



Article

Dokuchaevite, $\text{Cu}_8\text{O}_2(\text{VO}_4)_3\text{Cl}_3$, a new mineral with remarkably diverse Cu^{2+} mixed-ligand coordination environments

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Abstract

Dokuchaevite, ideally $\text{Cu}_8\text{O}_2(\text{VO}_4)_3\text{Cl}_3$, was found in the Yadovitaya fumarole of the Second scoria cone of the North Breach of the Great Tolbachik Fissure Eruption (1975–1976), Tolbachik volcano, Kamchatka Peninsula, Russia. Dokuchaevite occurs on the crusts of various copper sulfate exhalative minerals (such as kamchatkite and euchlorine) as individual prismatic crystals. Dokuchaevite is triclinic, $P\bar{1}$, $a = 6.332(3)$, $b = 8.204(4)$, $c = 15.562(8)$ Å, $\alpha = 90.498(8)$, $\beta = 97.173(7)$, $\gamma = 90.896(13)^\circ$, $V = 801.9(7)$ Å³ and $R_1 = 0.057$. The eight strongest lines of the X-ray powder diffraction pattern are (d , Å) (I)(hkl): (15.4396)(18)(00 $\bar{1}$), (7.2762)(27)(0 $\bar{1}1$), (5.5957)(43)(012), (4.8571)(33)($\bar{1}11$), (3.1929)(29)(023), (2.7915)(30)(202), (2.5645)(21)(032), (2.5220)(100)($\bar{1}30$), (2.4906)(18)(130) and (2.3267)(71)($\bar{2}22$). The chemical composition determined by electron-microprobe analysis is (wt.%): CuO 60.87, ZnO 0.50, FeO 0.36, V_2O_5 19.85, As_2O_5 6.96, SO_3 0.44, MoO_3 1.41, SiO_2 0.20, P_2O_5 0.22, Cl 10.66, $-\text{O} = \text{Cl}_2$ 2.41, total 99.06. The empirical formula calculated on the basis of 17 anions per formula unit is $(\text{Cu}_{7.72}\text{Zn}_{0.06}\text{Fe}_{0.05})_{\Sigma 7.83}(\text{V}_{2.20}\text{As}_{0.61}\text{Mo}_{0.10}\text{S}_{0.06}\text{P}_{0.03}\text{Si}_{0.03})_{\Sigma 3.03}\text{O}_{13.96}\text{Cl}_{3.04}$.

The crystal structure of dokuchaevite represents a new structure type with eight Cu sites, which demonstrate the remarkable diversity of Cu^{2+} mixed-ligand coordination environments. The crystal structure of dokuchaevite is based on OCu_4 tetrahedra that share common corners thus forming $[\text{O}_2\text{Cu}_6]^{8+}$ single chains. Two of the eight symmetrically independent copper atoms do not form Cu–O bonds with additional oxygen atoms, and thus are not part of the OCu_4 tetrahedra, but provide the three-dimensional integrity of the $[\text{O}_2\text{Cu}_6]^{8+}$ chains into a framework. TO_4 mixed tetrahedral groups are located within the cavities of the framework. The structural formula of dokuchaevite can be represented as $\text{Cu}_2[\text{Cu}_6\text{O}_2](\text{VO}_4)_3\text{Cl}_3$.

Keywords: dokuchaevite, new minerals, copper, vanadates, oxocentred tetrahedra, Tolbachik volcano

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Introduction

With the exception of few anhydrous vanadates, known to date as anthropogenic phases (Witzke and Ruger, 1998), most of the anhydrous vanadate minerals originate from the fumaroles of Izalco volcano, El Salvador (Hughes and Stoiber, 1985) and Tolbachik volcano, Kamchatka Peninsula, Russia (Pekov *et al.*, 2013; Vergasova and Filatov, 2016). The former is especially famous for exceptionally vanadium-rich exhalative mineral assemblages. Geochemical environments that led to this type of mineralisation on the fumaroles of both volcanos were discussed by Hughes and Birnie (1980) and Zelensky *et al.* (2011). None of these works could give a definite answer to explain such V-rich mineralisation. Basaltic scoria on both localities show similar concentrations of V as compared to common Earth's basalts.

Exhalative mineral assemblages from fumaroles of the First and Second scoria cones, Great Fissure Tolbachik eruption 1975–76 are well-known for their exceptional diversity of Cu oxy-salt minerals. Yadovitaya fumarole located on top of the Second scoria cone of the Great Fissure Tolbachik eruption is a type locality for 21 mineral species. Fifteen of them contain considerable amounts of Cu^{2+} (Pekov *et al.*, 2018).

Herein we report on the chemical composition, structure and properties of dokuchaevite (Cyrillic: докучаевит), $\text{Cu}_8\text{O}_2(\text{VO}_4)_3\text{Cl}_3$. The mineral is named in honour of Prof Vasily V. Dokuchaev (Cyrillic: Василий Васильевич Докучаев) (1846–1903). V.V. Dokuchaev is a founder of Soil Science. He was a professor in the Department of Mineralogy and from 1879, lectured on mineralogy and crystallography at St. Petersburg State University. The term 'dokuchaevite' has been used as a synonym of delafossite from Dzhezkazgan mining district, Karaganda, Kazakhstan. The usage of the term is not in a wide circulation, thus it should not be confused with the new fumarolic mineral described in this paper. Both the mineral and the mineral name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical

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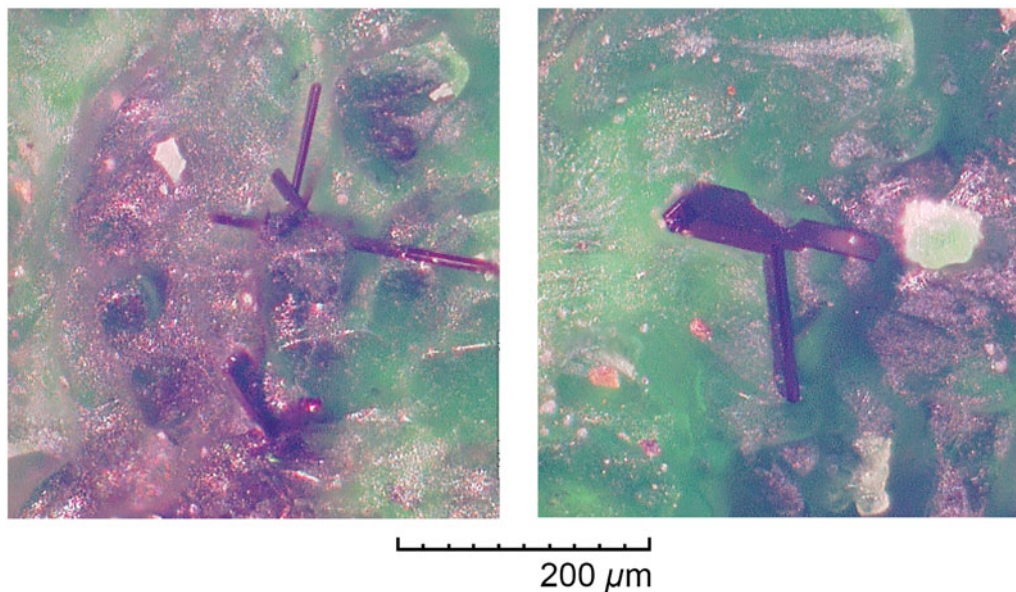


Fig. 1. Dark-red prismatic crystals of dokuchaevite associated with kamchatkite (yellow–green), euchlorine (emerald-green) and langbeinite (white).

Association (IMA2018-012, Siidra *et al.* 2018b). Type material is deposited at the Mineralogical Museum, St. Petersburg State University, St. Petersburg, Russia (catalogue no. 1/19664).

Occurrence and association

Dokuchaevite occurs as a product of fumarolic activity. It was found in June, 2016 in the Yadovitaya fumarole, Second scoria cone, Northern Breakthrough (North Breach), Great Tolbachik

Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. The Second scoria cone is located ~18 km SSW of the active shield volcano Ploskiy Tolbachik (Fedotov and Markhinin, 1983). Dokuchaevite closely associates with kamchatkite, euchlorine and langbeinite (Fig. 1). Other associated minerals are alumoklyuchevskite, lyonsite, pseudolyonsite, tenorite, hematite and

Table 1. Reflectance values for dokuchaevite (SiC standard in air).

λ (nm)	R_{\max} (%)	R_{\min} (%)	λ (nm)	R_{\max} (%)	R_{\min} (%)
400	12.15	11.07	560	13.84	13.01
420	12.62	11.55	580	13.88	13.03
440	12.97	11.92	589	13.87	13.02
460	13.20	12.22	600	13.86	13.01
470	13.30	12.36	620	13.83	12.96
480	13.40	12.50	640	13.79	12.88
500	13.55	12.67	650	13.75	12.84
520	13.69	12.82	660	13.71	12.79
540	13.79	12.94	680	13.57	12.65
546	13.81	12.96	700	13.44	12.47

The values required by the Commission on Ore Mineralogy are given in bold.

Table 2. Analytical data (wt.%) for dokuchaevite.

Constituent	Mean	Range	S.D.	Probe standard
CuO	60.87	59.15–61.85	0.99	Cu
ZnO	0.50	0.22–0.53	0.12	Zn
FeO	0.36	0.25–0.44	0.10	Hematite
V ₂ O ₅	19.85	18.44–22.98	1.68	V
As ₂ O ₅	6.96	3.14–8.00	1.97	GaAs
SO ₃	0.44	0.19–0.51	0.22	Baryte
MoO ₃	1.41	1.21–1.90	0.44	Mo
SiO ₂	0.20	0.11–0.33	0.08	Diopside
P ₂ O ₅	0.22	0.14–0.35	0.08	Apatite
Cl	10.66	10.12–10.99	0.30	NaCl
–O = Cl ₂	2.41			
Total	99.06			

S.D. – standard deviation

Table 3. Powder X-ray diffraction data (d in Å) for dokuchaevite.

l_{meas}	d_{calc}	d_{meas}	hkl
18	15.4396	15.4396	0 0 $\bar{1}$
27	7.2762	7.2762	0 $\bar{1}$ 1
6	6.0899	6.07188	$\bar{1}$ 0 1
43	5.5918	5.5957	0 1 2
6	5.2008	5.1929	$\bar{1}$ 0 2
5	5.1465, 5.0280	5.2133	0 0 3, 1 $\bar{1}$ 0
33	4.8615	4.8571	$\bar{1}$ $\bar{1}$ 1
7	4.5735	4.5796	1 1 1
12	4.4058	4.3945	$\bar{1}$ 1 2
14	4.3386	4.3395	0 1 3
5	4.2499	4.2377	$\bar{1}$ 0 3
8	3.8599, 3.7774, 3.7695	3.9189	0 0 4, $\bar{1}$ 1 3, $\bar{1}$ $\bar{1}$ 3
13	3.2243	3.2203	0 $\bar{2}$ 3
29	3.1908	3.1929	0 2 3
5	3.0328	3.0346	1 2 2
8	2.9307	2.9348	$\bar{2}$ $\bar{1}$ 1
7	2.8659	2.8690	$\bar{2}$ 1 2
30	2.7898	2.7915	2 0 2
15	2.7484, 2.7460	2.7477	$\bar{1}$ 1 5, 1 2 3
15	2.6873	2.6866	0 3 1
21	2.5686	2.5645	0 3 2
100	2.5226	2.5220	1 $\bar{1}$ 0
18	2.4916	2.4906	1 3 0
7	2.4543	2.4566	0 2 5
8	2.4254	2.4237	0 $\bar{3}$ 3
4	2.4162, 2.4134, 2.4039	2.4251	2 1 3, $\bar{1}$ $\bar{3}$ 2, 0 3 3
3	2.3810	2.3826	$\bar{1}$ $\bar{2}$ 5
71	2.3272	2.3267	2 $\bar{1}$ 2
2	2.1799	2.1803	$\bar{2}$ $\bar{2}$ 3
3	2.0558, 2.0515, 2.0513, 2.0506	2.0582	$\bar{2}$ $\bar{1}$ 6, $\bar{2}$ $\bar{3}$ 1, $\bar{3}$ 1 1, 0 4 0
4	2.0037	2.0048	2 1 5
5	1.9724	1.9706	3 1 1

The strongest lines are given in bold.

Table 4. Crystallographic data and refinement parameters for dokuchaevite.

Crystal data	
Ideal formula	As _{0.20} Cl _{0.75} Cu ₂ O _{3.50} V _{0.55}
Crystal size (mm)	0.05 × 0.05 × 0.20
Crystal system, space group	Triclinic, P $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.332(3), 8.204(4), 15.562(8)
α , β , γ (°)	90.498(8), 97.173(7), 90.896(13)
<i>V</i> (Å ³)	801.9(7)
<i>Z</i>	8
μ (mm ⁻¹)	13.834
<i>D</i> _{calc} (g/cm ³)	4.188
Data collection	
Instrument	
Radiation type, wavelength (Å)	MoK α , 0.71073
θ -range (°)	2.483–23.450
No. of measured, independent and observed <i>F</i> _o ≥ 4 σ <i>F</i> reflections	3292, 2173, 1563
<i>R</i> _{int}	0.043
Indices range of <i>h</i> , <i>k</i> , <i>l</i>	−3 ≤ <i>h</i> ≤ 7, −9 ≤ <i>k</i> ≤ 6, −17 ≤ <i>l</i> ≤ 16
Refinement	
<i>R</i> _{<i>j</i>} , <i>R</i> _{<i>w</i>} (all)	0.057, 0.085
GoF	1.006
No. of refined parameters, restraints	257, 18
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e [−] Å ^{−3})	+1.567/−1.627

anhydrite (Fig. 1). Dokuchaevite is a fumarolic mineral that is deposited directly from volcanic gas emissions as a sublimate. The temperature of gases at the sampling location was ~300°C. All the recovered samples were packed and isolated when collected to avoid any contact with the external atmosphere.

Physical properties

Dokuchaevite occurs on the crusts (Fig. 1) of various copper sulfate exhalative minerals (such as kamchatkite and euchlorine) as

individual prismatic crystals up to 30 μm × 30 μm × 150 μm (but usually from 5 to 20 μm in size). Dokuchaevite is dark red, with a reddish black streak and close to adamantine lustre. It is brittle with no cleavage observed. Parting was not observed, and its fracture is uneven. The density could not be measured due to lack of sufficient material. The calculated density using the empirical formula derived from the analytical data given in Table 1 is 4.142 g cm^{−3}.

Dokuchaevite has a Vickers Hardness Number (VHN₂₀) of 55 kg mm^{−2} (*n* = 5, range 54–56 kg mm^{−2}), which corresponds to a Mohs' hardness of ~2.

Despite the transparency of dokuchaevite, its optical properties had to be investigated in reflected light, because of the high values of refractive indices typical of vanadates and arsenates. Reflectance measurements were made using a SiC standard in air in the range 400–700 nm (Table 1). In reflected light, dokuchaevite is grey with a yellowish tint. It is non-pleochroic, with abundant yellow–red internal reflections and a weak bireflectance. The measured anisotropy is $\Delta R_{589} = 0.85\%$.

Dokuchaevite is soluble in warm H₂O.

Chemical composition

Three crystals (34 × 9, 60 × 13 and 65 × 10 μm) of dokuchaevite were mounted in epoxy resin and polished with oil suspension. The mineral has been studied and analysed by both energy- and wavelength-dispersive spectrometry (EDS and WDS respectively).

Preliminary EDS analyses were obtained using a Hitachi S-3400N scanning electron microscope equipped with an Oxford Instruments X-Max 20 Energy Dispersive Spectrometer (installed in St. Petersburg State University). The electron beam accelerating voltage was 20 kV and the current 2.0 nA; both focused and defocused beam (1 to 3 μm spot size) were used and the X-ray

Table 5. Bond-valence sums (BVS), coordinates and isotropic and anisotropic displacement parameters (Å²) of atoms in dokuchaevite.

Atom	B.V.S.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
Cu1	1.99	0.0840(3)	0.5751(2)	0.66630(14)	0.0132(6)	0.0153(12)	0.0146(11)	0.0085(13)	−0.0027(9)	−0.0030(9)	0.0002(9)
Cu2	2.12	0.2457(4)	0.2504(3)	0.04469(15)	0.0206(6)	0.0266(13)	0.0218(12)	0.0136(14)	0.0027(10)	0.0020(11)	0.0052(10)
Cu3	2.07	−0.0513(3)	0.8275(2)	0.80017(14)	0.0125(6)	0.0125(11)	0.0150(11)	0.0101(13)	0.0007(9)	0.0012(9)	0.0042(9)
Cu4	2.06	−0.5452(3)	0.8029(2)	0.79464(14)	0.0124(6)	0.0106(11)	0.0161(11)	0.0096(13)	0.0025(9)	−0.0014(9)	−0.0009(9)
Cu5	2.14	0.1613(3)	0.9378(3)	0.65237(15)	0.0159(6)	0.0140(12)	0.0213(12)	0.0116(14)	0.0038(10)	−0.0021(10)	−0.0013(9)
Cu6	1.91	0.5594(3)	0.4215(3)	0.83355(15)	0.0196(6)	0.0249(13)	0.0185(12)	0.0145(14)	−0.0040(10)	−0.0015(11)	0.0072(10)
Cu7	1.93	0.2936(3)	0.8954(2)	0.08698(14)	0.0157(6)	0.0216(13)	0.0143(11)	0.0108(14)	−0.0023(10)	0.0001(10)	0.0030(9)
Cu8	2.17	−0.3485(3)	0.4078(2)	0.55875(14)	0.0138(6)	0.0097(11)	0.0163(12)	0.0144(14)	0.0039(10)	−0.0021(9)	0.0007(9)
T1*	5.19	−0.3331(4)	0.1032(3)	0.70749(17)	0.0117(12)	0.0110(16)	0.0142(16)	0.0098(19)	0.0001(11)	0.0009(11)	0.0001(10)
T2**	5.01	0.1153(4)	0.2878(3)	0.52405(17)	0.0095(12)	0.0097(17)	0.0159(17)	0.0022(19)	−0.0011(11)	−0.0021(11)	0.0008(11)
T3***	5.26	0.2426(3)	0.5926(3)	0.94484(16)	0.0125(10)	0.0137(15)	0.0162(15)	0.0074(17)	−0.0012(10)	0.0007(10)	0.0036(10)
O1	2.05	0.1752(16)	0.7619(12)	0.7383(8)	0.011(3)	0.007(5)	0.009(5)	0.018(6)	0.003(5)	0.000(5)	−0.005(4)
O2	2.01	−0.0303(17)	0.2539(13)	0.4246(8)	0.016(3)	0.017(7)	0.014(6)	0.016(8)	−0.002(6)	−0.002(6)	−0.011(5)
O3	2.10	−0.1036(17)	−0.0048(13)	0.7133(7)	0.013(3)	0.016(6)	0.018(6)	0.005(7)	0.001(5)	0.003(5)	0.002(5)
O4	2.16	0.0177(18)	0.6810(15)	0.8983(8)	0.021(3)	0.021(7)	0.035(8)	0.009(8)	0.009(6)	0.006(6)	0.012(6)
O5	2.08	0.3491(17)	0.4012(13)	0.5124(8)	0.014(3)	0.010(5)	0.021(5)	0.011(6)	−0.002(5)	−0.005(5)	−0.007(4)
O6	2.12	−0.0413(17)	0.4105(13)	0.5820(8)	0.017(3)	0.014(6)	0.023(7)	0.016(8)	0.002(6)	0.008(6)	0.005(5)
O7	2.05	0.1571(18)	0.1101(13)	0.5708(8)	0.021(3)	0.027(7)	0.017(7)	0.017(8)	0.004(6)	−0.009(6)	−0.004(6)
O8	2.23	0.2055(18)	0.3981(14)	0.9536(8)	0.018(3)	0.015(6)	0.031(7)	0.010(7)	0.007(6)	0.004(5)	0.004(5)
O9	2.09	0.4621(17)	0.6257(13)	0.8857(8)	0.015(3)	0.010(6)	0.014(6)	0.020(8)	0.001(6)	−0.001(5)	0.001(5)
O10	2.18	−0.5435(17)	−0.0329(15)	0.7051(8)	0.023(3)	0.007(6)	0.035(7)	0.024(8)	0.014(6)	−0.010(6)	−0.001(5)
O11	2.15	−0.3653(17)	0.2131(13)	0.6199(8)	0.018(3)	0.006(6)	0.020(7)	0.028(8)	0.010(6)	−0.004(6)	−0.006(5)
O12	2.16	−0.3263(19)	0.2180(13)	0.8037(8)	0.020(3)	0.034(8)	0.017(6)	0.011(8)	0.006(6)	0.005(6)	0.016(6)
O13	2.07	0.3173(18)	0.6753(13)	0.0464(8)	0.018(3)	0.025(6)	0.016(5)	0.012(6)	−0.009(5)	−0.002(5)	0.000(5)
O14	2.09	0.2904(15)	0.1076(11)	0.1372(7)	0.007(3)	0.006(6)	0.002(5)	0.012(7)	0.001(5)	0.002(5)	0.000(4)
Cl1	0.79	0.6806(7)	0.5864(5)	0.7168(3)	0.0179(11)	0.018(2)	0.021(2)	0.014(3)	−0.005(2)	0.004(2)	0.0006(18)
Cl2	0.81	0.2152(7)	0.3695(5)	0.7537(3)	0.0208(11)	0.024(2)	0.021(2)	0.014(3)	0.000(2)	−0.011(2)	0.0000(19)
Cl3	0.71	0.2441(8)	0.0187(5)	0.9493(3)	0.0247(12)	0.039(3)	0.019(2)	0.015(3)	−0.003(2)	0.000(2)	0.001(2)

*V_{0.75(2)}As_{0.25(2)}; **V_{0.84(2)}As_{0.16(2)}; ***V_{0.59(2)}As_{0.41(2)}. Bond-valence sums for mixed *T* sites were calculated using parameters for V⁵⁺–O bonds.

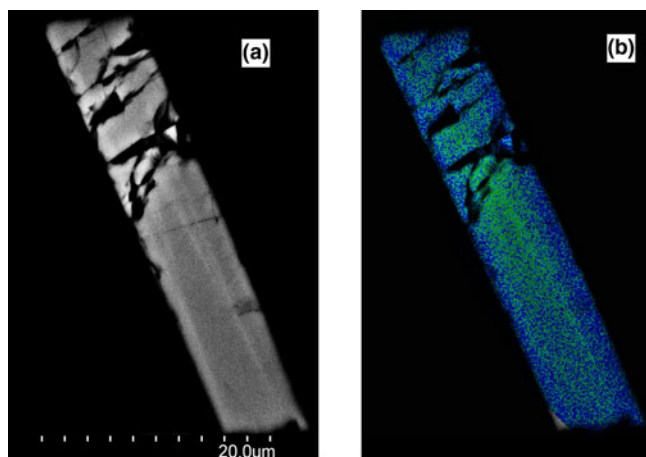


Fig. 2. Back-scatter electron image of (a) the zoned dokuchaevite crystal and (b) false colour X-ray element distribution map (V = blue and As = green).

acquisition time was 30 s. The following standards were used: Cu (Cu), Zn (Zn), FeS₂ (Fe), V (V), InAs (As), CaSO₄ (S), Mo (Mo), SiO₂ (Si), InP (P) and NaCl (Cl). However, there is a strong overlap for Mo ($L\alpha$ 2.293) and S ($K\alpha$ 2.307) lines in the ED spectrum.

The WDS analyses were obtained using a JEOL 8900 Superprobe (Universität Tübingen) and Cameca SX 100 (Natural History Museum, London), the accelerating voltage was 20 kV, beam current 15 nA and probe diameter 1 μ m. The ZAF method was used for data raw correction. Standard and analytical data are given in Table 2. Note, that Cl was analysed using two different standards – turgupite and NaCl.

The empirical formula calculated on the basis of 17 anions per formula unit is (Cu_{7.72}Zn_{0.06}Fe_{0.05})_{Σ7.83}(V_{2.20}As_{0.61}Mo_{0.10}S_{0.06}P_{0.03}Si_{0.03})_{Σ3.03}O_{13.96}Cl_{3.04}. The simplified formula is Cu₈O₂(VO₄)₃Cl₃. Ideally dokuchaevite contains CuO = 64.18 wt.%, V₂O₅ = 27.52 wt.%, Cl = 10.73 wt.%, -O = Cl₂ = 2.42 wt.%, total = 100.00 wt.%.

X-ray crystallography

Experiment

Powder X-ray diffraction data were collected using a Rigaku R-Axis Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye-Scherrer geometry (CoK α radiation, $d = 127.4$ mm). Data (in \AA) are given in Table 3. Unit-cell parameters refined from the powder data processed using *osc2xrd* software (Britvin et al. 2017) are as follows: triclinic, space group $P\bar{1}$, $a = 6.3335(4)$ \AA , $b = 8.2088(5)$ \AA , $c = 15.556(1)$ \AA , $\alpha = 90.509(6)^\circ$, $\beta = 97.239(7)^\circ$, $\gamma = 90.911(6)^\circ$, $V = 802.20(7)$ \AA^3 and $Z = 2$.

A dark red transparent crystal fragment of dokuchaevite was mounted on a thin glass fibre for X-ray diffraction analysis using a Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with MoK α radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multi-scan type model implemented in the Bruker programs APEX and SADABS (Bruker-AXS, 2014). More than a hemisphere of X-ray diffraction data was collected. The refinement in the $P\bar{1}$ space group converged to $R_1 = 0.057$ (Table 4). The final model included anisotropic displacement parameters for all atoms. The final atomic coordinates,

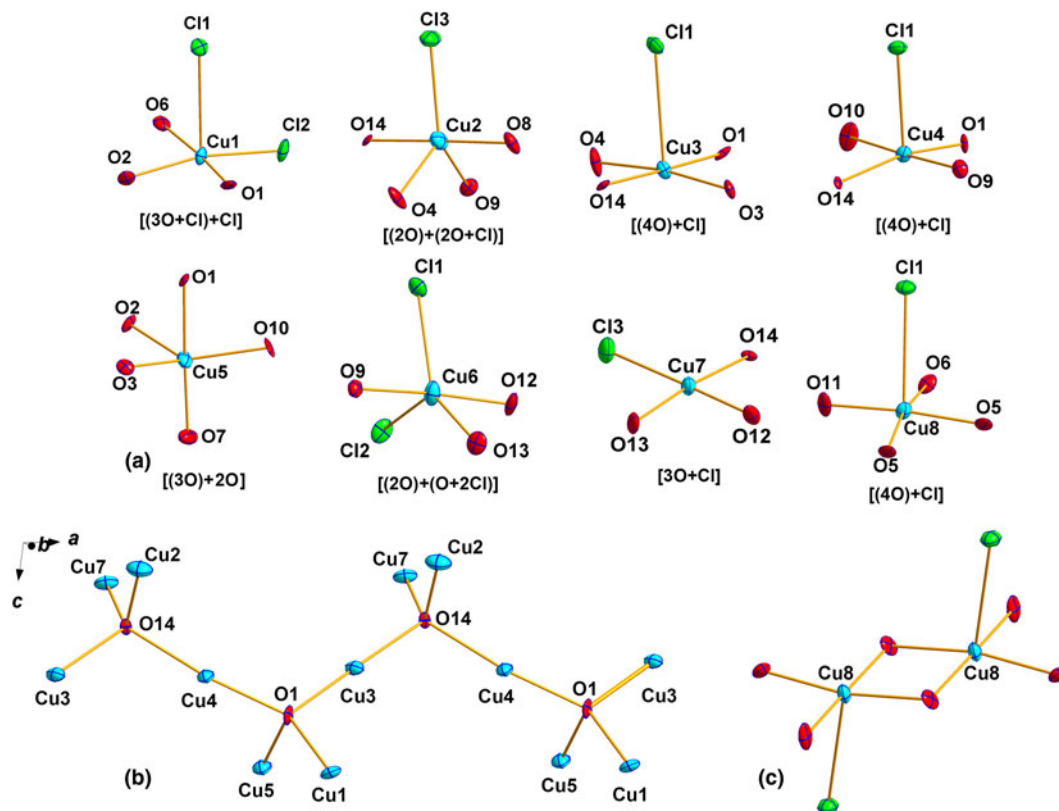


Fig. 3. (a) Cu²⁺ cation coordination environments; (b) general projection of [O₂Cu₆]⁸⁺ chains in dokuchaevite; and (c) Cu₈-centred dimeric units.

Table 6. Selected interatomic distances (Å) in dokuchaevite.

Cu1–O1	1.928(11)	Cu2–O14	1.862(11)	Cu3–O1	1.906(10)	Cu4–O1	1.899(11)	Cu5–O7	1.906(12)	Cu6–O12	1.907(10)	Cu7–O14	1.904(10)
Cu1–O6	1.963(12)	Cu2–O8	1.868(12)	Cu3–O3	1.940(11)	Cu4–O14	1.946(11)	Cu5–O10	1.956(12)	Cu6–O9	1.994(11)	Cu7–O13	1.922(11)
Cu1–O2	2.003(11)	Cu2–O4	2.068(11)	Cu3–O4	1.962(11)	Cu4–O10	1.947(12)	Cu5–O1	1.972(11)	Cu6–O13	2.101(12)	Cu7–O12	1.937(12)
Cu1–Cl2	2.278(5)	Cu2–O9	2.247(12)	Cu3–O14	1.977(10)	Cu4–O9	2.036(11)	Cu5–O2	2.067(12)	Cu6–Cl2	2.399(5)	Cu7–Cl3	2.364(5)
Cu1–Cl1	2.767(5)	Cu2–Cl3	2.401(5)	Cu3–Cl1	2.789(4)	Cu4–Cl1	2.672(4)	Cu5–O3	2.085(10)	Cu6–Cl1	2.466(5)		
Cu8–O11	1.875(11)	T1–O11	1.635(12)	T2–O7	1.646(11)	T3–O8	1.619(12)	O1–Cu4	1.898(10)	O14–Cu2	1.861(10)		
Cu8–O5	1.926(11)	T1–O3	1.707(10)	T2–O2	1.719(12)	T3–O4	1.692(11)	O1–Cu3	1.906(12)	O14–Cu7	1.903(10)		
Cu8–O6	1.934(11)	T1–O10	1.721(12)	T2–O6	1.745(10)	T3–O13	1.722(12)	O1–Cu1	1.929(11)	O14–Cu4	1.947(9)		
Cu8–O5	1.960(11)	T1–O12	1.757(12)	T2–O5	1.765(11)	T3–O9	1.779(11)	O1–Cu5	1.972(11)	O14–Cu3	1.978(11)		
Cu8–Cl1	2.837(4)	<T1–O>	1.705	<T2–O>	1.719	<T3–O>	1.703	<O1–Cu>	1.926	<O2–Cu>	1.922		

anisotropic displacement parameters and bond-valence sums are given in Table 5. All bond-valence parameters were taken from Brese and O’Keeffe (1991). All of the bond-valence sums are in good agreement with the expected oxidation states for all atoms. Lists of observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Cation coordination

The crystal structure of dokuchaevite contains eight symmetrically independent Cu sites (Fig. 3a, Table 6) with different

coordination environments. All of the copper sites, except for Cu5, demonstrate mixed-ligand coordination. All of the Cu–Cl bonds <3.3 Å were taken into consideration. Cu3, Cu4 and Cu8 have similar distorted square pyramidal [(4O)+Cl] mixed-ligand coordination, common for copper oxychloride minerals and synthetic compounds. The Cu2 atom has also five-fold but [(2O)+(2O+Cl)] coordination. CuO₃Cl₂ polyhedra with [(3O+Cl)+Cl] and [(2O)+(O+2Cl)] coordination environments are observed for Cu1 and Cu6 atoms, respectively. The Cu7 atom has exceptionally rare planar square [3O+Cl] mixed-ligand coordination, which has been described previously only in ilinskite NaCu₅O₂(SeO₃)₂Cl₃ (Krivovichev *et al.*, 2013a). Cu5 has a strongly distorted [(3O)+2O] trigonal bipyramid formed exclusively by O atoms. Interestingly, none of the copper sites in dokuchaevite demonstrate Jahn–Teller distorted octahedral coordination environments typical for Cu²⁺ cations.

There are three symmetrically independent tetrahedral *T* sites occupied predominantly by V⁵⁺ in dokuchaevite. In addition, all of the *T* sites contain a considerable amount of As⁵⁺ (Table 5). However, the *T*–O bond lengths and angles fall within the range typically observed in vanadate structures. The refined V/As ratio is in good agreement with the microprobe data, taking into account zonation of the dokuchaevite crystals (Fig. 2) and presence of other cations (Mo, S, Si or P) in the tetrahedral sites.

The oxygen atoms O2–O13 are each bonded strongly in TO₄ tetrahedra. The O1 and O14 sites belong to additional oxygen atoms (Krivovichev *et al.*, 2013b) being coordinated tetrahedrally by four Cu atoms each (Fig. 3b). The O1 atom is coordinated tetrahedrally by Cu1, Cu3, Cu4 and Cu5 atoms thus forming an O1Cu₄ oxocentred tetrahedron. Similarly, the O2 atom is central in the O2Cu₄ tetrahedron with Cu2, Cu3, Cu4 and Cu7 in the vertices. The average <O1–Cu> and <O2–Cu> bond lengths in dokuchaevite are 1.926 and 1.922 Å, respectively. Both values are in good agreement with the typical <O–Cu> bond length in oxocentred OCu₄ tetrahedra (Filatov *et al.* 1992).

Description of the crystal structure

In the structure of dokuchaevite, OCu₄ tetrahedra share common corners thus forming [O₂Cu₆]⁸⁺ single chains shown in Fig. 3b. Each of the OCu₄ tetrahedra is bidentate. The topology of the [O₂Cu₆]⁸⁺ chain in dokuchaevite is very similar to the [Si₂O₆]^{4–} silicate chain in the minerals of the pyroxene group (Liebau, 1985), where each SiO₄ tetrahedron is replaced by an oxocentred OCu₄ tetrahedron. [O₂Cu₆]⁸⁺ chains in dokuchaevite are well-known in Cu²⁺ oxysalts and can be described as fragments of kagome-nets (Kovrugin *et al.*, 2015; Siidra *et al.*, 2018a). Note,

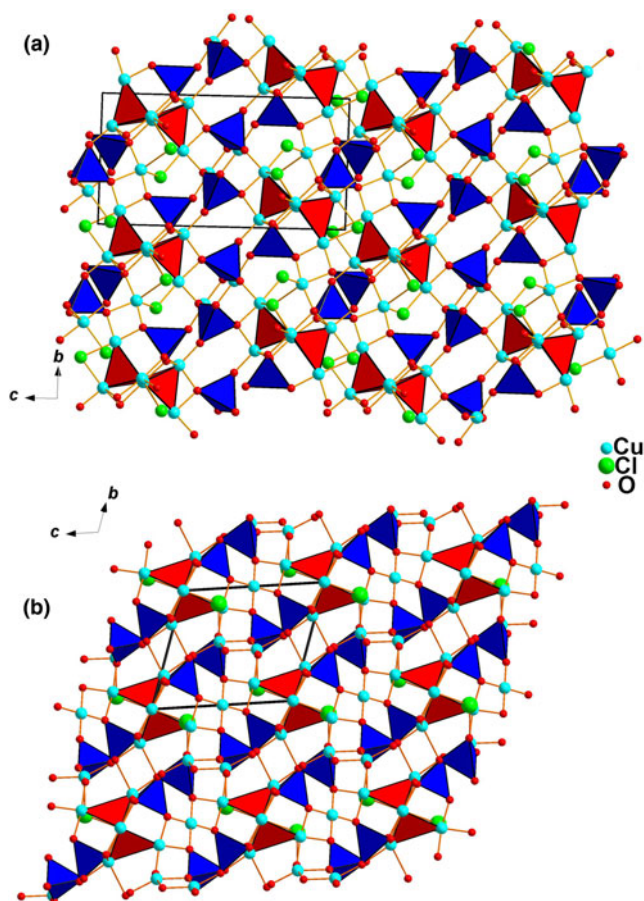


Fig. 4. General projection of the crystal structure of (a) dokuchaevite and (b) yaroshevskite (OCu₄ = red; VO₄ = blue) along the *a* axis.

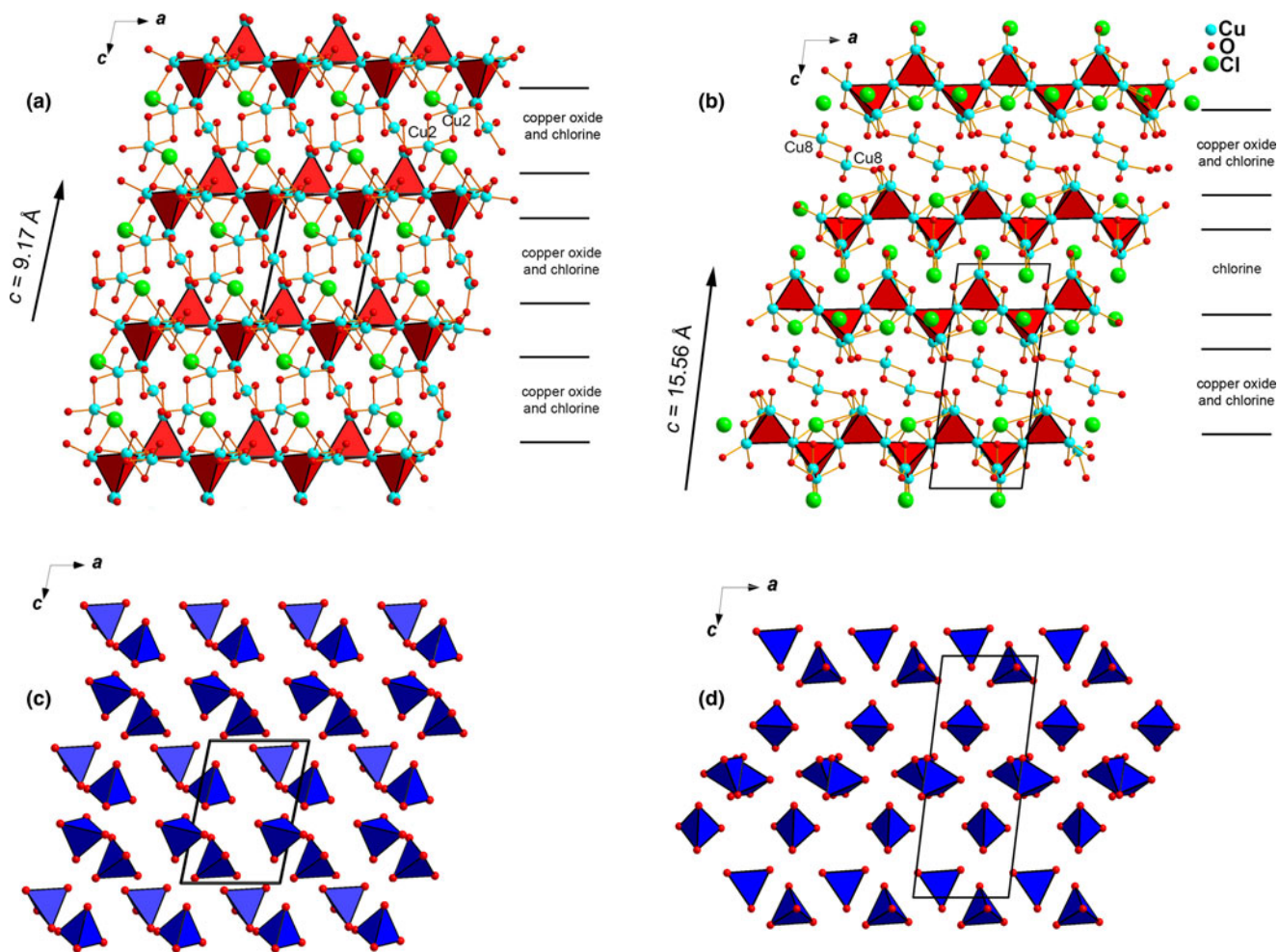


Fig. 5. General projection of the crystal structure of (a) yaroshevskite and (b) dokuchaevite ($\text{OCu}_4 = \text{red}$) along the b axis. VO_4 tetrahedra are omitted for clarity. Cu8-centred dimeric units in dokuchaevite are labelled. Increase of the c parameter value is highlighted. (c, d) The arrangement of VO_4 tetrahedra in the structure of yaroshevskite and dokuchaevite, respectively.

Cu_6 and Cu_8 do not form Cu-O bonds with additional oxygen atoms, and thus are not part of the oxocentred tetrahedra. Cu_6 polyhedra are isolated one from each other, whereas Cu_8 -centred polyhedra form dimers depicted in Fig. 3c. Cu_6 - and Cu_8 -centred polyhedra provide the three-dimensional integrity of the $[\text{O}_2\text{Cu}_6]^{8+}$ chains into the copper-oxide framework. TO_4 mixed tetrahedral groups are located within the cavities of the framework (Fig. 4a). Thus the structural formula of dokuchaevite can be written as $\text{Cu}_2[\text{Cu}_6\text{O}_2](\text{VO}_4)_3\text{Cl}_3$.

Discussion

Dokuchaevite is a new structure type and a new member of the structural family of minerals and synthetic compounds that are based upon $(\text{OCu}_4)^{6+}$ oxocentred tetrahedral groups (Krivovichev *et al.*, 2013). No synthetic copper vanadate-chlorides without additional cations and anions are known to date. Dokuchaevite is structurally and compositionally related to yaroshevskite $\text{Cu}_3[\text{Cu}_6\text{O}_2][\text{VO}_4]_4\text{Cl}_2$ (Pekov *et al.*, 2013) (Table 7) with the crystal structure (Fig. 4b) also based on the similar $[\text{O}_2\text{Cu}_6]^{8+}$ chains. However yaroshevskite is characterised by lower Cl content and higher Cu amount per formula unit. a and b unit-cell parameters are also similar in dokuchaevite and

yaroshevskite (Table 7), whereas the c parameter is enlarged significantly in dokuchaevite. An increase of Cl content in dokuchaevite is responsible for the enlargement of the c parameter from 9.1726(16) Å in yaroshevskite to 15.562(8) Å. Notably Cu^{2+} coordination environments show considerable diversity in dokuchaevite. This is in strong contrast to yaroshevskite, where most of the Cu sites (except for Cu_2) are coordinated exclusively

Table 7. Crystal chemical data for dokuchaevite and yaroshevskite.

Mineral	Dokuchaevite	Yaroshevskite
Formula	$\text{Cu}_6\text{O}_2(\text{VO}_4)_3\text{Cl}_3 = \text{Cu}_2[\text{Cu}_6\text{O}_2](\text{VO}_4)_3\text{Cl}_3$	$\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2 = \text{Cu}_3[\text{Cu}_6\text{O}_2][\text{VO}_4]_4\text{Cl}_2$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.332(3)	6.4344(11)
b (Å)	8.204(4)	8.3232(13)
c (Å)	15.562(8)	9.1726(16)
α (°)	90.498(8)	105.338(14)
β (°)	97.173(7)	96.113(14)
γ (°)	90.896(13)	107.642(15)
V (Å ³)	801.9(7)	442.05(13)
Z	2	1
R_1 (%)	5.7	7.4

by oxygen atoms. The space between the $[\text{O}_2\text{Cu}_6]^{8+}$ chains in yaroshevskite (Fig. 5a) is filled by Cu₂-centred dimeric units similar to those in dokuchaevite (Fig. 3c). In dokuchaevite two possible fillings are possible. One is represented by the Cu-centred polyhedra similar to yaroshevskite, whereas another one contains Cl atoms only (Fig. 5b). The arrangements of the vanadate tetrahedra are very different in both minerals (Fig. 5c,d).

Other copper vanadate–chloride minerals known to date with additional cations include: leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ (Siidra *et al.*, 2007), averievite $\text{Cu}_5\text{O}_2(\text{VO}_4)_n\text{MCl}_x$ ($M = \text{Cu, Cs, Rb}$ or K) (Krivovichev *et al.*, 2015) and aleutite $[\text{Cu}_5\text{O}_2](\text{AsO}_4)(\text{VO}_4)(\text{Cu}_{0.5}\square_{0.5})\text{Cl}$ (Siidra *et al.*, 2019). Coparsite $\text{Cu}_4\text{O}_2((\text{As, V})\text{O}_4)\text{Cl}$ (Starova *et al.*, 1998) contains, similarly to dokuchaevite, mixed tetrahedral sites but with the slight predominance of As^{5+} over V^{5+} . Notably, all of these minerals originate from the fumarolic environments of the Second scoria cone, of the Great Tolbachik Fissure Eruption. Crystal structures of coparsite and averievite are also based on the oxocentred units formed by OCu_4 tetrahedra. Copper oxyvanadates with ‘additional’ O atoms are common, not only in the fumaroles of the Scoria cones of Tolbachik volcano, but are also characteristic for the fumaroles of the Izalco volcano, El Salvador (e.g. stoiberite, $\text{Cu}_5\text{O}_2(\text{VO}_4)_2$ (Birnie and Hughes, 1979) and fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ (Finger, 1985).

The crystal structure of dokuchaevite demonstrates the remarkable diversity of Cu^{2+} mixed-ligand coordination environments. The very complex copper-oxide substructure in dokuchaevite suggests interesting magnetic properties worthy of study for its synthetic analogue.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2019.41>

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