

Averievite $\text{Cu}_5(\text{VO}_4)_2\text{O}_2 \cdot n\text{MX}$ —a New Mineral of Volcanic Exhalations

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Averievite is a product of the fumarole activity of the Great Tolbachik fissure eruption (Kamchatka, 1975–1976) [1]. It is represented by a single finding. Apart from the novelty, the actuality of mineral investigation is determined by the presence in it of the rare elements Rb and Cs, which are the geochemical indicators of postmagmatic processes characterizing the interaction of fumarole gases with the surrounding rocks.

The averievite crystals were detected in the sample taken in 1976 from the exhalation deposits of various compounds of copper along the fissure (the visible depth 10–15 cm) in the eruptive lump slag ashmaterial of the crater zone. The fissure was traced within the south-eastern internal slope of the second cone of the Northern breakthrough near the crater edge (1.5 m westward from the Yadovitaya fumarole) [2]. The temperature of gases during sampling corresponded to 294–310°C. The deposits, chiefly in the form of cryptocrystalline masses of brown-yellow-green color, filled the voids between large lumps of pyroclastics along the fissure. The mossy and setiform aggregations of crystals were encountered in lesser amounts. Oxo sulfates of Cu dominated in the composition of the deposits. The basic mineral is pyipite $\text{K}_4\text{Cu}_4\text{O}_2(\text{SO}_4)_4 \cdot \text{MeCl}$, the secondary ones are alumoklyuchevskite $\text{K}_3\text{Cu}_3(\text{Al,Fe})\text{O}_2(\text{SO}_4)_4$ and langbeinite $\text{K}_2\text{Mg}_2(\text{SO}_4)_4$ [3]. With respect to the above-mentioned phases, averievite falls into the group of subordinate minerals that are mostly encountered as amorphous pith-black, opaque segregations, less than 0.1 mm in size, chiefly intergrown with pyipite. The following compounds of Cu were established in them by microprobe analysis: vanadates, tellurate, arsenate vanadate, arsenate $\text{Cu}_3(\text{AsO}_4)$, and oxide CuO. Averievite differs from them in relatively greater dimensionality of grains, flattened shape, and pseudohexagonal habit of individuals (the maximum dimension in the flattened plane does not exceed 0.3 mm in length and 0.05 mm thickness) (Fig. 1). The

averievite crystals are opaque and black-colored with a resinous to metallic luster and black streak. The mineral is stable in an atmosphere of air, practically insoluble in alcohol and water, and readily soluble in diluted HCl. Sampling of the monomineral fraction is extremely difficult because of its microscopic dimensions and rarity.

The X-ray investigation of monocrystals with the application of an X-ray goniometer RGNS-2 and autodiffractometer Syntex P2₁ showed that the averievite crystals relate to trigonal syngony with the following characteristics: space group $P\bar{3}$ or $P\bar{3}$, $a = 6.375(1)$, $c = 8.399(1)$ Å, $V = 295.6(1)$ Å³, $Z = 1$, $D_x = 4.01$ g/cm³. The crystal structure is determined in space group $P\bar{3}$ (the R -factor is 0.052). The Debyeogram of averievite (the photometod, RKD-57.3 camera, rubber ball, radiation $\text{CuK}\alpha$, internal standard Ge) contains the following diagnostic lines (I - d - hkl): 7-3.43-102, 2-3.048-111, 4-2.810-003, 10-2.315-202, 3-2.131-113, 2-1.871-212, 4-1.598-220, and 2-1.494-115 (Table 1). The indexing

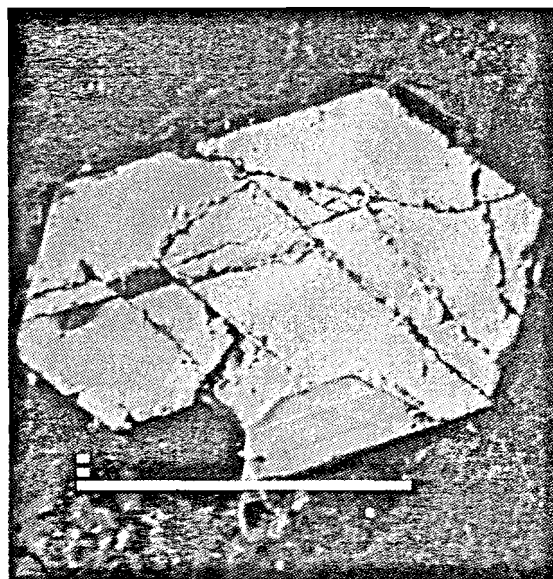


Fig. 1. Averievite crystal (magn. 650).

was carried out with the use of intensities obtained from the monocrystal. The elementary cell parameters, calculated from the Debyeogram, are equal to: $a = 6.39(1)$, $c = 8.40(2)$ Å, $V = 297(2)$ Å³.

Investigation of the chemical composition of averievite was performed on the Camebax microprobe. The polished section was prepared from several grains 20–100 µm in size. The mineral composition was estimated as the average from 17 analyses (Table 2). The valences of elements are adopted on the basis of the oxidative formation environment.

The crystallochemical formula $\text{Cu}_5(\text{VO}_4)_2\text{O}_2 \cdot \text{CuCl}_2$, obtained as a result of decoding the crystal structure of averievite, allowed us to understand and explain the relationship of elements established through the microprobe investigation. A wide and sufficiently exotic set of alkaline metals (Table 2) in averievite can be explained by the presence of large ($R \geq 3.2$ Å) free channels in its structure (Fig. 2), capable of accommodating both neutral molecules and charged particles with a sufficiently large volume. The empirical formula of averievite, estimated from cations, looks as follows: $\text{Cu}_{5.00}(\text{V}_{1.87}\text{Mo}_{0.08}\text{Fe}_{0.05})_{2.00}\text{O}_{7.78}\text{O}_{2.19} \cdot (\text{Cu}_{0.56}^{2+}\text{Cl}_{1.12}) \cdot (\text{Cs}_{0.17}\text{Rb}_{0.06}\text{K}_{0.15})_{0.38}\text{Cl}_{0.40}$. In the averievite structure, the charge of the tetrahedral lattice of $\{\text{OCu}_4\}^{6+}$ is completely neutralized by the charges of the $[\text{VO}_4]^{3+}$ groups. The particles, arranged within the channels, do not participate in the structure formation (i.e., do not coordinate atoms). Therefore, it can be supposed, with a high degree of probability, that the nature of these particles depends on the environment, within which the mineral crystals grow. Then, the idealized formula of the sample studied can be presented in the form: $\text{Cu}_5(\text{VO}_4)_2\text{O}_2 \cdot (\text{CuCl}_2) \cdot (\text{MCl})$, where $\text{M} = \text{Cs}$, K , or Rb , while the idealized formula of the mineral in the more general form will look as follows: $\text{Cu}_5(\text{VO}_4)_2\text{O}_2 \cdot n\text{MX}$, where M and X are the cation and anion, respectively, which depend on the environment of mineral formation. This formula, undoubtedly, is in need of further study.

The left-hand portion of the averievite formula coincides completely with the formula of stoiberite [4, 5] found in the fumarole products of the Izalco Volcano (El Salvador), however, the XRD data and the original structure of averievite differ from those of stoiberite (Table 3), which allows us to distinguish averievite as an independent mineral.

Averievite is the second new vanadate detected in the fumarole products of the Great Tolbachik fissure eruption. The first one was leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$, described earlier [6].

The mineral density estimated is 3.98 g/cm³, in accordance with the empirical formula, and 4.01 g/cm³, in accordance with the idealized formula. The experimental value of density ($D_{\text{exp}} = 3.54$ g/cm³), obtained by means of immersion of mineral grains in the Clerichi liquid + distilled water mixture and comparison of

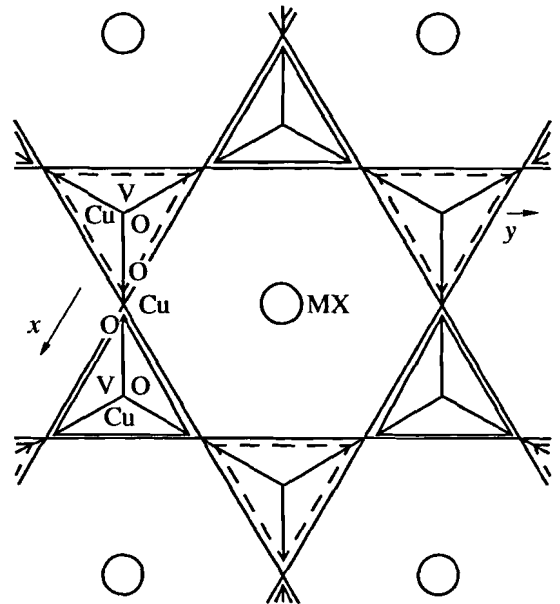


Fig. 2. Projection of the averievite structure on the XY plane.

their densities, is underestimated with respect to the calculated one, evidently, because of the adhesion of air bubbles to the microscopic grains of the mineral.

The averievite crystals possess good cleavage along $(10\bar{1}0)$ and are brittle. The shapes are simple: monohedrons $\{0001\}$ and $\{000\bar{1}\}$ and trigonal prisms $\{10\bar{1}0\}$ and $\{01\bar{1}0\}$. Frequently one of them is more developed than the other.

The microhardness, studied at the Department of Mineralogy, St. Petersburg State University, by G.A. Il'inskii

Table 1. Debyeogram of averievite

l	d/n_{exp}	d/n_{est}	hkl
7	3.43	3.34	102
2	3.048	2.980	111
4	2.810	2.800	003
10	2.315	2.307	202
3	2.131	2.104	113
2	1.871	1.869	212
2	1.679	1.671	204
4	1.598	1.594	220
2	1.494	1.486	115
1	1.425	1.435	205
2	1.377	1.385	223
1	1.309	1.311	402
		1.308	215
2	1.262	1.269	224
1	1.159	1.158	412
		1.153	404
1	1.017	1.013	422
1	0.983	0.981	208

Table 2. Chemical composition of averievite

No.	CuO	Fe ₂ O ₃	K ₂ O	Cs ₂ O	Rb ₂ O	V ₂ O ₅	MoO ₃	Cl	O=Cl	Total
1	63.14	0.35	0.63	2.70	0.69	23.02	3.13	7.93	-1.79	99.85
2	62.66	0.53	0.71	3.02	0.56	23.62	1.55	7.82	-1.55	98.71
3	62.50	0.51	0.69	2.89	0.69	22.67	2.90	7.75	-1.75	98.85
4	63.14	0.43	1.03	3.71	0.93	23.97	0.88	7.66	-1.73	99.98
5	63.03	0.72	0.75	3.06	0.69	23.41	1.92	7.74	-1.75	99.58
6	63.41	0.55	1.28	3.33	1.11	24.31	0.74	7.50	-1.69	100.54
7	62.45	0.69	1.18	3.51	1.06	24.30	0.44	7.46	-1.68	99.41
8	62.55	0.76	1.20	3.50	1.13	24.36	0.42	7.50	-1.69	99.73
9	60.47	0.87	0.72	4.04	0.61	22.82	2.44	7.60	-1.71	97.86
10	60.52	1.06	0.65	3.84	0.70	22.70	2.55	7.49	-1.69	97.82
11	63.09	0.58	1.22	3.30	1.05	24.26	0.64	7.49	-1.69	99.94
12	63.19	0.64	1.20	3.38	1.08	24.29	0.61	7.55	-1.70	100.24
13	61.28	0.41	0.85	2.80	0.55	23.35	2.84	7.56	-1.70	97.94
14	61.42	0.63	0.83	2.94	0.61	23.23	2.73	7.52	-1.70	98.21
15	60.52	0.70	1.23	3.47	0.73	25.16	0.55	7.41	-1.67	98.10
16	60.78	0.59	1.27	3.42	0.88	24.97	0.55	7.32	-1.65	98.13
17	60.06	0.57	1.17	4.11	0.84	24.77	0.75	7.26	-1.64	97.89
Average	62.01	0.62	0.98	3.35	0.82	23.84	1.51	7.56	-1.70	98.99

Note: Conditions of photography: Camebax microprobe, voltage 20 kV, current 40 nA, exposition 5 s. Standards: Fe₂O₃ (Fe), CuO (Cu), Ca molybdate (Mo), synthetic chlorapatite (Cl), orthoclase (K), synthetic pollucite (Cs), synthetic V₂O₅ (V), and lepidolite with the Rb admixture (Rb).

Table 3. Basic parameters of averievite and stoiberite

	Averievite	Stoiberite
Formula	Cu ₅ (VO ₄) ₂ O ₂ · nMX	Cu ₅ (VO ₄) ₂ O ₂
Appearance of crystals	Laminated (pseudo-hexagonal prism)	Laminated (bevelled parallelepiped)
Space group	<i>P</i> 3	<i>P</i> 2/ <i>n</i>
<i>a</i> , Å	6.375(1)	15.654(15)
<i>b</i> , Å	6.375(1)	6.054(4)
<i>c</i> , Å	8.399(1)	8.385(11)
<i>Z</i>	1	4
<i>b</i> , degree		102.29(12)
<i>D_x</i> , g/cm ³	4.01	4.96
Structural pattern of [OCu ₄] tetrahedrons	⊥ [001] lattice of six-membered rings	Ribbons [010]

on the PMT-3 instrument ($P = 0.002$ kg, $n = 4$), yielded $H_{av} = 258$ kg/mm that corresponds to the hardness class 4.3.

The mineral was called "averievite" in honor of Russian volcanologist V.V. Averiev (1929–1968). The name and mineral was approved by the International Commission on New Minerals, September 13, 1995.

The specimen was submitted to the Museum of Mines, St. Petersburg Institute of Mines.

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