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Urusovite, $Cu[AlAsO_5]$, a new mineral from the Tolbachik volcano, Kamchatka, Russia

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Abstract: Urusovite, ideally $Cu[AlAsO_5]$, has been found in a fumarole in the North Breach of the great fissure Tolbachik eruption (1975-76, Kamchatka peninsula, Russia). It occurs as light-green plates up to 0.4 mm in maximal dimension, tabular on {100}, elongated along [001]; well-developed forms are {100}, {010}, {110}, {011}, {111}. Associated minerals are: ponomarevite, piypite, sylvite, dolerophanite, euchlorine, tenorite, hematite and two unknown As-bearing minerals. Urusovite is brittle and has a perfect cleavage on (100), a vitreous luster and a white streak. H = 378 kg/mm^2. Biaxial, optically negative. $\alpha = 1.672(2)$, $\beta = 1.718(2)$, $\gamma = 1.722(2)$, $2V_{meas} \sim 30(2)^o$, $2V_{calc} = 32.2^o$. Optical orientation is $b = \beta$, $c \sim \alpha$. Pleochroism is in the light-green tones: α - colourless, β - light-green, γ - light-green. The mineral is monoclinic, space group $P2_1/c$, $a = 7.314(2)$, $b = 10.223(3)$, $c = 5.576(2)$ Å, $\beta = 99.79(3)^o$, $V = 410.9(2)$ Å^3. The diagnostic lines of the X-ray powder diffraction pattern are (I-d-hkl): 100-7.20-100; 9-4.844-011; 23-4.327-$\bar{1}11$; 10-3.604-200; 10-3.174-121; 20-3.125-$\bar{2}11$; 6-2.656-012; 8-2.458-221. Urusovite is isostructural with $Fe^{2+}[AlPO_5]$. Microprobe analysis gave the following chemical composition (wt. %): CuO 32.23 (30.97-32.82), Al_2O_3 20.89 (20.44-21.44), Fe_2O_3 0.32 (0.10-0.72), ZnO 0.25 (0.10-0.43), As_2O_5 46.02 (44.97-47.17), V_2O_5 0.12 (0.00-0.40), Σ 99.83 (98.71-100.64). The empirical formula of urusovite, $(Cu_{0.99}Zn_{0.01})_{\Sigma 1.00}Al_{1.00}As_{0.98}O_{5.00}$, calculated on the basis of 5 O atoms, is close to the ideal one, $Cu[AlAsO_5]$, confirmed by crystal-structure analysis. The mineral is named urusovite in honour of Vadim Sergeevich Urusov (1936–), crystal chemist, Corresponding Member of the Russian Academy of Sciences, chair of the Department of Crystallography and Crystal Chemistry of Moscow State University.

Key-words: urusovite, new mineral, arsenate, Tolbachik volcano, Kamchatka (Russia).

Introduction

A new copper aluminoarsenate, $Cu[AlAsO_5]$, has been discovered in a fumarole of the North Breakthrough of the Great fissure Tolbachik eruption (GFTE) (1975-76, Kamchatka peninsula, Russia). The mineral is named urusovite in honour of Vadim Sergeevich Urusov, crystal chemist, Corresponding Member of the Russian Academy of Sciences, chair of the Department of Crystallography and Crystal Chemistry of Moscow State University. The type specimen is

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deposited in the Mining Museum, Mining Institute, St. Petersburg. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (proposal no. 98-067).

Locality and occurrence

The GFTE is the greatest basaltic eruption in modern history (Fedotov, 1984). It was active in 1975-76 and consists of two breaches (North and South) and seven cones. Urusovite occurs in the products of fumarolic activity on the second cinder cone of the North Breach. The crystals of the mineral were found in 1983 in exhalative deposits of the fumarole named "Novaya" ("New"). The temperature of the gases in this fumarole at the time of sampling was about 410-420°C. The most common minerals in the sample are dark-red ponomarevite, $K_4Cu_4OCl_{10}$ (Vergasova *et al.*, 1988), emerald-green piypite, $K_4Cu_4O_2(SO_4)_4 \cdot MCl$ (= caratiite, discredited name; Vergasova *et al.*, 1984; Filatov & Vergasova, 1989) and sylvite. Other minerals present are dolerophanite, $Cu_2O(SO_4)$, euchlorine, $KNaCu_3O(SO_4)_3$ (Scordari *et al.*, 1989), tenorite, hematite and two unknown As-bearing minerals. Urusovite occurs as elongated light-green plates, often in intergrowths with other minerals.

Chemical composition

Chemical analyses of urusovite were performed with a Camebax electron microprobe using an operating voltage of 15 kV and a beam current of 20 nA for all elements. The following standards were used for calibration: CuO (Cu), $MgAl_2O_4$ (Al), Fe_2O_3 (Fe), ZnO (Zn), $Cu_3(AsO_4)_2$ (As), V_2O_5 (V). No elements other than those mentioned above have been detected. The results of the analyses are summarized in Table 1. The empirical formula of urusovite, $(Cu_{0.99}Zn_{0.01})_{\Sigma 1.00}Al_{1.00}As_{0.98}O_{5.00}$, calculated for O = 5, is close to the ideal one, $Cu[AlAsO_5]$, confirmed by crystal-structure analysis. The valence state of Cu (2+) has been confirmed by bond-valence calculations on the basis of local coordination of Cu atoms in the crystal structure. After lammerite, $Cu_3(AsO_4)_2$ (Filatov *et al.*, 1984), alarsite, $AlAsO_4$ (Semenova *et al.*, 1994), and coparsite, $Cu_4O_2((As,V)O_4)Cl$ (Vergasova *et al.*, 1999), urusovite is the fourth arsenate mineral found as a product of fumarolic activity of GFTE.

Table 1. Electron-microprobe analyses of urusovite (wt. %).

CuO	Al_2O_3	Fe_2O_3	ZnO	As_2O_5	V_2O_5	Σ
31.92	20.44	0.72	0.43	45.07	0.40	98.98
32.45	21.07	0.10	0.33	45.43	0.08	99.46
32.14	20.53	0.21	0.29	45.82	0.00	98.99
32.47	20.73	0.57	0.28	44.97	0.28	99.30
30.97	21.20	0.10	0.10	46.35	0.00	98.71
31.84	20.91	0.17	0.17	45.86	0.00	98.96
32.48	21.44	0.17	0.19	46.79	0.19	101.07
32.09	21.07	0.12	0.13	46.18	0.00	99.60
32.36	21.08	0.48	0.25	47.17	0.00	101.35
31.87	20.99	0.38	0.33	46.95	0.00	100.52
32.34	20.61	0.58	0.33	45.51	0.24	99.61
32.82	20.85	0.30	0.23	46.27	0.17	100.64
32.48	20.91	0.19	0.24	46.76	0.00	100.58
32.49	20.79	0.48	0.30	45.33	0.39	99.79
32.70	20.67	0.27	0.21	45.80	0.01	99.65
32.23	**20.89**	**0.32**	**0.25**	**46.02**	**0.10**	**99.81**

X-ray crystallography

Unit-cell parameters of urusovite were preliminarily determined using a Weissenberg camera and were further refined from X-ray powder diffraction data (DRON-2 diffractometer, Cu$K\alpha$ radiation, Ge internal standard). The experimental data, together with intensities calculated from the crystal structure, are given in Table 2. The diagnostic lines of the X-ray powder diffraction pattern are (I-d-hkl): 100-7.20-100; 9-4.844-011; 23-4.327-$\bar{1}$11; 10-3.604-200; 10-3.174-121; 20-3.125-$\bar{2}$11; 6-2.656-012; 8-2.458-221. The discrepancy between measured and calculated intensities (Table 2) can be explained by preferred orientation of urusovite grains due to the perfect cleavage parallel to (100) and plate morphology (see below).

The mineral is monoclinic, space group $P2_1/c$, a = 7.314(2), b = 10.223(3), c = 5.576(2) Å, β = 99.79(3)°, V = 410.9(2) Å^3.

Crystal structure

The crystal structure of urusovite has been solved by direct methods in the space group $P2_1/c$ and refined to $R(F)$ = 0.048 from 1134 unique observed reflections. The cell dimensions obtained by the structure analysis [a = 7.335(1), b = 10.225(1), c = 5.599(1) Å, β = 99.79(1)°, V = 415.0(1) Å^3] are in good agreement with the parameters refined from powder diffraction data.

Table 2. X-ray powder diffraction pattern of urusovite.

$I/I_{1\ meas}$	d_{meas}, Å	*hkl*	$I/I_{1\ calc}$	d_{calc}, Å
100	7.20	100	100	7.21
3	5.88	110	10	5.89
2	5.10	020	6	5.11
9	4.844	011	33	4.840
23	4.327	$\bar{1}11$	73	4.329
10	3.604	200	5	3.604
3	3.398	210	3	3.399
10	3.174	121	65	3.174
20	3.125	$\bar{2}11$	97	3.123
3	3.080	130	30	3.081
2	2.944	220	5	2.945
2	2.752	002	14	2.747
2	2.700	211	10	2.703
6	2.656	012	39	2.653
3	2.637	$\bar{1}12$	7	2.634
2	2.558	040	13	2.556
8	2.458	221	43	2.458
5	2.403	300	4	2.403
2	2.338	310	3	2.339
5	2.167	$\bar{2}22$	4	2.165
		231	7	2.165
3	2.138	032	9	2.139
		$\bar{3}21$	5	2.137
2	2.127	$\bar{1}32$	7	2.129
3	1.982	$\bar{3}02$	11	1.983
		132	1	1.980
4	1.964	330	14	1.964
2	1.872	042	8	1.871
3	1.801	400	2	1.802

a = 7.314(2), b = 10.223(3), c = 5.576(2) Å,
β = 99.79(3)°, V = 410.9(2) Å^3

* $I/I_{1\ calc}$ are based on crystal-structure data.

A detailed description of the structure is given by Krivovichev *et al.* (2000). The structure is based upon $[AlAsO_5]^{2-}$ sheets parallel to the (100) plane. The sheets are built from corner-sharing chains of $[AlO_4]$ tetrahedra extended along [100] which are linked with each other through $[AsO_4]$ tetrahedra. Cu atoms are located between the sheets to link them into a three-dimensional framework. There is one symmetrically independent Cu atom in urusovite that is in square-pyramidal fivefold coordination [Cu-O = 1.960(5), 1.971(5), 1.972(5), 1.975(5), 2.370(5) Å]. Urusovite is isostructural with $Fe^{2+}[AlPO_5]$ and $Mg[AlPO_5]$ (Hesse & Cemič, 1994a, b).

Crystal morphology and physical properties

The crystal morphology of urusovite was studied by the measurements of five crystals up to 0.4 mm in maximal dimension with a two-circle reflection goniometer. Crystals of urusovite are platy on (100) and elongated along [001]. The well-developed forms are {100}, {010}, {110}, {011}, {111} (Fig. 1a). The *a:b:c* relations calculated from morphology and from unit-cell parameters obtained from single-crystal data are equal to 0.698 : 1 : 0.541 and 0.715 : 1 : 0.545, respectively.

The mineral is light-green with a vitreous luster and white streak. Urusovite has a perfect cleavage parallel to (100), which corresponds to the aluminoarsenate sheets in the structure. The calculated density is 3.93 g/cm^3. The experimental density was not measured due to the small amount of

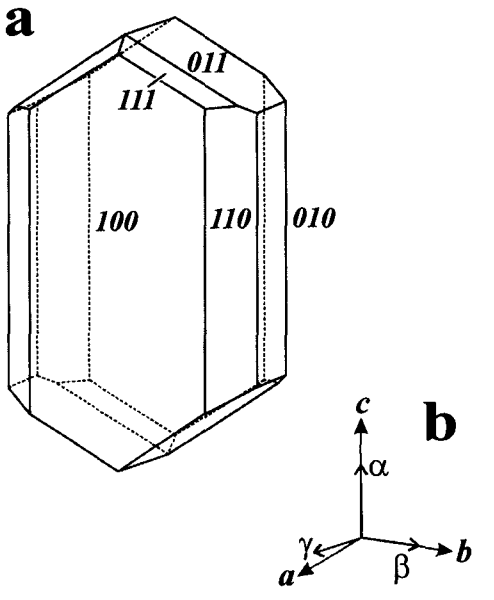

Fig. 1. The crystal morphology of urusovite (a) and its optical orientation (b).

material. The mineral is brittle. The hardness H = 378 kg/mm^2 was measured by micro-indentation (VHN load 10 g, range 337-441 kg/mm^2). Urusovite is stable at room temperature and pressure and is practically unsoluble in water and alcohol. The mineral does not fluoresce in either short- or long-wave ultraviolet radiation.

Optical properties

In transmitted light the mineral is transparent. Urusovite is biaxial and optically negative. The refractive indices were measured in immersion liquids: $\alpha = 1.672(2)$, $\beta = 1.718(2)$, $\gamma = 1.722(2)$, $2V_{meas} \sim 30(2)^o$, $2V_{calc} = 32.2^o$. Optical orientation is $b = \beta$, $c \sim \alpha$ (Fig. 1b). Urusovite shows slight pleochroism in the light-green tones: α - colourless, β - light-green, γ - light-green. The Gladstone-Dale compatibility $[1-(K_P/K_C)]$ is equal to –0.030; thus the compatibility is excellent.

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