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Yaroshevskite, $Cu_9O_2(VO_4)_4Cl_2$, a new mineral from the Tolbachik volcano, Kamchatka, Russia

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ABSTRACT

A new mineral, yaroshevskite, ideally $Cu_9O_2(VO_4)_4Cl_2$, occurs in sublimates collected from the Yadovitaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with euchlorine, fedotovite, hematite, tenorite, lyonsite, melanothallite, atlasovite, kamchatkite and secondary avdoninite, belloite and chalcanthite. Yaroshevskite forms isolated prismatic crystals, up to $0.1 \times 0.15 \times 0.3$ mm in size, on the surface of euchlorine crusts. The mineral is opaque and black, with a reddish black streak and lustre between metallic and adamantine. Yaroshevskite is brittle, no cleavage was observed and the fracture is uneven. The Mohs hardness is ~3½ (corresponding to a mean VHN micro-indentation hardness of 172 kg mm^{-2}) and the calculated density is 4.26 g cm^{-3}. In reflected light, yaroshevskite is grey with a weak bluish hue. Pleochroism, internal reflections and bireflectance were not observed. Anisotropy is very weak. The composition (wt.%) determined by electron microprobe is: CuO 61.82, ZnO 0.53, Fe_2O_3 0.04, V_2O_5 31.07, As_2O_5 0.32, MoO_3 1.56, Cl 6.23, O=Cl_2 −1.41; total 100.16. The empirical formula, calculated on the basis of 20 (O + Cl) anions is $(Cu_{8.80}Zn_{0.07}Fe_{0.01})_{\Sigma 8.88}(V_{3.87}Mo_{0.12}As_{0.03})_{\Sigma 4.02}O_{18.01}Cl_{1.99}$. Yaroshevskite is triclinic, space group $P\bar{1}$, a = 6.4344(11), b = 8.3232(13), c = 9.1726(16) Å, α = 105.338(14), β = 96.113(14), γ = 107.642(1)º, V = 442.05(13) Å^3 and Z = 1. The nine strongest reflections in the X-ray powder pattern [d_{obs} in Å(I)(hkl)] are as follows: 8.65(100)(001); 6.84(83)(0$\bar{1}$1); 6.01(75)(100); 5.52(60)($\bar{1}$01); 4.965(55)(011); 4.198(67)($\bar{1}\bar{1}$1); 4.055(65)(110); 3.120(55)(021); 2.896(60)(2$\bar{1}$1,003,$\bar{2}$20). The crystal structure was solved by direct methods from single-crystal X-ray diffraction data and refined to R = 0.0737. The yaroshevskite structure is unique. It is based on corrugated layers made up of chains of edge-sharing flat squares with central Cu^{2+} cations [Cu(1), Cu(4) and Cu(5)]; neighbouring chains are connected via groups consisting of three Cu^{2+}-centred squares [two Cu(3) and Cu(6)]. Neighbouring layers are connected via pairs of $Cu(2)O_4Cl$ five-coordinate polyhedra and isolated VO_4 tetrahedra. The structure of yaroshevskite can also be considered in terms of oxygen-centred tetrahedra: $O(7)Cu_4$ tetrahedra are connected via common Cu(4) and Cu(5) vertices to form pyroxene-like chains $[O_2Cu_6]^{\infty}$. In this context, the structural formula can be written $Cu_3[O_2Cu_6][VO_4]_4Cl_2$. The mineral name honours the Russian geochemist Alexei A. Yaroshevsky (b. 1934) of Moscow State University.

Keywords: yaroshevskite, new mineral, vanadate, copper oxysalt, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka.

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Introduction

A diverse assemblage of vanadium minerals is present in sublimates from fumaroles related to the Great Tolbachik Fissure Eruption (GTFE) of 1975–1976 at the Tolbachik volcano, Kamchatka Peninsula, Far East Asia, Russia. These include ten anhydrous vanadate minerals, five of which were first reported from fumaroles of the Second scoria cone of the Northern Breakthrough of the GTFE, namely: leningradite, $PbCu_3(VO_4)_2Cl_2$ (Vergasova *et al*., 1990); averievite, $Cu_6O_2(VO_4)_2Cl_2 \cdot n(K,Cs,Rb)Cl$ (Vergasova *et al*., 1998); pseudo-lyonsite, $Cu_3(VO_4)_2$ (Zelenski *et al*., 2011); starovaite, $KCu_5O(VO_4)_3$ (Pekov *et al*., 2012); and yaroshevskite, $Cu_9O_2(VO_4)_4Cl_2$, which is described herein. Other vanadates found in the GTFE fumaroles include ziesite, β-$Cu_2V_2O_7$ (Vergasova and Filatov, 1993); lyonsite, $Cu_{3+x}(Fe^{3+}_{4-2x}Cu_{2x})(VO_4)_6$, with $0 \leqslant x \leqslant 1$ (Pekov *et al*., 2013); fingerite, $Cu_{11}O_2(VO_4)_6$; blossite, α-$Cu_2V_2O_7$; and schäferite, $NaCa_2Mg_2(VO_4)_3$ (I.V. Pekov, unpublished data). In addition to the vanadate minerals listed above, the vanadyl sulfate pauflerite, β-$VO(SO_4)$ (Krivovichev *et al*., 2007), and the vanadium-bearing oxides shcherbinaite, V_2O_5 (Glavatskikh, 1982), and bannermanite, $(Na,K)_xV^{4+}_xV^{5+}_{6-x}O_{15}$ (I.V. Pekov, unpublished data), have also been identified. A general discussion of the formation of vanadate minerals in fumaroles is provided by Hughes and Birnie (1980) and Zelenski *et al*. (2011).

TABLE 1. Reflectance data for yaroshevskite.

Wavelength (nm)	Reflectance (%)
400	15.8
420	16.2
440	16.3
460	16.2
480	16.0
500	15.8
520	15.5
540	15.3
560	15.2
580	14.9
600	14.7
620	14.5
640	14.4
660	14.2
680	14.0
700	13.8

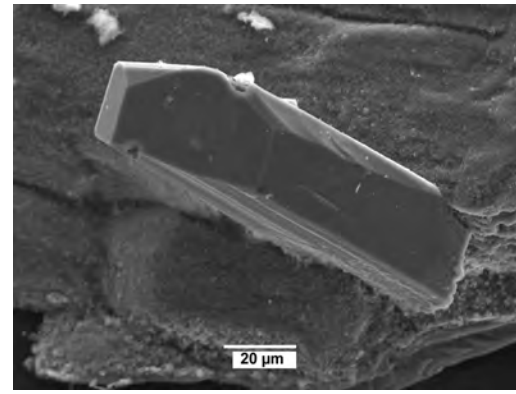

FIG. 1. A scanning electron microscope image of a crystal of yaroshevskite on euchlorine.

The new mineral yaroshevskite (Cyrillic: ярошевскит), described herein, is named in honour of the Russian geochemist Alexei Andreevich Yaroshevsky (b. 1934), Professor in the Department of Geochemistry at the Faculty of Geology of Moscow State University. The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2012-003). The type specimen of yaroshevskite has been deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, under registration number 4240/1.

Occurrence and general appearance

The specimens of yaroshevskite were collected in 2009 by one of the authors (MEZ) in the Yadovitaya (i.e. Poisonous) fumarole at the

TABLE 2. Composition data for yaroshevskite.

Oxide	Mean* (wt.%)	Range
CuO	61.82	60.8–62.4
ZnO	0.53	0.4–0.8
Fe_2O_3	0.04	0.00–0.07
V_2O_5	31.07	30.5–31.7
As_2O_5	0.32	0.2–0.4
MoO_3	1.56	1.0–1.9
Cl	6.23	6.0–6.6
$O{=}Cl_2$	−1.41	
Total	100.16	

* Mean of five analyses.

Second scoria cone of the Northern Breakthrough of the GTFE. This scoria cone, which was formed in 1975, is 300 m high and approximately 0.1 km^3 in volume (Fedotov and Markhinin, 1983). The Yadovitaya fumarole is an open cave about 1.5 m wide and 2 m deep with an interior temperature of up to 340ºC (as measured in 2010). The walls of the cave are thickly encrusted by a diverse assemblage of minerals, dominantly sulfates.

Yaroshevskite occurs very rarely on crusts mainly consisting of bright green euchlorine. Associated minerals include fedotovite, hematite, tenorite, a Cu-rich variety of lyonsite (Pekov *et al.*, 2013), melanothallite, atlasovite, kamchatkite and secondary supergene avdoninite, belloite (both these hydrous chlorides replace melanothallite) and chalcanthite. Yaroshevskite occurs as isolated prismatic crystals (Fig. 1) typically up to $0.03 \times 0.07 \times 0.12$ mm, and very rarely up to $0.1 \times 0.15 \times 0.3$ mm in size.

Physical properties and optical data

Yaroshevskite is opaque and black with a reddish black streak. Its lustre is intermediate between

TABLE 3. X-ray powder-diffraction data for yaroshevskite.

I_{obs}	d_{obs} (Å)	I_{calc}	d_{calc} (Å)*	*h k l*
100	**8.65**	32	8.661	0 0 1
83	**6.84**	89	6.844	0 $\bar{1}$ 1
75	**6.01**	42	6.004	1 0 0
60	**5.52**	65	5.483	$\bar{1}$ 0 1
55	**4.965**	40	4.966	0 1 1
47	4.702	27	4.703	$\bar{1}$ 1 1
49	4.526	24	4.523	1 0 1
51	4.318	14	4.331	0 0 2
67	**4.198**	43	4.205	$\bar{1}$ $\bar{1}$ 1
65	**4.055**	67	4.061	1 1 0
52	3.930	21	3.909	$\bar{1}$ 0 2
34	3.567	37	3.555	$\bar{1}$ $\bar{1}$ 2
39	3.340	97	3.331	0 1 2
50	3.199	14, 64, 12	3.216, 3.194, 3.191	1 0 2, $\bar{2}$ 1 0, 1 $\bar{2}$ 2
55	**3.120**	100	3.115	0 2 1
60	**2.896**	37, 93, 35	2.919, 2.887, 2.882	2 $\bar{1}$ 1, 0 0 3, $\bar{2}$ 2 0
48	2.704	22, 38, 46, 55	2.743, 2.742, 2.699, 2.679	1 $\bar{3}$ 1, $\bar{2}$ 0 2, $\bar{2}$ 2 1, $\bar{2}$ 1 2
48	2.505	49	2.507	2 1 0
45	2.266	65, 9, 48	2.279, 2.262, 2.249	0 $\bar{1}$ 4, 2 0 2, 2 1 1
31	2.083	20, 11, 13	2.092, 2.075, 2.072	$\bar{3}$ 2 0, 1 3 0, 1 1 3
14	2.008	16	2.030	2 2 0
43	1.971	24, 22	1.974, 1.970	0 $\bar{3}$ 4, $\bar{2}$ 3 2
27	1.919	10, 8	1.922, 1.917	$\bar{2}$ 4 0, 1 0 4
21	1.833	19	1.828	$\bar{3}$ 0 3
20	1.741	25, 12	1.749, 1.741	$\bar{1}$ $\bar{2}$ 5, 1 2 3
16	1.636	6, 8, 18	1.640, 1.634, 1.629	3 $\bar{4}$ 2, 3 $\bar{3}$ 3, $\bar{3}$ 4 1
37	1.585	10, 7, 18, 9, 28	1.588, 1.584, 1.583, 1.581, 1.580	$\bar{2}$ $\bar{3}$ 4, $\bar{2}$ 5 0, $\bar{1}$ $\bar{4}$ 4, 1 0 5, $\bar{4}$ 1 0
28	1.513	9, 17	1.515, 1.511	2 $\bar{2}$ 5, $\bar{1}$ 3 4
26	1.445	4, 18	1.445, 1.444	1 $\bar{2}$ 6, 0 0 6
21	1.406	4, 4	1.406, 1.404	$\bar{3}$ 3 4, 3 $\bar{5}$ 3
17	1.371	4, 7, 15	1.372, 1.371, 1.369	2 $\bar{6}$ 2, $\bar{4}$ 0 4, 2 $\bar{6}$ 1
15	1.339	8, 9	1.340, 1.337	$\bar{4}$ 2 4, 4 0 2
16	1.311	5, 4, 4, 7	1.315, 1.314, 1.308, 1.307	2 $\bar{3}$ 6, 2 $\bar{2}$ 6, 1 $\bar{6}$ 4, 4 $\bar{1}$ 3
12	1.273	8	1.272	$\bar{3}$ $\bar{3}$ 5

* Calculated using unit-cell parameters obtained from single-crystal data.
The nine strongest lines in the powder pattern are listed in bold.

metallic and adamantine. Yaroshevskite is brittle. Its mean micro-indentation hardness (VHN) is 172 kg mm^{-2} with a range of 165–179 kg mm^{-2} (under a 20 g load). The Mohs hardness was not measured directly because of the small size of the crystals; the value calculated from the VHN measurement is ~3½. Cleavage and parting were not observed; fracture is uneven (observed under the scanning electron microscope). The density could not be measured because of the paucity of available material for volumetric methods and the lack of suitable heavy liquids. The calculated density, D_{calc}, is 4.26 g cm^{-3} (from the empirical formula).

In reflected light, yaroshevskite is grey with a weak bluish hue. Pleochroism, internal reflections and bireflectance were not observed. The anisotropy is very weak. The reflectance values were measured in St Petersburg State University using a MSF-21 microspectrophotometer (LOMO, Russia) with a SiC standard (Zeiss, No. 545). As the mineral is almost isotropic only one *R* value was measured at each wavelength (Table 1).

Chemical composition

Chemical data for yaroshevskite were obtained using a JEOL JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer at Moscow State University. Operating conditions were an accelerating voltage of 20 kV, current of 20 nA and beam diameter of 2 μm. The following standards and lines were used: $CuFeS_2$ (Cu*K*α, Fe*K*α), ZnS (Zn*K*α), FeAsS (As*K*α), V (V*K*α), $CaMoO_4$ (Mo*L*α) and KCl (Cl*K*α). As the S*K*α and Mo*L*α lines overlap, the Mo content was checked using the Mo*K*α line in slightly different operating conditions (30 kV with a 30 nA beam current); this produced similar results, showing that there is no contribution to the Mo*L*α line intensity from S*K*α and therefore that S is below the instrumental detection limit in yaroshevskite. The composition of yaroshevskite is reported in Table 2. Elements with atomic numbers greater than 8, other than those listed, are below detection limits.

TABLE 4. Crystal data, data collection information and structure refinement details for yaroshevskite.

Formula	$Cu_9O_2(VO_4)_4Cl_2$
Formula mass	567.26
Temperature (K)	293(2)
Radiation and wavelength (Å)	Mo*K*α; 0.71073
Crystal system, space group, *Z*	Triclinic, $P\bar{1}$, 1
Unit cell dimensions (Å, º)	a = 6.4344(11) α = 105.338(14)
	b = 8.3232(13) β = 96.113(14)
	c = 9.1726(16) γ = 107.642(15)
V (Å^3)	442.05(13)
Density (calculated) (g cm^{-3})	4.262
Absorption coefficient μ (mm^{-1})	12.976
F_{000}	531
Crystal size (mm)	0.03 × 0.09 × 0.23
Diffractometer	Xcalibur S CCD
θ range for data collection (º)	2.70–30.51
Index ranges	$-9 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $-13 \leqslant l \leqslant 13$
Reflections collected	12,451
Independent reflections	2693 (R_{int} = 0.1316)
Independent reflections with $I>2\sigma(I)$	2026
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	154
R_F / wR (F^2)	0.0737 / 0.1741
GoF	1.083
Largest diff. peak and hole (e Å^{-3})	2.465 and −1.733

TABLE 5. Atom coordinates and equivalent isotropic-displacement parameters, U_{eq}, (Å^2) for yaroshevskite.

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
Cu(1)	0.14053(18)	0.71747(16)	0.02236(13)	0.0145(3)
Cu(2)	0.41589(19)	0.54353(17)	−0.35783(13)	0.0183(3)
Cu(3)	0.1708(2)	0.83232(16)	−0.31239(13)	0.0162(3)
Cu(4)	½	0	0	0.0150(4)
Cu(5)	0	0	0	0.0160(4)
Cu(6)	0	0	½	0.0256(4)
V(1)	−0.1105(2)	0.4159(2)	−0.34993(17)	0.0111(3)
V(2)	0.3253(2)	0.2519(2)	−0.14950(17)	0.0106(3)
Cl	0.6545(5)	0.8717(4)	−0.2796(3)	0.0300(6)
O(1)	0.3919(11)	0.4395(9)	−0.1925(8)	0.0172(13)
O(2)	0.1372(10)	0.5891(9)	−0.3400(7)	0.0126(12)
O(3)	0.3394(10)	0.5365(10)	−0.5833(8)	0.0193(15)
O(4)	0.0879(11)	0.7799(9)	−0.5388(7)	0.0181(14)
O(5)	0.1076(12)	0.5833(10)	0.1675(7)	0.0189(14)
O(6)	−0.1301(10)	0.7664(9)	0.0347(8)	0.0176(14)
O(7)	0.1910(10)	0.8865(8)	−0.0960(7)	0.0121(12)
O(8)	0.4521(10)	0.7763(9)	0.0517(8)	0.0159(13)
O(9)	0.2109(11)	0.0703(9)	−0.3170(7)	0.0188(14)

The empirical formula calculated on the basis of 20 (O + Cl) anions p.f.u. is $(Cu_{8.80}Zn_{0.07}Fe_{0.01})_{\Sigma 8.88}(V_{3.87}Mo_{0.12}As_{0.03})_{\Sigma 4.02}O_{18.01}Cl_{1.99}$. The ideal formula is $Cu_9O_2(VO_4)_4Cl_2$, which requires CuO 63.10, V_2O_5 32.06, Cl 6.25, O=Cl_2 −1.41, total 100.00 wt.%.

X-ray crystallography

The X-ray powder-diffraction data for yaroshevskite were obtained at St Petersburg State University using a STOE IPDS II single-crystal diffractometer (Mo*K*α radiation) equipped with an image-plate detector (distance between sample

TABLE 6. Selected interatomic distances (Å) in the yaroshevskite structure.

Cu(1)−O(8)	1.885(6)	Cu(5)−O(7)	1.916(6) × 2
Cu(1)−O(6)	1.913(6)	Cu(5)−O(6)	1.995(6) × 2
Cu(1)−O(5)	1.941(7)		
Cu(1)−O(7)	1.967(6)	Cu(6)−O(9)	1.875(7) × 2
		Cu(6)−O(4)	2.032(7) × 2
Cu(2)−O(1)	1.934(7)		
Cu(2)−O(2)	1.957(6)	V(1)−O(5)	1.670(7)
Cu(2)−O(3)	1.960(6)	V(1)−O(3)	1.729(6)
Cu(2)−O(3)	2.055(7)	V(1)−O(4)	1.737(7)
Cu(2)−Cl	2.553(3)	V(1)−O(2)	1.771(6)
Cu(3)−O(7)	1.897(6)	V(2)−O(1)	1.653(7)
Cu(3)−O(2)	1.913(6)	V(2)−O(8)	1.718(6)
Cu(3)−O(9)	1.931(7)	V(2)−O(6)	1.721(6)
Cu(3)−O(4)	1.983(6)	V(2)−O(9)	1.745(7)
Cu(4)−O(7)	1.916(6) × 2		
Cu(4)−O(8)	1.984(7) × 2		

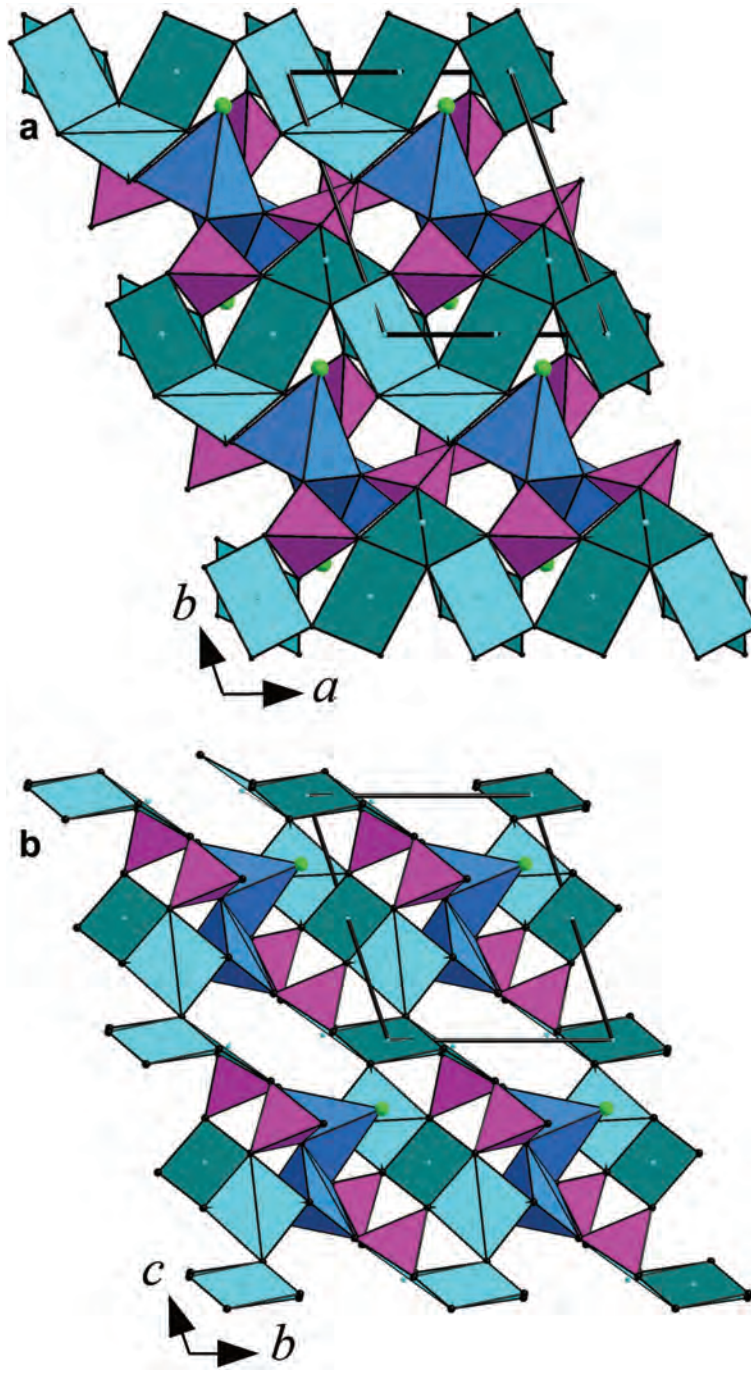

FIG. 2. Crystal structure of yaroshevskite in the (*a*) *ab* and (*b*) *bc* planes. The VO_4 tetrahedra are purple; the CuO_4 squares are light blue; and the CuO_4Cl polyhedra are dark blue. Green spheres mark the positions of Cl atoms.

and detector 200 mm) using the Gandolfi method. The X-ray powder-diffraction pattern (Table 3) is unique. The triclinic unit-cell parameters calculated from the powder data using *UnitCell* (Holland and Redfern, 1997) are a = 6.4528(3), b = 8.3121(5), c = 9.1700(4) Å, α = 105.208(5), β = 96.147(5), γ = 107.881(5)º, V = 442.16(3) Å^3 and Z = 1.

Single-crystal X-ray studies of yaroshevskite and its crystal structure determination were carried out using an Xcalibur S diffractometer equipped with a CCD detector at Moscow State University. The structure was solved by direct methods and refined using *SHELX* (Sheldrick, 2008) to R = 0.0737 for 2026 unique reflections with $I>2\sigma(I)$. Crystal data, data collection information and structure refinement details are given in Table 4, atom coordinates and equivalent isotropic-displacement parameters in Table 5 and selected interatomic distances in Table 6.

Crystal structure: description and discussion

The crystal structure of yaroshevskite (Fig. 2) is based on corrugated layers, which are coplanar with *ac* (Fig. 3), and made up of chains of edge-sharing flat squares with central Cu^{2+} cations [of the Cu(1), Cu(4) and Cu(5) sites]; neighbouring chains are linked by groups consisting of three Cu^{2+}-centred squares [two Cu(3) and one Cu(6)]. These triads are connected by common edges and linked to the chains by common vertices. Neighbouring layers are connected via pairs of $Cu(2)O_4Cl$ five-coordinate polyhedra and isolated VO_4 tetrahedra.

Yaroshevskite has a unique structure; no related mineral or synthetic compound is known. The two other natural chlorovanadates that are known only from the fumaroles of the Tolbachik volcano, leningradite (Siidra *et al.*, 2007) and averievite (Starova *et al.*, 1997), have structures that are different to yaroshevskite. Howardevansite, $NaCuFe_2^{3+}(VO_4)_3$, which has similar lattice parameters and a triclinic unit cell [a = 8.198, b = 9.773, c = 6.651 Å, α = 103.82, β = 101.99, γ = 106.74º (Hughes *et al.*, 1988)], has a structure that is very different to yaroshevskite.

Yaroshevskite is a representative of large group of natural and synthetic compounds with so-called additional anions. Their structures contain anionic complexes with central cations that have a high valence, and anions (in yaroshevskite O^{2-} and Cl^-) which do not participate in the formation of these complexes and can be considered to be coordination centres. In most cases such anion-centred polyhedra are tetrahedrally coordinated with oxygen atoms at their centre and they can be described as OMe_4 units. Many minerals with structures that can be described in terms of OCu_4 tetrahedra are known in sublimates from the fumaroles related to the GTFE (Krivovichev, 2009). In yaroshevskite, $O(7)Cu_4$ tetrahedra formed by Cu(1), Cu(3), Cu(4) and Cu(5) atoms are connected to each other via common Cu(4) and Cu(5) vertices to form pyroxene-like chains, $[O_2Cu_6]^{\infty}$, which extend along the a axis (Fig. 4*a*). Pyroxene-like chains of OCu_4 tetrahedra are present in kamchatkite, $K_2[O_2Cu_6][SO_4]_4Cl_2$ (Varaksina *et al.*, 1990); chloromenite, $Cu_3[O_2Cu_6][SeO_3]_4Cl_6$ (Krivovichev *et al.*, 1998); vergasovaite, $[O_2Cu_6][(Mo,S)O_4SO_4]_2$ (Berlepsch *et al.*, 1999); cupromolybdite, $[O_2Cu_6][MoO_4]_4$ (Zelenski *et al.*, 2012); and other compounds. In yaroshevskite these chains are connected to V^{5+} and additional Cu^{2+} cations to form a specific framework (Fig. 4*b*). Taking into account the above-mentioned structural features, the formula of yaroshevskite can be written $Cu_3[O_2Cu_6][VO_4]_4Cl_2$.

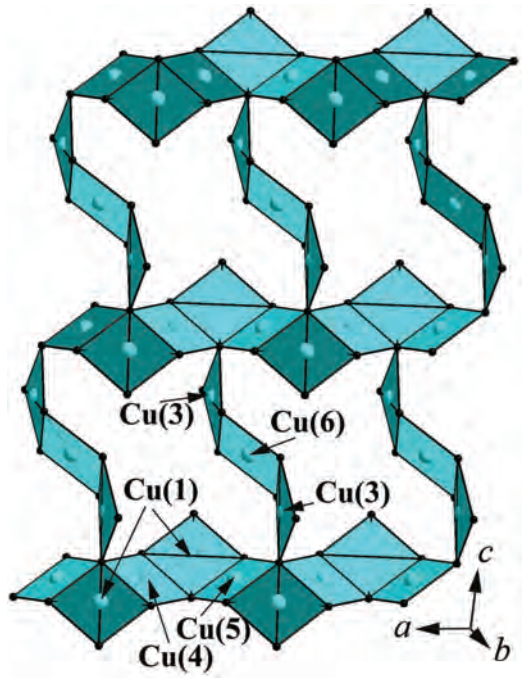

FIG. 3. Corrugated layers formed by the CuO_4 squares in yaroshevskite.

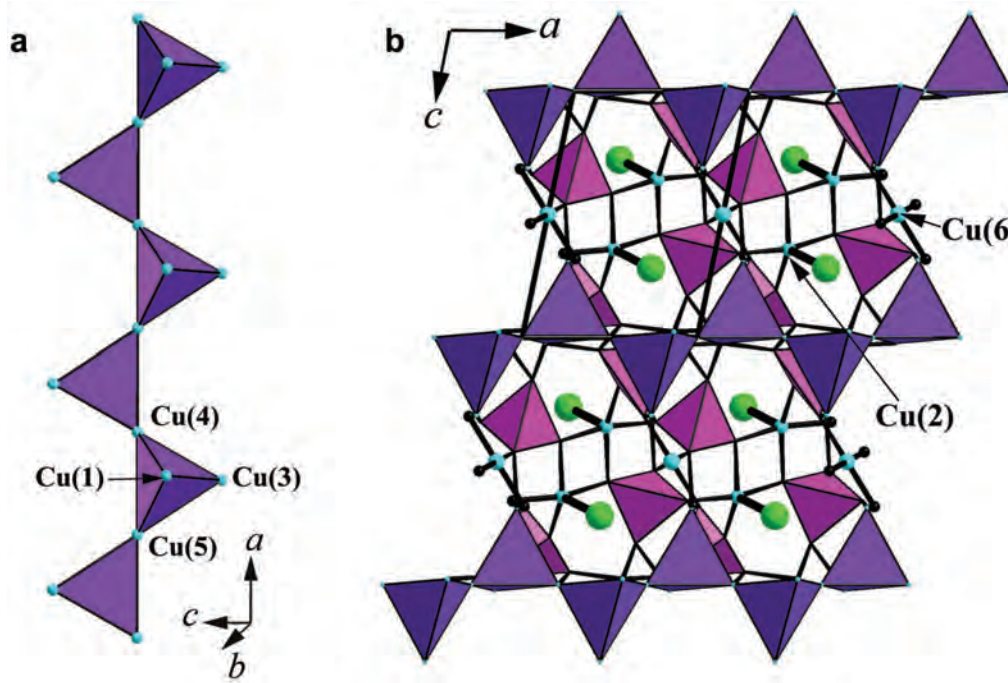

FIG. 4. (*a*) Pyroxene-like chains $[O_2Cu_6]^{\infty}$ and (*b*) the framework formed by these chains in yaroshevskite; VO_4 tetrahedra are purple and the position of additional Cu^{2+} cations are shown.

An interesting crystallochemical feature of yaroshevskite is the substitution of Mo^{6+} for V^{5+} in the tetrahedral sites. This type of substitution is not uncommon in vanadates from the Yadovitaya fumarole, as well as yaroshevskite, it has been noted in pseudolyonsite (Zelenski *et al*., 2011), starovaite (Pekov *et al*., 2012) and lyonsite (Pekov *et al*., 2013); it has not been reported in minerals from other localities. Although it is a relatively exotic phenomenon in minerals, the substitution of Mo^{6+} for V^{5+} is well known in synthetic compounds of many different structural types. It has been described in numerous (V,Mo)-disordered molybdovanadates and vanadomolybdates [e.g. $Bi_{0.93}(V^{5+}_{0.79}Mo^{6+}_{0.21})O_4$, $Bi_{0.88}(V^{5+}_{0.63}Mo^{6+}_{0.37})O_4$ and $Bi_{0.82}(Mo^{6+}_{0.55}V^{5+}_{0.45})O_4$ (Cesari *et al*., 1971); $K_{0.13}(Mo^{6+}_{0.87}V^{5+}_{0.13})O_3$ (Darriet and Galy, 1973); $Mn_{0.47}(Mo^{6+}_{1.06}V^{5+}_{0.94})O_6$ (Kozlowski and Stadnicka, 1981); $Ag_{0.5}Cu_3[(V^{5+}_{0.5}Mo^{6+}_{0.5})O_4][Mo^{6+}O_4]_2$ (Szillat and Müller-Buschbaum, 1995); $Mg_{2.54}(V^{5+}_{1.08}Mo^{6+}_{0.92})O_8$ (Wang *et al*., 1996); $(Mg_{0.53}Fe_{0.47})(Mo^{6+}_{1.53}V^{5+}_{0.47})O_7$ (Wang *et al*., 2002); and $K_{0.23}(V^{5+}_{5.35}Mo^{6+}_{0.65})O_{15}$ and $K_{0.32}(V^{5+}_{5.48}Mo^{6+}_{0.52})O_{15}$ (Zema *et al*., 2007)].

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