

Starovaite, $\text{KCu}_5\text{O}(\text{VO}_4)_3$, a new mineral from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia

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Abstract: The new mineral species starovaite, ideally $\text{KCu}_5\text{O}(\text{VO}_4)_3$, has been found in the sublimates of the Yadovitaya fumarole at the Second scoria cone of the Northern Breach of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. The mineral is associated with lammerite, hematite, palmierite, tenorite, piypite, rutile, orthoclase, lyonsite, pseudolyonsite, lammerite- β , langbeinite, calciolangbeinite, and cupromolybdate. Starovaite occurs as prismatic crystals up to $3 \times 6 \times 20 \mu\text{m}$ or divergent long-prismatic crystals up to $1 \times 3 \times 70 \mu\text{m}$. The crystals are combined in sprays, sheaf-like aggregates or crusts up to $0.3 \times 0.5 \text{ mm}$ overgrowing lammerite. Starovaite is golden brown to reddish brown with a semi-metallic luster. The mineral is brittle, VHN is 182 (range 165–195) kg mm^{-2} . Cleavage and parting were not observed, fracture is uneven. $D(\text{calc.}) = 4.54 \text{ g cm}^{-3}$. In reflected light, starovaite is grey with a brownish hue. Bireflectance is weak, internal reflections are distinct red-brown, anisotropy is weak. The reflectance values [R_1 – R_2 , % (λ , nm)] are: 14.2–12.45 (470), 13.2–11.6 (546), 13.0–11.4 (589), 12.6–11.35 (650). The chemical composition (wt%, electron microprobe data) is: K₂O 4.90, CaO 0.04, PbO 1.29, CuO 48.20, ZnO 5.59, Al₂O₃ 0.08, Fe₂O₃ 0.10, P₂O₅ 0.05, As₂O₅ 4.49, V₂O₅ 31.89, SO₃ 0.19, MoO₃ 2.34, total 99.16. The empirical formula calculated on the basis of 13 O *apfu* is: $(\text{K}_{0.76}\text{Pb}_{0.04}\text{Ca}_{0.01})_{\Sigma 0.81}(\text{Cu}_{4.45}\text{Zn}_{0.51}\text{Al}_{0.01}\text{Fe}_{0.01})_{\Sigma 4.98}(\text{V}_{2.58}\text{As}_{0.29}\text{Mo}_{0.12}\text{S}_{0.02}\text{P}_{0.01})_{\Sigma 3.02}\text{O}_{13}$. Starovaite is triclinic, $P-1$, $a = 6.08(4)$, $b = 8.26(5)$, $c = 10.71(6)$ Å, $\alpha = 97.8(1)$, $\beta = 92.4(1)$, $\gamma = 90.4(1)^\circ$, $V = 532(2)$ Å³, and $Z = 2$. The strongest reflections of the X-ray powder diffraction pattern [d , Å (l , %) (hkl)] are: 10.62 (32) (001); 8.18 (46) (010); 3.047 (41) (022, 200, 12-2); 2.745 (47) (2-1-1, 03-1); 2.526 (100) (031, 2-12, 2-1-2, 023, 1-31, 13-1); 2.322 (98) (03-3, 21-3, 221, 22-2); 1.867 (23) (302); 1.410 (23) (24-5, 053, 41-3, 03-7). Starovaite is a natural analogue of synthetic $\text{KCu}_5\text{O}(\text{VO}_4)_3$. The mineral is named in honour of the Russian crystallographer and crystal chemist Galina L. Starova (b. 1946) for her contributions to the crystal chemistry of minerals from the Tolbachik fumaroles.

Key-words: starovaite, new mineral species, potassium copper vanadate, copper oxysalt, fumarole sublimate, Tolbachik volcano, Kamchatka.

1. Introduction

A new copper and potassium vanadate mineral was found in the sublimates of an active fumarole related to the Great Tolbachik Fissure Eruption (1975–76), Tolbachik volcano, Kamchatka Peninsula, Russia. The mineral is named starovaite (Cyrillic: староваит) in honour of the Russian crystallographer and crystal chemist Galina Leonidovna Starova (b. 1946), Associate Professor of the Chemical Faculty of St. Petersburg State University, a specialist in single-crystal X-ray diffraction analysis, for her contributions to the crystal chemistry of minerals from the Tolbachik fumaroles.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2011-085). The type specimen of

starovaite is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow under catalogue number 4196/1.

2. Occurrence and general appearance

Specimens containing starovaite were collected in 2008–10 by the authors (M.E.Z. and M.N.M) in the Yadovitaya (Poisonous) fumarole at the Second scoria cone of the Northern Breach of the Great Tolbachik Fissure Eruption. The cone, which is 300 m high and about 0.1 km³ in volume, is a monogenetic volcano formed in 1975 (Fedotov & Markhinin, 1983). Numerous gas vents at the apical parts of the cone are still hot, with temperatures up to 480 °C as measured in 2010. The fumarolic

gases are chemically similar to the atmospheric air with less than 1 % of water vapour and less than 0.1 % of acid species (mainly CO₂, HF and HCl; unpublished data by M.E.Z.). The Yadovitaya fumarole is a cave about 1.5 m wide and 2 m deep. The temperature inside Yadovitaya is still high (up to 340 °C in 2010). Walls of the cave are covered by thick incrustations of different minerals, mainly sulphates. Mineral associations of fumarole sublimate crusts are different in different parts of the cave.

Starovaite is a rare mineral. It was found only on the surface of coarse crystals (up to 1 mm) of dark-green lammerite (Fig. 1a) typically located on fine-crystalline crusts of iron-black hematite covering the surface of basaltic scoria. Other associated minerals are palmierite, tenorite (Fig. 1), piypite, langbeinite, rutile (the Fe- and Sb-bearing variety intermediate between rutile and tripuhyte), orthoclase (an As- and Zn-bearing variety intermediate between orthoclase and filatovite), lyonsite and the recently discovered species pseudolyonsite (Zelenski *et al.*, 2011), lammerite-β (Starova *et al.*, 2011), calcio-langbeinite (Pekov *et al.*, 2012a) and cupromolybdate (Zelenski *et al.*, 2012). The hydrous copper chlorides belloite and avdoninite and the chloride-sulphate chlorothionite are secondary minerals in this assemblage.

Starovaite forms prismatic, sometimes lath- or bar-shaped crystals up to 3 × 6 × 20 μm in size, or long-prismatic crystals up to 1 × 3 × 70 μm that are typically divergent and curved. They are combined in sprays,

sheaf-like aggregates (Fig. 1a–c) or in almost monomineralic, thin crystalline crusts (Fig. 1d) up to 0.3 × 0.5 mm in size.

3. Physical properties and optical characteristics

Starovaite is golden brown to reddish brown with a semi-metallic luster. The streak is yellowish-brown. The mineral is brittle. The mean micro-indentation hardness (VHN) is 182 with the range 165–195 kg mm⁻² (load 20 g). Mohs' hardness was not measured directly because of the tiny size of the available crystals; the value calculated from the VHN is 3½–4. Cleavage and parting were not observed, and the fracture is uneven (observed under the scanning electron microscope). Density could not be measured because of the small grain size and lack of heavy liquids of necessary density. $D(\text{calc.}) = 4.54 \text{ g cm}^{-3}$ (using the empirical formula).

Under the microscope in reflected light, starovaite is grey with a brownish hue, pleochroism was not observed. Bireflectance is weak, $\Delta R = 1.5 \%$ (589 nm). Internal reflections are distinct red-brown. Anisotropy is weak. The reflectance values measured by means of the MSF-21 microspectrophotometer (LOMO, Russia) using the SiC standard (Zeiss, No. 545) are given in Table 1.

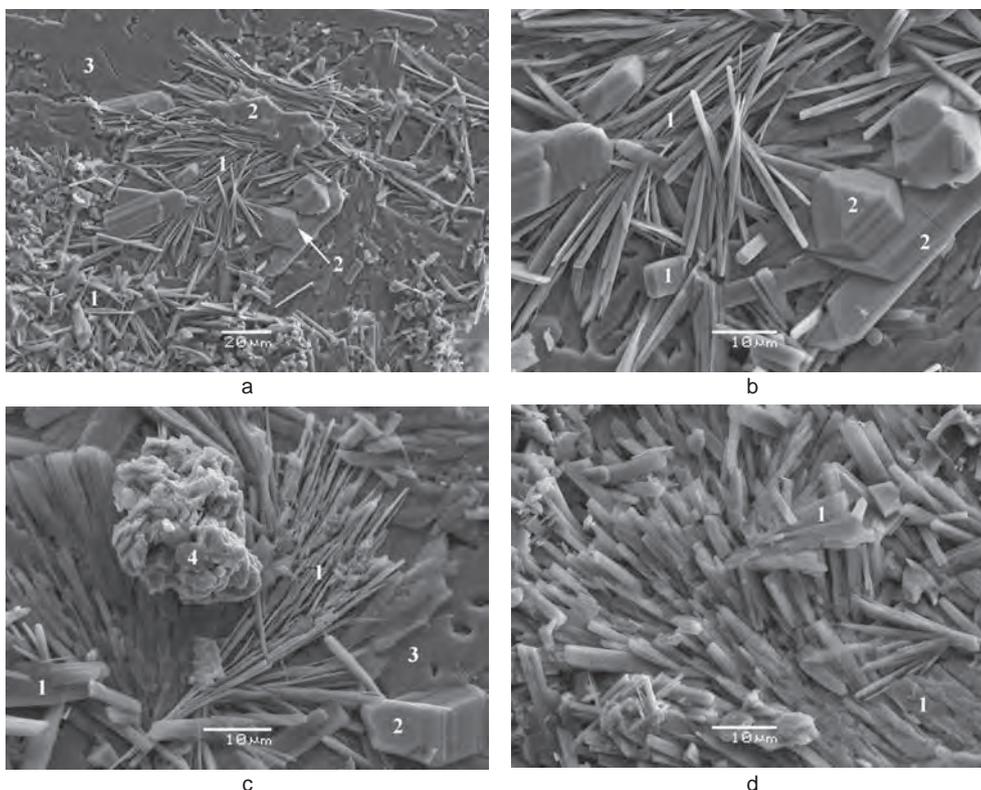


Fig. 1. Aggregates of starovaite (1) and associated minerals palmierite (2), lammerite (3), and tenorite (4): SEM (SE) image.

Table 1. The reflectance data of starovaite.

λ (nm)	R_1 (%)	R_2 (%)	λ (nm)	R_1 (%)	R_2 (%)
400	15.8	14.6	560	13.1	11.5
420	15.2	13.8	580	13.0	11.4
440	14.8	13.1	600	12.9	11.4
460	14.4	12.6	620	12.8	11.3
480	14.0	12.3	640	12.7	11.3
500	13.7	12.0	660	12.5	11.2
520	13.5	11.8	680	12.4	11.2
540	13.3	11.6	700	12.3	11.1

4. X-ray crystallography

Single-crystal studies of starovaite were not carried out because of the tiny crystal size and their curved and divergent morphology (Fig. 1). The X-ray powder-diffraction data (Table 2) were collected with a STOE IPDS II single-crystal diffractometer equipped with an Image Plate detector using the Gandolfi method by employing the MoK α radiation and a sample–detector distance of 200 mm. The X-ray diffraction powder pattern was indexed by comparison with the theoretical pattern calculated for synthetic KCu₅O(VO₄)₃ (Martin & Müller-Buschbaum, 1994). Starovaite is triclinic, $P\bar{1}$, $a = 6.08(4)$, $b = 8.26(5)$, $c = 10.71(6)$ Å, $\alpha = 97.8(1)$, $\beta = 92.4(1)$, $\gamma = 90.4(1)^\circ$, $V = 532(2)$ Å³, and $Z = 2$.

5. Chemical data

Chemical data for starovaite were obtained using a JEOL JSM-6480LV scanning electron microscope equipped with the INCA-Wave 500 wavelength-dispersive spectrometer under operating conditions of 20 kV and 20 nA with an electron-beam diameter of 2 μ m. The following standards were used: orthoclase (K), CaWO₄ (Ca), PbTe (Pb), CuFeS₂ (Cu, Fe), ZnS (Zn, S), Al₂O₃ (Al), GaP (P), FeAsS (As), V metal (V) and CaMoO₄ (Mo). To avoid problems caused by the partial overlap of the SK α and MoL α lines, control measurements of the Mo content were carried out with an accelerating voltage of 30 kV and a beam current of 30 nA, using the MoK α line, which produced very similar results.

The chemical composition of starovaite (wt%, mean of 8 analyses, range in parentheses) is: K₂O 4.90 (4.5–5.5), CaO 0.04 (0.00–0.1), PbO 1.29 (0.3–2.3), CuO 48.20 (46.5–49.0), ZnO 5.59 (4.7–8.2), Al₂O₃ 0.08 (0.00–0.2), Fe₂O₃ 0.10 (0.00–0.2), P₂O₅ 0.05 (0.00–0.2), As₂O₅ 4.49 (3.3–7.9), V₂O₅ 31.89 (28.1–35.8), SO₃ 0.19 (0.05–0.5), MoO₃ 2.34 (1.7–3.3), total 99.16. The contents of other elements with atomic number higher than 8 are below detection limits.

The empirical formula calculated on the basis of 13 O *apfu* is: (K_{0.76}Pb_{0.04}Ca_{0.01}) Σ 0.81 (Cu_{4.45}Zn_{0.51}Al_{0.01}Fe_{0.01}) Σ 4.98 (V_{2.58}As_{0.29}Mo_{0.12}S_{0.02}P_{0.01}) Σ 3.02O₁₃. The simplified, end-member formula is KCu₅V₃O₁₃ [= KCu₅O(VO₄)₃], which requires K₂O 6.56, CuO 55.43, V₂O₅ 38.01, total 100.00 wt%.

6. Discussion

The stoichiometry and X-ray powder diffraction data clearly show that starovaite is a natural analogue of synthetic KCu₅O(VO₄)₃, characterized by Martin & Müller-Buschbaum (1994) (Table 3). The synthetic compound TiCu₅O(VO₄)₃ with the same structure is also known (Moser & Jung, 2000). Starovaite, its synthetic analogue and its Tl counterpart are representatives of the large group of inorganic compounds with additional anions. Along with the anionic complexes centred by high-valence cations, their structures contain additional O²⁻ ions that can be considered as coordination centres for oxocentred OMe₄ tetrahedra that can form diverse structural units. Many copper minerals with structures that could be described in terms of the OCu₄ tetrahedra have been discovered in sublimates of the Tolbachik fumaroles (Starova *et al.*, 1997; Krivovichev, 2009). On the basis of the structure data for synthetic KCu₅O(VO₄)₃ (Martin & Müller-Buschbaum, 1994), we conclude that, in starovaite, OCu₄ tetrahedra are isolated.

Fingerite, Cu₁₁O₂(VO₄)₆, is a mineral found in fumarole sublimates on the Izalco volcano, El Salvador. It crystallizes in the same space group, $P\bar{1}$, and shows a stoichiometry similar to that of starovaite: its formula can be formally presented as Cu_{0.5}Cu₅O(VO₄)₃. However, fingerite strongly differs from starovaite and its synthetic analogue in terms of X-ray diffraction powder data, unit-cell dimensions and crystal structure (Finger, 1985; Hughes & Hadidiacos, 1985).

More than 180 minerals with species-defining vanadium are known presently. Among them, 30 species are anhydrous vanadates with different cations, including 12 minerals with Cu as species-defining element. All these anhydrous copper vanadate minerals were first described in the fumarole sublimates from two active volcanoes: Izalco (7 species) and Tolbachik (5 species). Izalco is the type locality for stoiberite Cu₅O₂(VO₄)₂ (Birmie & Hughes, 1979), ziesite β -Cu₂V₂O₇ (Hughes & Birmie, 1980), fingerite Cu₁₁O₂(VO₄)₆ (Hughes & Hadidiacos, 1985), blossomite α -Cu₂V₂O₇ (Robinson *et al.*, 1987), lyon-site Cu_{3+x}(Fe³⁺_{4-2x}Cu_{2x})(VO₄)₆, with $0 \leq x \leq 1$ (Hughes *et al.*, 1987a), mcbirneyite Cu₃(VO₄)₂ (Hughes *et al.*, 1987b), and howardevansite NaCuFe³⁺₂(VO₄)₃ (Hughes *et al.*, 1988). Copper vanadates discovered in Tolbachik

Table 2. X-ray powder diffraction data for starovaite and its synthetic end-member analogue.

Starovaite	Synthetic $\text{KCu}_5\text{O}(\text{VO}_4)_3^a$				<i>hkl</i>	
	d_{meas} (Å)	d_{calc} (Å)	I_{calc}	d_{calc} (Å)		
32	10.65	10.601		63	10.585	001
46	8.18	8.183		100	8.183	010
9	5.319	5.371, 5.301		5, 17	5.371, 5.293	10-1, 002
15	4.834	4.848		11	4.848	110
20	4.043	4.082, 4.005		17, 1	4.078, 4.005	10-2, 02-1
14	3.499	3.534		21	3.528	003
22	3.402	3.418		38	3.414	01-3
41	3.047	3.045, 3.040, 3.037		20, 64, 29	3.042, 3.040, 3.038	022, 200, 12-2
13	2.860	2.859		12	2.863	2-10
47	2.745	2.756, 2.733		23, 25	2.758, 2.733	2-1-1, 03-1
9	2.629	2.628, 2.625		29, 22	2.625, 2.623	01-4, 12-3
100	2.526	2.559, 2.524, 2.511, 2.509, 2.494, 2.491	24, 18, 19, 18, 11, 16	24, 18, 19, 18, 11, 16	2.558, 2.527, 2.510, 2.508, 2.496, 2.490	031, 2-12, 2-1-2, 023, 1-31, 13-1
7	2.420	2.424, 2.424, 2.415, 2.414	4, 6, 4, 14	4, 6, 4, 14	2.424, 2.424, 2.419, 2.415	220, 22-1, 2-21, 212
98	2.322	2.317, 2.313, 2.307, 2.306	4, 3, 19, 4	4, 3, 19, 4	2.317, 2.311, 2.306, 2.306	03-3, 21-3, 221, 22-2
3	2.174	2.188		2	2.189	2-2-2
7	2.097	2.124, 2.123, 2.114		7, 2, 1	2.123, 2.121, 2.114	213, 01-5, 222
13	2.062	2.062		35	2.062	04-1
12	2.046	2.046, 2.045, 2.042		23, 10, 1	2.046, 2.045, 2.044	040, 2-30, 03-4
10	1.993	1.997, 1.988		1, 3	1.995, 1.985	02-5, 015
6	1.949	1.955, 1.953, 1.946		22, 1, 2	1.956, 1.954, 1.947	204, 31-1, 1-40
5	1.909	1.917, 1.904		2, 3	1.914, 1.903	12-5, 14-2
23	1.867	1.865		3	1.867	302
4	1.798	1.797, 1.795		3, 2	1.796, 1.795	1-43, 03-5
5	1.779	1.786, 1.783, 1.775		8, 2, 9	1.783, 1.782, 1.773	025, 034, 20-5
6	1.735	1.738, 1.736, 1.733		6, 4, 4	1.739, 1.737, 1.731	3-22, 04-4, 1-2-5
13	1.705	1.709, 1.704		2, 6	1.707, 1.704	02-6, 205
9	1.684	1.688, 1.681, 1.679		1, 1, 3	1.686, 1.678, 1.678	1-16, 016, 14-4
7	1.666	1.669, 1.663, 1.662		10, 1, 10	1.671, 1.664, 1.663	2-42, 1-44, 313
5	1.611	1.610		3	1.609	24-3
14	1.578	1.584, 1.584, 1.575		15, 2, 3	1.584, 1.583, 1.576	2-4-2, 04-5, 3-14
10	1.529	1.528, 1.527		4, 3	1.528, 1.527	2-35, 151
17	1.507	1.514, 1.508, 1.507		13, 9, 2	1.512, 1.507, 1.507	007, 2-16, 052
6	1.468	1.471		4	1.471	1-5-2
6	1.444	1.448, 1.447		6, 1	1.450, 1.447	2-50, 243
23	1.410	1.417, 1.413, 1.408, 1.407		21, 3, 3, 8	1.416, 1.413, 1.407, 1.407	24-5, 053, 41-3, 03-7
17	1.377	1.380, 1.378, 1.377, 1.375, 1.375		7, 2, 1, 2, 5	1.380, 1.379, 1.377, 1.374, 1.374	2-4-4, 4-2-2, 06-1, 235, 1-3-6

^aCalculated from the structure data by Martin & Müller-Buschbaum (1994) using the LAZY PULVERIX program (Yvon *et al.*, 1977).

Table 3. Comparative crystal data for starovaite and its synthetic end-member analogue.

Mineral/compound Idealized formula	Starovaite $\text{KCu}_5\text{O}(\text{VO}_4)_3$	Synthetic $\text{KCu}_5\text{O}(\text{VO}_4)_3$
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a , Å	6.08(4)	6.086(3)
b , Å	8.26(5)	8.261(3)
c , Å	10.71(6)	10.694(3)
α , °	97.8(1)	97.82(3)
β , °	92.4(1)	92.32(3)
γ , °	90.4(1)	90.48(3)
V , Å ³	532	532.2
Z	2	2
D_{calc} , g cm ⁻³	4.54 ^a	4.48
References	This work	Martin & Müller-Buschbaum (1994)

^aThe higher density of starovaite in comparison with its synthetic end-member analogue is caused by the presence of admixtures of heavier elements, namely Pb, Zn, As and Mo, in the mineral.

fumaroles are leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ (Vergasova *et al.*, 1990), averievite $\text{Cu}_6\text{O}_2(\text{VO}_4)_2 \text{Cl}_2 \cdot n(\text{K,Cs,Rb})\text{Cl}$ (Vergasova *et al.*, 1998), pseudolyonsite $\text{Cu}_3(\text{VO}_4)_2$ (Zelenski *et al.*, 2011), yaroshevskite $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$ (Pekov *et al.*, 2012b), and starovaite $\text{KCu}_5\text{O}(\text{VO}_4)_3$. We were able to find four of the above-mentioned Izalco type minerals in Tolbachik fumaroles: ziesite (Vergasova & Filatov, 1993), lyonsite (Pekov *et al.*, 2012c), fingerite, and blossomite. From anhydrous copper vanadate minerals, only lyonsite was found in other locality, namely, in burned dumps of the Lichtenberg uranium mine near Ronneburg, Thuringia, Germany (Witzke & Rüger, 1998), whereas eleven other species are endemic minerals of volcanic fumaroles (for genetic features of fumarolic vanadates see: Hughes & Birnie, 1980; Zelenski *et al.*, 2011). Note that lyonsite in burned dumps of the Lichtenberg mine was formed under very similar physico-chemical conditions.

Schäferite $\text{NaCa}_2\text{Mg}_2(\text{VO}_4)_3$ is the only non-copper vanadate that has been found in fumaroles. It was originally discovered in paleo-fumarole deposits related to the Quaternary volcanism of the Eifel area, Rheinland-Pfalz, Germany (Krause *et al.*, 1999), and recently we have found this mineral at Tolbachik. Vanadium oxides of fumarolic origin are represented by shcherbinaite V_2O_5 and bannermanite $(\text{Na,K})_x\text{V}^{4+}_x\text{V}^{5+}_{6-x}\text{O}_{15}$ known from three volcanoes: Bezmyannyi in Kamchatka (Borisenko, 1972; our data), Izalco (Hughes *et al.*, 1983a and b) and Tolbachik (Glavatskikh, 1982; our data). The vanadyl sulphate paulferite $\beta\text{-VO}(\text{SO}_4)$ is an endemic mineral of the Tolbachik fumaroles (Krivovichev *et al.*, 2007).

Seven natural hydrous vanadates with species-defining copper are known: mottramite $\text{PbCuVO}_4(\text{OH})$, namibite $\text{Cu}(\text{BiO})_2\text{VO}_4(\text{OH})$, sengierite $\text{Cu}_3(\text{UO}_2)(\text{VO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, tangeite $\text{CaCuVO}_4(\text{OH})$, turanite $\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$, vesigneite $\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$, and volborthite $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. All these minerals are of supergene origin.

Thus, natural anhydrous and hydrous copper vanadates strongly differ in their formation conditions, first of all, in terms of the temperature of crystallization (the pressure seems to be close to atmospheric in all cases), and belong to essentially different geological formations.

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