

# Vlodavetsite, $\text{AlCa}_2(\text{SO}_4)_2\text{F}_2\text{Cl}\cdot 4\text{H}_2\text{O}$ , a New Mineral from Volcanic Exhalations<sup>1</sup>

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Vlodavetsite<sup>2</sup> is a product of fumarole activity associated with the Great Tolbachik fissure eruption in Kamchatka in 1974 and 1976 [1]. It was discovered in newly formed material produced by vent-facies fumaroles in the second cone of the North Breach. It is present as minute particles, among which we sometimes found segregations of micron-size flakes and transparent plates (Fig. 1). Besides forming hygroscopic and other finely dispersed phases, the mineral occurs as pastelike clusters of wet, soft material with an intense light-yellow color. This paste coats sizable wall areas in open fissures (to a depth of over 1 m) on the west and east sides of a 100 m long grabenlike trough that has developed on the second cone, within its main fumarole field (on the southeast inner slope of the cone near crater rim, temperature about 100° C).

Vlodavetsite is always accompanied by fine-particle pyroclastic material, which has been variously altered so that it now consists of semitransparent, dark to light cream-yellow grains of cindery appearance. The admixed hygroscopic phases are films, mainly of chlorides of sodium and potassium and, less commonly, of those of iron, magnesium and calcium, that coat the individual vlodavetsite grains. X-ray analysis revealed gypsum, sellaite and bischofite among the above small-particle phases. Very thin gypsum laths are visible as well in immersion liquids. The presence of calcium sulfate was also confirmed by analyses of aqueous extracts (pH 4.1). The creamy yellow-white small particle material with vlodavetsite commonly contains black spinel octahedra—the relicts of an ore phase in erupted magnesian basalt of moderate alkalinity, subsequently altered by fumarole activity. Among the new minerals discovered in products of the Tolbachik eruption [2], vlodavetsite is the first (highest temperature) crystal hydrate. This is explained by the fact that a drop in the temperature of mineral formation promotes the capture of atmospheric water by the nascent phase.

We used a RGNS X-ray goniometer and an automatic Syntex-P2<sub>1</sub> diffractometer to find that vlodavetsite single crystals belong to the tetragonal system, the point group 4/m and the diffraction

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<sup>2</sup>Name approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, on August 2, 1993.

Table 1

## Powder pattern of vlodavetsite

$l/l_1$	$d/n_{\text{meas}}$	$d/n_{\text{calc}}$	$hkl$	$l/l_1$	$d/n_{\text{meas}}$	$d/n_{\text{calc}}$	$hkl$	$l/l_1$	$d/n_{\text{meas}}$	$d/n_{\text{calc}}$	$hkl$
60	6.67	6.66	002	40	2.483	2.484	105			2.011	215
50	3.922	3.920	112	15	2.424	2.424	220	20	1.833	1.834	107
40	3.729	3.728	103	15	2.390	2.389	204	10	1.733	1.735	305
100	3.431	3.428	200	10	2.279	2.278	222	5	1.714	1.714	400
80	3.335	3.331	004	10	2.222	2.221	006	20	1.549	1.551	316
40	3.052	3.048	202	30	2.168	2.168	310			1.548	325
30	2.991	2.988	-211	10	2.060	2.062	312	10	1.533	1.533	420
5	2.525	2.523	213	30	2.012	2.019	116				



Fig. 1. Photograph of vlodavetsite crystals (30×).

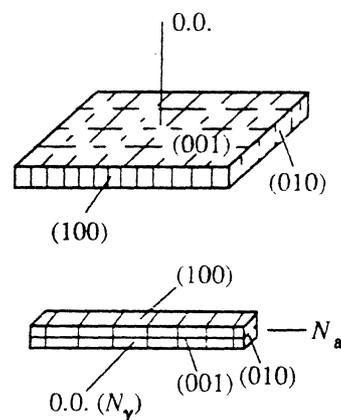


Fig. 2. Optical orientation and cleavage in vlodavetsite grains.

group  $I\bar{4}$  (law of  $hkl$  maxima,  $h + k + l = 2n$ ), which includes the space groups  $I4/m$ ,  $I4$  and  $I\bar{4}$ . The unit cell with  $a$  and  $c$  parameters of 6.87 (1) and 13.342 (2) Å, respectively, contains two formula units; the X-ray density  $D_x$  is 2.35 g·cm<sup>-3</sup>. The structure was resolved in the space group  $I4/m$  ( $R$  factor 0.046 [3]).

The X-ray investigation of vlodavetsite polycrystals was done on a DRON-2 diffractometer in  $\text{CoK}\alpha$  radiation, with germanium as the internal standard. The powder pattern of the mineral (Table 1) was indexed using the cell parameters measured on the single crystal (see above), so we were able to eliminate the lines due to impurity phases. The thus-improved cell parameters and volume are:  $a = 6.856$  (1) and  $c = 13.325$  (3) Å,  $V = 626.2$  (4) Å<sup>3</sup>. The diagnostic lines of the powder pattern ( $l-d/n-hkl$ ) are: 60-6.67-002, 50-3.92-112, 40-3.73-103, 100-3.431-200, 80-3.335-004, 40-3.052-202, 20-2.991-211, 40-2.483-105, 30-2.168-310, 30-2.012-214 and 115.

Table 2

Chemical composition of vlodavetsite (in weight percent), as determined by microprobe analysis of sample 201 (second cone, Great Tolbachik fissure eruption, collected in 1977)

Anal. No.	Al <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>	Cl	O <sub>2</sub> =Cl	Total
1	13.15	25.24	32.15	6.00	-1.35	75.19
2	12.91	24.02	34.56	5.64	-1.27	75.86
3	12.01	24.95	36.39	4.89	-1.10	77.14
4	11.21	25.31	35.38	4.01	-0.90	75.01
5	12.55	24.65	34.90	5.33	-1.20	76.23
6	12.47	25.31	35.69	3.95	-0.89	76.53
7	11.75	24.91	37.24	4.82	-1.09	77.63
8	13.10	23.07	35.65	4.46	-1.00	75.28
9	11.97	25.85	38.08	4.25	-0.96	79.19
10	13.41	26.55	38.06	3.50	-0.79	80.73
11	11.61	26.33	37.54	3.65	-0.82	78.31
Average	12.37	25.11	35.97	4.59	-1.03	77.01

Note. Conditions: Camebax microprobe, accelerating voltage 20 kV, current 25 nA, exposure time 3 s. Standards: dolerophanite for S; albite for Na, Al and Si; sanidine for K; blue diopside for C and Mg; chlorapatite for Cl. The analytical lines for all components were  $K_{\alpha 1}$ .

We were not able to extract a monomineralic vlodavetsite fraction for a complete chemical analysis. We therefore determined the composition of individual mineral flakes, placed on a glass plate, with a *Camebax* microprobe. We deposited carbon on the alcohol-washed flakes, and studied the natural surfaces of the plane-parallel faces of the mineral. Its incomplete chemical composition was computed from an average of 11 analyses (Table 2). The constant slight impurities in vlodavetsite are: SiO<sub>2</sub> 0.42 weight percent (range 0.11 to 0.76 percent) and Na<sub>2</sub>O 0.18 (0.01 to 0.32), which may have come from the supporting glass plate. Chlorine displays much volatility, as indicated by the fact that its concentrations vary by a factor of almost two (Table 2). This suggests that its computed average content (4.59 weight percent) is too low.

A complete chemical analysis of sample 201 revealed a much higher chlorine content (10.6 weight percent) and also disclosed fluorine (15.5) and H<sub>2</sub>O<sup>+</sup> (7.2 weight percent). After the sample had been treated with distilled water, we found under the microscope virtually nothing but vlodavetsite and some altered ash. The content of chlorine in such a washed sample was 6.08, and that of fluorine 8.1 weight percent; the Cl:F atomic ratio was 1:2.5. No other components could be determined because of the small amount of the available material.

The content of chlorine and fluorine in the mineral was defined more accurately when the atomic structure of its crystals was deciphered by means of single-crystal X-ray diffraction analysis. Their structure ( $R$  factor = 0.046) allows for two sets of positions for fluorine and chlorine atoms with 2 and 4 atoms, respectively. Both positions fit into the coordination polyhedron of calcium and are at distances of 2.689 and 2.233 Å from it, respectively. The difference between these values (0.456 Å) is virtually equal to that between the ionic radii of chlorine and fluorine (0.43). Therefore, two chlorine atoms can be fitted into positions with the larger interatomic distances and four fluorine atoms in the positions with the smaller distances. In

the unit cell, moreover, there are eight water molecules, i.e., the Cl:F:H<sub>2</sub>O atomic ratio becomes 1:2:4. Therefore, the idealized chemical formula of the mineral becomes AlCa<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>F<sub>2</sub>Cl·4H<sub>2</sub>O, which fits the following chemical composition: Al<sub>2</sub>O<sub>3</sub> 11.46 weight percent, CaO 25.22, SO<sub>3</sub> 30, Cl 7.97, F 8.54, H<sub>2</sub>O<sup>+</sup> 16.21, Σ 105.4, minus O - Cl + F (5.4), Σ 100. Consequently, structural data have confirmed that the chlorine and fluorine contents determined by chemical analysis are much too low. By compensating the negative charge deficiency with this in mind, we get the following empirical formula for vlodavetsite (based on O = 15): Al<sub>1.09</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>2.01</sub>Cl<sub>0.77</sub>·F<sub>1.94</sub>4H<sub>2</sub>O.

Optical investigation of vlodavetsite crystals showed that the mineral is transparent and colorless. Most crystals are thin and tabular that do not become transparent under crossed nicols (section ⊥0.0.) and have square outlines with {100} prism faces (data of single-crystal X-ray analysis). They display very perfect {100} prism cleavage (Fig. 2). Grains lying on {100} prism faces, i.e., parallel to 0.0., are less common. They have rectangular outlines, negative elongation and parallel extinction. The mineral is uniaxial and optically positive ( $\gamma \parallel L_4$ );  $\epsilon = 1.526$  (3),  $\omega = 1.509$  (2),  $\gamma - \alpha = 0.017$ .

The mineral density, computed from the idealized formula for  $Z = 2$ , is 2.35 g·cm<sup>-3</sup>, but according to the empirical formula it is 2.1 g·cm<sup>-3</sup>. The density could not be determined experimentally because of the small grain size.

Individual crystals of vlodavetsite are colorless and transparent with a glassy luster. Its aggregates are white, the streak being white as well. The mineral hardness was studied by G.A. Il'inskiy of the Department of Mineralogy of our University, using a PMT-3 instrument. At the minimum load ( $P = 0.002$  kg), the crystals split along perfect (100) cleavage planes, so their hardness could not be measured.

After washing with alcohol to remove impurity phases, the vlodavetsite flakes are comparatively stable in air and, therefore, can be investigated in various ways. Prolonged exposure to air leads to the clouding of flakes, presumably as a result of their dehydration. The mineral is virtually insoluble in distilled water, but in acids it dissolves well.

This mineral has been called vlodavetsite after the volcanologist V.I. Vlodavets (1893 to 1993). A specimen has been sent for custody to the Mining Museum, St. Petersburg Mining Institute.

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