4Cu_9]^{10+}$ 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 $Cu_5O_2(AsO_4)_2$ and dolerophanite $Cu_2O(SO_4)$ according to the scheme $Cu_9O_4(AsO_4)_2(SO_4)_2 = Cu_5O_2(AsO_4)_2 + 2Cu_2O(SO_4)$. 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 Vasiliy 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