LENINGRADITE PbCU$_3$(VO$_4$)$_2$Cl$_2$, A NEW MINERAL

FROM VOLCANIC EXHALATIONS[*][1]

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(Presented by Academician V.A. Zharikov, March 21, 1989)

Leningradite is the product of fumarole activity in the Great Tolbachik Fissure Eruption (FTFE, Kamchatka, 1975-76) [1]. It occurs in relatively small amounts in fumarole incrustations on the southwestern crest of the second slag cone of the Northern Breakthrough of the eruption, above the vent, where it was deposited in the upper parts of the vugs. Owing to high gas concentrations, the temperature at the sampling site could not be measured. The temperature of the vapor-gas mixture at fumarole vent was 140° C. The mineral was found both as single poorly faceted red-brown rhomboidal crystals or flakes, or as intergrowths of fine tabular crystals. The crystals and flakes measured a maximum of 0.3 mm across (ordinarily 0.1 mm) in the plane of flattening and were about 0.3 mm thick. The intergrowth aggregates had the appearance of microscopic spheres or globules (Fig. 1) up to 0.6 mm in diameter (usually 0.2 to 0.3 mm), with rough maroon-brown surfaces. Internally, some of the spherical particles resembled spherulites, with the crystals oriented in an orderly fashion from the center to the edges (Fig. 2a); in other cases the crystals were in a spiral arrangement (Fig. 2b). The mineral was found in association with anglesite PbSO$_4$, hematite Fe$_2$O$_3$, and lammerite Cu$_3$[(As, P)O$_4$]$_2$ in a tangled fibrous mass of tolbachite CuCl$_2$ [3]. It is relatively stable in air and insoluble in water.

Under the binocular microscope, the crystals have an intense red color, a strong vitreous luster, and perfect cleavage along the (010) plane. The streak is orange-red. The microindentation hardness (PMT-3 instrument, $P = 0.010$ kg, $n = 23$) is 180 to 345 kg/m^2, with $H_{av} = 247$ kg/m^2 (hardness class 4.25). The variation in hardness is due to the brittleness of the mineral. The density calculated from the empirical formula, with $Z = 4$, is 4.97 g/cm^3. The density of 4.8(1) g/cm^3, measured in microburettes using quartz as a reference, is lower than the calculated value, apparently owing to the presence of microscopic admixtures of lighter minerals.

In transmitted light, very thin grains (< 0.02 mm thick) are transparent and golden-red in color. No optical dispersion is evident. The elongation is positive and the extinction is direct or symmetrical. The optical axes are in the (100) plane, and $N_g = c, N_m = a, N_p = b$ (Fig. 3). The refractive indices are: $\gamma = 2.35(1)$, $\beta = 2.29(1)$. The value of α could not be measured because of the perfect cleavage of the mineral along the (010) plane, while a cleaved chip placed on edge ceases to be transparent. No pleochroism was found in the (010) plane (containing the γ and β axis); the color corresponding to the α axis could not be observed. The conascopic figure in the cleavage chip was a broad ualtese cross with a transmission angle of about 30°. In view of the very high refractive indices, this indicates that the section is perpendicular to the acute bisectrix and that the angle $2V$ is large. Thus the mineral is biaxial and optically negative.

The crystals have a thin tabular habit. The {010} pinacoid faces are the most highly developed. The contours of the tablets are irregular, or less often near-rhomboidal, owing to the development of the {101} prism faces. There are a few crystals elongated in the c direction, which in addition to the prismatic faces also had developed {100} pinacoidal faces and less often {001} pinacoidal faces. In the latter case, the contour of the tablets is nearly rectangular, with slightly truncated corners. The measured angle between the prismatic faces is 87.9(5)°, and that calculated from the unit cell parameters is 87.8°.
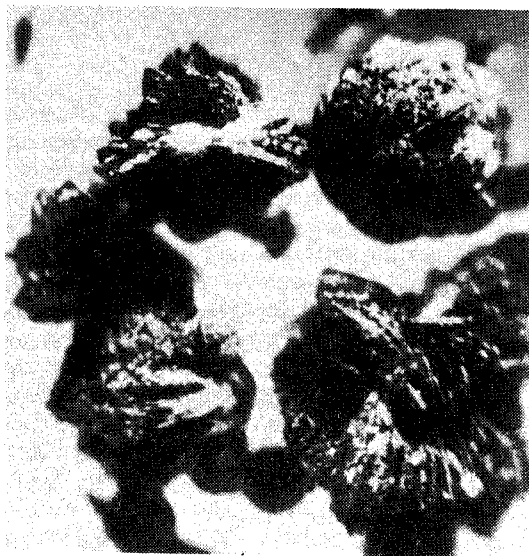
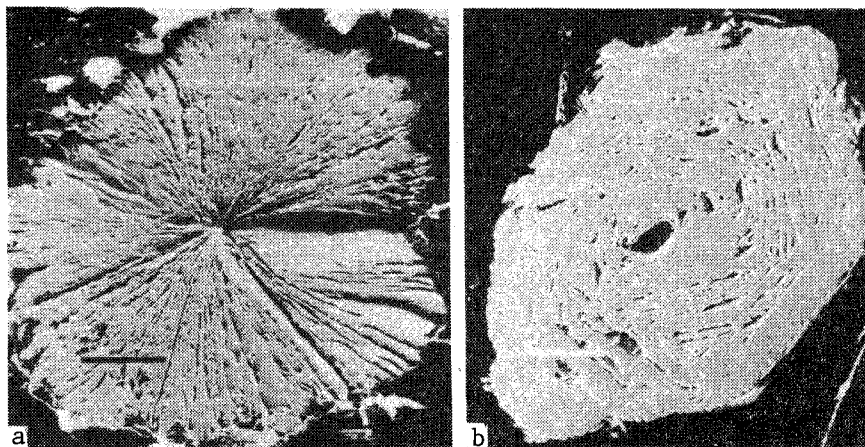Fig. 1. Aggregates of intergrowths of leningradite crystals.
25×, reproduction 2/3 size.

Fig. 2. Cross sections of spheroidal leningradite aggregates. Secondary—electron image.
Camebax microprobe, 150×.

The composition of leningradite was investigated on five grains (10 determina-
tions) with Camebax microprobe[2]. The highest valences of the cations were assumed;
in partiuclar, for vanadium and arsenic we assumed valences of 5, because the mineral
is formed in an oxygen-rich medium and the cations of the accessory minerals (lam-
merite, hematite, alglesite, tolbachite and the like) also have the highest valence.
The average composition (percent by weight) was PbO 32.13 (31.73-32.51), CuO 32.84
(32.44-33.20), ZnO 0.32 (0.18-0.47), V_2O_5 (26.22 (25.39-26.90), As O 0.49 (0.17-
0.94), Cl 9.60 (9.35-9.81), O = Cl_2 -2.17 (2.11-2.21). The chemical composition of

[2]Analysis conditions accelerating voltage 20 kV, current to specimen 40 nA, exposure 10 sec,
standards V_2O_5 (for V), CuO (for Cu), FeS (for Fe), ZnO (for Zn), PbS (for Pb), FeAsS (for As), and
NaCl (for Cl). Analytical lines: M_{α_1} for Rb, L_{α_1} for As, K_{α_1} for the others. Relative intensities
converted to concentrations by the MBXCOR program, with the help of Reed mass absorption coefficients
[4]. In calculating the formula, the iron found in two analyses was treated as mechanical by admixed
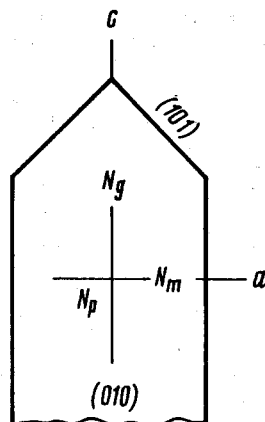hematite.

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Fig. 3. Optical orientation of leningradite.

Table 1

Powder pattern of leningradite

I/I_1	d_{meas}, A	d_{calc}, A	hkl	I/I_1	d_{meas}, A	d_{calc}, A	hkl
19	6,982	6,981	110	5	1,930	1,931	134
49	5,545	5,542	020	1	1,901	1,902	422
21	4,494	4,494	200	49	1,847	1,847	060
18	4,214	4,212	121	2	1,787	1,788	044
26	3,887	3,887	112	5	1,743	1,742	440
34	3,489	3,490	220	13	1,707	1,708	260
100	3,418	3,417	130			1,707	215
62	3,242	3,241	202	13	1,6598	1,6611	244
3	2,891	2,892	310			1,6591	512
95	2,763	2,771	040	6	1,6343	1,6352	442
		2,760	132			1,6350	433
19	2,732	2,730	231	7	1,6196	1,6207	404
66	2,548	2,548	141	9	1,6160	1,6164	530
24	2,459	2,460	312	10	1,6047	1,6049	262
25	2,384	2,384	042	12	1,5592	1,5599	006
73	2,358	2,358	240			1,5593	170
16	2,327	2,327	330	10	1,5263	1,5261	325
10	2,246	2,247	400	31	1,4793	1,4794	172
2	2,219	2,219	114	4	1,4486	1,4499	064
15	2,153	2,152	150	11	1,4262	1,4269	460
4	2,106	2,106	242			1,4267	602
		2,106	233			1,4263	415
30	2,082	2,082	420	6	1,4141	1,4138	514
8	2,012	2,013	323	9	1,3991	1,3999	370
8	1,986	1,988	341			1,3990	444
18	1,956	1,955	152	4	1,3549	1,3548	181
7	1,944	1,945	251	8	1,3405	1,3412	372
		1,944	224			1,3403	435

the mineral exhibited little variation. Within crystals, the distribution of the mineral-forming elements was practically uniform. The ubiquitous minor impurities in leningradite were zinc and arsenic cations. The formula of the mineral, calculated under the assumption that $O + Cl = 10$, is $Pb_{1,01}(Cu_{2,89} Zn_{0,05})_{\Sigma2,94} \cdot [(V_{1,01} As_{0,01})_{\Sigma1,02}O_4]_2(Cl_{1,90}O_{0,10})_{\Sigma2,00}$. The ideal formula is $PbCu_3(VO_4)_2Cl_2$, giving the ultimate analysis of Pb 29.66, Cu 27.29, V 14.58, O 18.32, Cl 10.15, total 100.00 percent by weight.

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The Laue patterns, oscillating-crystal radiograms and X-ray goniometric scans of three layer lines obtained with rotation about the c axis in an RGNS-2 chamber (radiation from Cu) indicate that the mineral belongs to the rhomboid system and to the mmm point group, with the space groups *Ibam* and *Iba2* as possible candidates, and with $Z = 4$. The structure of the mineral was determined with a $P2_1$ automatic single-crystal diffractometer ($R = 0.042$), and confirmed the *Ibam* space group. The structure consists of Cu(O, Cl)$_6$ octahedra (4O-Cu = 1.957-1.973 Å, 2Cl-Cu = 2.759-2.995 Å), joined at their edges and vertices. The octahedra are also joined by (VO$_4$)$^{3-}$ tetrahedra. The Pb cations exist in an eightfold coordination (4O + 4Cl).

The powder of the mineral was investigated with a DRON-2 diffractometer, using CoK_α radiation, with germanium as an internal standard or with no standard. The power patterns were indexed (Table 1) in terms of the cell parameters measured by the single-crystal method. The unit cell parameters, improved by means of the powder pattern and calculated by the least-squares method were $a = 8,988(2)$, $b = 11,083(2)$, $c = 9,360(6)$ Å, $V = 932,4(9)$ Å^3. The strongest lines in the powder pattern ($I-d-hkl$): were 49-5.545-0.20, 34-3.489-220, 100-3.418-130, 62-3.242-202, 95-2.763-0.40.132, 66-2.548-141, 73-2.358-240, 30-2.082-420, 49-1.847-060. The powder pattern of leningradite obtained from the same preparation after storage in air for half a year showed no changes.

Heating followed by X-ray analysis indicated that the mineral is stable on heating in air to 425 ± 25° C, at which it breaks down to vanadinite Pb$_5$(VO$_4$)$_3$Cl plus by products.

The mineral is named *leningradite* in honor of the city of Leningrad, at whose university this and several other new minerals from volcanic exhalations were investigated. No natural or synthetic compounds have the composition of the X-ray properties of this mineral.

The specimen has been transferred to the Mining Museum of the Leningrad Mining Institute.

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