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Dravertite, $CuMg(SO_4)_2$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia

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Abstract: The new mineral dravertite, ideally $CuMg(SO_4)_2$, was found in sublimates of two active fumaroles at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. In the Arsenatnaya fumarole, dravertite (holotype) is closely associated with dolerophanite, euchlorine, tenorite, hematite, langbeinite, steklite, fedotovite, wulffite, anhydrite and anglesite. In the Yadovitaya fumarole, it is associated with euchlorine, chalcocyanite, steklite, alumoklyuchevskite, piypite, parawulffite, cryptochalcite, dolerophanite, hematite, tenorite, vergasovaite, cupromolybdite, yaroshevskite and ziesite. Dravertite occurs as crude equant crystals up to 0.08 mm across forming compact clusters or spherulitic crusts up to $5 \times 5\,cm^2$ in area and up to 1-cm thick on basalt scoria. Dravertite is transparent in small grains and translucent in aggregates, with a vitreous lustre. It is light blue to colourless (Arsenatnaya) or light brown (Yadovitaya). The mineral is brittle, with Mohs' hardness *ca.* 3½. Cleavage is imperfect, the fracture is uneven. $D_{calc} = 3.508\,g\,cm^{-3}$ (based on the empirical formula). Dravertite is optically biaxial (–), $\alpha = 1.624(3)$, $\beta = 1.661(3)$, $\gamma = 1.663(3)$ and $2V_{meas} = 35(10)°$. The infrared spectrum is reported. The chemical composition (holotype, average of 7 analyses) is: MgO 11.00, MnO 0.16, CuO 31.16, ZnO 2.62, SO_3 54.76, total 99.72 wt.%. The empirical formula based on 8 O apfu is: $Mg_{0.79}Mn_{0.01}Cu_{1.14}Zn_{0.09}S_{1.99}O_8$. Dravertite is monoclinic, $P2_1/n$, $a = 4.8141(3)$, $b = 8.4443(5)$, $c = 6.7731(4)$ Å, $\beta = 94.598(5)°$, $V = 274.45(3)$ Å^3 and $Z = 2$. The strongest reflections of the powder X-ray diffraction (XRD) pattern [d, Å(I)($h\,k\,l$)] are: 4.175(68)(1 1 0), 3.666(64)(–1 1 1), 3.579(63)(0 2 1), 3.443(59)(1 1 1), 2.719(41) (–1 1 2), 2.637(100)(0 2 2), 2.430(68)(1 3 0) and 1.791(24)(0 4 2). The crystal structure, solved from single-crystal XRD data ($R = 0.0591$), contains chains of alternating edge-sharing octahedra centred by Cu^{2+} and Mg. The CuO_6 octahedra show significant Jahn–Teller distortion while MgO_6 octahedra are much more regular. The octahedral chains are connected *via* isolated SO_4 tetrahedra to form a pseudo-framework. In terms of structure, dravertite can be considered as a monoclinically distorted, cation-ordered derivative of orthorhombic (*Pnma*) chalcocyanite $CuSO_4$. The mineral is named in honour of the Russian mineralogist and geologist Petr Lyudovikovich Dravert (1879–1945).

Key-words: dravertite; new mineral; copper magnesium sulfate; crystal structure; bivalent cation ordering; chalcocyanite; fumarole; Tolbachik volcano; Kamchatka.

1. Introduction

Synthetic simple anhydrous sulfates of medium-size bivalent cations with the general formula $M^{2+}SO_4$, where M = Mg, Mn, Fe, Co, Ni, Cu, Zn or Cd, are well-known (Rentzeperis & Soldatos, 1958; Coing-Boyat, 1961; Will, 1965; Samaras & Coing-Boyat, 1970; Wildner & Giester, 1988; Wildner, 1990; Burns & Hawthorne, 1993; Weil, 2007a,b). However, from these compounds only, chalcocyanite $CuSO_4$ is found in nature. It was reported from deposits of hot fumaroles containing copper oxysalt mineralization at three active volcanoes: Vesuvius in Campania, Italy (type locality), Tolbachik in Kamchatka, Russia, and Izalco in El Salvador (Palache *et al.*, 1951; Anthony *et al.*, 2003). At the same time, no information on natural or synthetic double anhydrous sulfates containing only the above-listed cations that would be ordered in a crystal structure is found in literature and databases. It came therefore as a surprise to find in fumarolic exhalations of the Tolbachik volcano a cation-ordered sulfate with the idealized formula $CuMg(SO_4)_2$, structurally related to chalcocyanite.

This new mineral is described in the present paper. It was named dravertite (Cyrillic: дравертит) in honour of the Russian mineralogist and geologist Petr

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Lyudovikovich Dravert (1879–1945), who made significant contribution to the mineralogy of Siberia and to studies of Siberian mineral deposits. Both the mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-104). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 95001.

2. Occurrence and general appearance

The new mineral was first detected in the material collected by us in July 2013 as an anhydrous sulfate of copper, magnesium and zinc (Cu > Mg > Zn) which has some relation to chalcocyanite in its powder X-ray diffraction (XRD) pattern and infrared (IR) spectrum (Table 1). In July 2014, we found the sample of the same mineral from which a single crystal suitable for crystal structure analysis was extracted. This specimen became the holotype of dravertite.

The material was collected from the northern part of the Arsenatnaya fumarole located near the summit of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′ N 160°14′ E, 1200 m asl). This scoria cone, a monogenetic volcano about 300-m high and approximately 0.1 km^3 in volume formed in 1975 (Fedotov & Markhinin, 1983), shows strong fumarolic activity to present day.

Arsenatnaya is one of the brightest in the world mineralogical objects of the fumarolic formation. More than one hundred (!) minerals are found there on an area of less than 40 m^2, including more than twenty new species first discovered in this fumarole. The general description of Arsenatnaya is given by Pekov *et al.* (2014). As our observations show, richly mineralized hot chambers belonging to this fumarole form a chain of about 15-m long elongated in meridional direction and located at depths from 0.3 to 4 m below day surface.

Areas strongly enriched in copper sulfates occur at less than 1.5-m depths. In some of them dravertite is a common constituent, an important mineral form of copper. It is closely associated with dolerophanite, euchlorine, tenorite, hematite, langbeinite, steklite, fedotovite, wulffite, anhydrite, anglesite and an incompletely characterized Na–Cu–Mg sulfate. The temperature measured by us using a chromel–alumel thermocouple in these areas (inside cracks and chambers) immediately after their uncovering was 360–370 °C. Only H-free minerals occur in this hot zone. Upwards, near day surface, in the areas with temperatures lower than 100–150 °C, the "dry" sulfate mineralization alters under the influence of atmospheric humidity with formation of the supergene assemblage including hydrous sulfates, typically chalcantite, bonattite, kaliochalcite, epsomite, hexahydrite and gypsum.

In the Arsenatnaya fumarole, dravertite occurs as crusts up to 5 × 5 cm^2 in area and up to 3 mm, rarely up to 1-cm thick, overgrowing basalt scoria altered by fumarolic gas. The outer part of a dravertite crust typically consists of its coarse spherulites (Fig. 1a) with a rough surface formed by crude crystals (Fig. 2a) up to 0.02 mm across. The crusts contain numerous micro-cracks and caverns and sometimes look like dried bread in structure. Dravertite forms intimate intergrowths with dolerophanite and/or euchlorine, and its aggregates are commonly impregnated by micro-inclusions of a Na- and Cu-bearing variety of langbeinite and an incompletely characterized Na–Cu–Mg sulfate. Rarely, dravertite occurs as compact clusters of crude equant crystals (or polyhedral single-crystal grains) up to 0.08 mm in size (Fig. 2b). Polysynthetic twins were observed in some grains under the microscope: very thin twin lamellae form "belts" crossing a grain.

In July 2015, dravertite was also found in the Yadovitaya (Poisonous) fumarole located 15 m west of Arsenatnaya. The temperature measured in the zone where it occurs was 290–300 °C. The new mineral forms here crusts up to 1 × 2 cm^2 in area and up to 1-mm thick which consist of its spherulites up to 1 mm in diameter (Fig. 1b). Associated

Table 1. Comparative data for dravertite and chalcocyanite.

Mineral	Dravertite	Chalcocyanite
Formula	$CuMg(SO_4)_2$	$CuSO_4$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbnm**
Unit cell data		
a, Å	4.814	4.833
b, Å	8.444	8.409
c, Å	6.773	6.709
β, °	94.6	90
V, $Å^3$	274.5	272.7
Z	2	4
Strongest reflections of the X-ray powder pattern: *d*,Å – *I*	4.175–68	4.187–75
	3.666–64	3.549–100
	3.579–63	2.620–95
	3.443–59	2.420–50
	2.719–41	1.775–30
	2.637–100	1.433–20
	2.430–68	1.430–18
Wavenumbers of strong and characteristic absorption bands in the IR spectrum	1165, 1142	1152
	992	964
	703	705
	658	
	607	608, 589
	492	491
	370	
Optical data		
α	1.624	1.724
β	1.661	1.733
γ	1.663	1.739
Optical sign, 2*V*	(–), 35°	(–), large
D_{calc}, g cm^{-3}	3.51	3.89
Sources	This work	Wildner & Giester (1988), Anthony *et al.* (2003), Chukanov (2014)

* For orthorhombic chalcocyanite the setting was changed from the standard space group *Pnma* reported by Wildner & Giester (1988) to *Pbnm* to obtain the same order of the unit-cell parameters as in monoclinic dravertite.

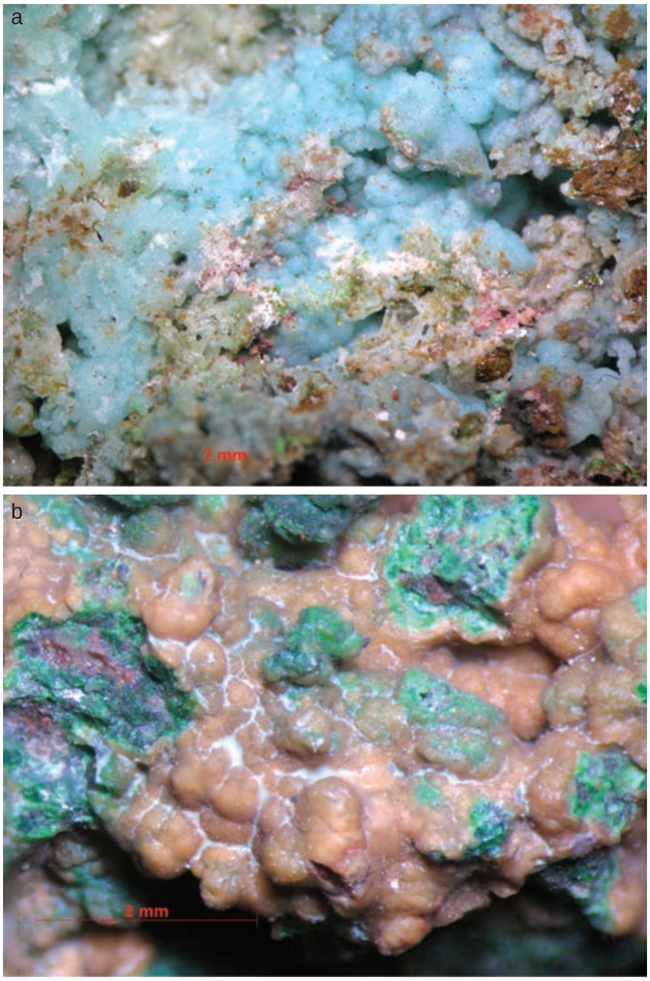

Fig. 1. Spherulitic crusts of dravertite: (a) light-blue crust from the Arsenatnaya fumarole (the holotype); (b) light-brown crust on green euchlorine from the Yadovitaya fumarole. Field of view: (a) 14.6 mm, (b) 2.9 mm. Photo: A.V. Kasatkin & I.V. Pekov.

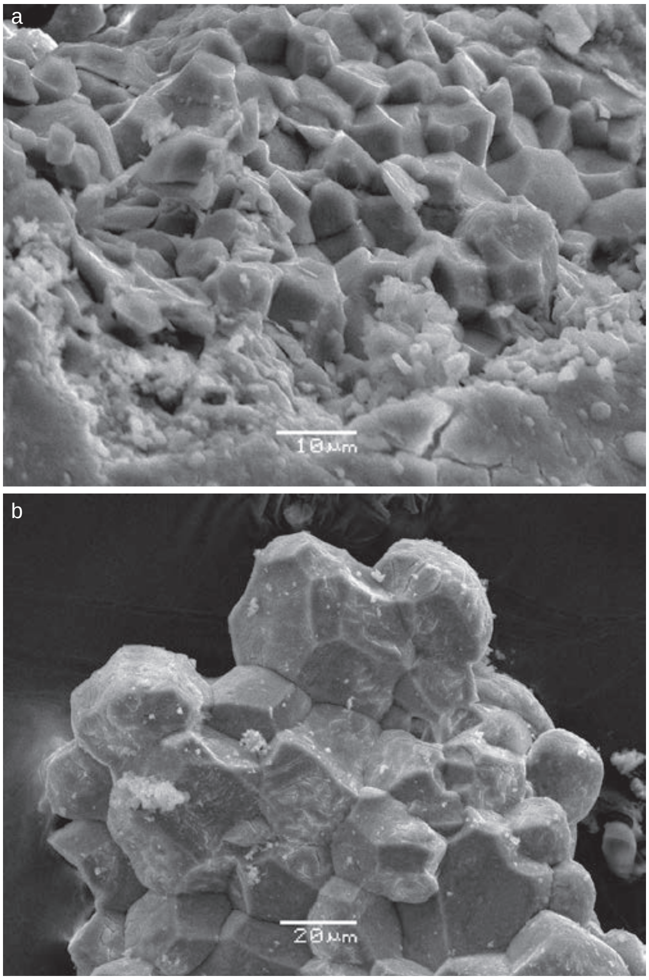

Fig. 2. Crude crystals of dravertite (the holotype) forming (a) the surface of a crust and (b) a compact cluster. Scanning electron microscope (secondary electrons) images.

minerals are euchlorine, chalcocyanite, steklite, alumoklyuchevskite, piypite, parawulffite, cryptochalcite (IMA2014-106), dolerophanite, hematite, tenorite, vergasovaite, cupromolybdite, yaroshevskite and ziesite. Dravertite is one of the latest sublimate sulfates there. Its crusts overgrow encrustations of euchlorine sometimes covering chalcocyanite crystals. Thus, the sequence of deposition of major copper sulfates forming this assemblage is: chalcocyanite $CuSO_4$ → euchlorine $KNaCu_3O(SO_4)_3$ → dravertite $CuMg(SO_4)_2$. It should be noted that, unlike Yadovitaya, dravertite in Arsenatnaya was not observed in close association with chalcocyanite, a typical mineral of similar sulfate associations (with euchlorine, fedotovite, dolerophanite, *etc.*) in other areas of the fumarole.

3. Physical properties and optical data

Dravertite is transparent in small grains and translucent in aggregates. Samples from Arsenatnaya are light blue to colourless, sometimes with a greenish hue, while the mineral from Yadovitaya is light brown. The streak is white. The lustre is vitreous. The mineral is non-fluorescent under ultraviolet rays or an electron beam. Dravertite is brittle. One direction of imperfect cleavage was observed under the microscope, the fracture is uneven. Its Mohs' hardness is *ca.* 3½. Density could not be measured because of the micro-cavernous character of aggregates and the presence of abundant micro-inclusions of other phases. The density calculated from the empirical formula is 3.508 g cm^{-3}.

Dravertite is optically biaxial (–), $\alpha = 1.624(3)$, $\beta = 1.661(3)$, $\gamma = 1.663(3)$ (589 nm). The $2V$ value estimated by the curvature of conoscopic interference figure on the section perpendicular to the optical axis is 35 (10)° and $2V_{calc} = 26°$. Dispersion of optical axes is distinct, $r > v$. In plane-polarized light, the mineral is non-pleochroic, colourless or with a slight bluish hue.

4. Infrared spectroscopy

The IR absorption spectrum of dravertite was obtained for a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm^{-1}. Sampling scan number was 16. The IR spectrum of a pure KBr disc was subtracted from the overall spectrum.

Absorption bands in the IR spectrum of dravertite (Fig. 3) and their assignments are (cm^{-1}, s – strong band, w – weak band, sh – shoulder): 2228w, 1963w (overtones of S–O stretching modes), 1270sh, 1225sh (overtones of O–S–O bending modes), 1165s, 1142s, 1097s [$\nu_3(F_2)$ – asymmetric stretching vibrations of SO_4^{2-} anions], 992s [$\nu_1(A_1)$ – symmetric stretching vibrations of SO_4^{2-} anions), 703, 658, 635w, 607 [$\nu_4(F_2)$ – bending vibrations of SO_4^{2-} anions], 492, 395sh, 370 [lattice modes involving Cu–O and Mg–O stretching vibrations and/or ν_2(E) bending mode of SO_4^{2-} anions]. The weak band at 1025 cm^{-1} may be due to Fermi resonance between an overtone of the 492 cm^{-1} band and symmetric stretching vibrations of SO_4^{2-} anions.

The rather high intensity of the non-degenerate $\nu_1(A_1)$ band at 992 cm^{-1}, as well as the splitting of the band of asymmetric stretching vibrations of SO_4^{2-} anions (the triplet $1097 + 1142 + 1165$ cm^{-1}) reflect a rather strong distortion of SO_4 tetrahedra (see below). The IR spectrum of dravertite is similar to that of chalcocyanite but contains more absorption bands (Table 1) because of cation ordering and lower symmetry of the new mineral.

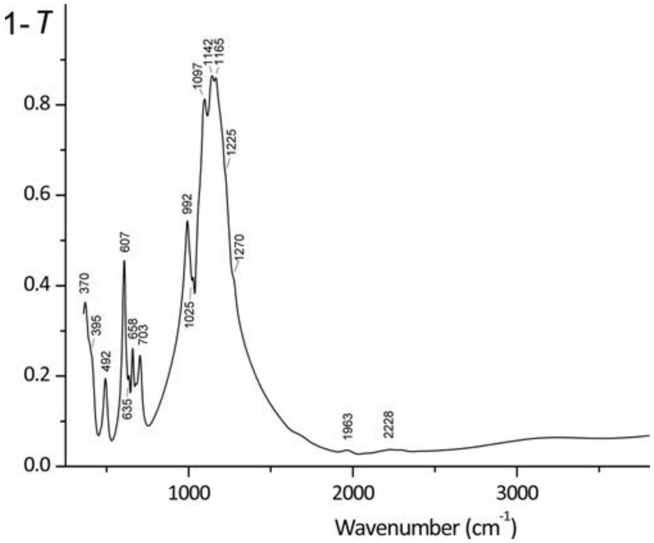

Fig. 3. The powder IR absorption spectrum of dravertite (*T*= transmittance).

Characteristic bands of BO_3^{3-}, CO_3^{2-}, NO_3^{-} and hydrogen-bearing groups are absent in the IR spectrum of dravertite.

5. Chemical data

Chemical data for dravertite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 3-μm beam diameter. The following standards were used: diopside (Mg), $MnTiO_3$ (Mn), $CuFeS_2$ (Cu) and ZnS (Zn and S). Contents of other elements with atomic numbers higher than carbon are below their detection limits.

The chemical composition of dravertite is given in Table 2. The mineral exhibits wide variations in ratios of essential M^{2+} cations, species-defining Cu and Mg and admixed Zn. The empirical formula of the holotype sample calculated for its average composition on the basis of 8 O apfu is $Mg_{0.79}Mn_{0.01}Cu_{1.14}Zn_{0.09}S_{1.99}O_8$. The crystal separated from the holotype and used for the structure study has the average composition $Mg_{0.65}Mn_{0.01}Cu_{1.25}Zn_{0.09}S_{2.00}O_8$. In general, chemical variations determined for the holotype specimen are $Mg_{0.63–0.97}Mn_{0.00–0.01}Cu_{1.01–1.30}Zn_{0.07–0.11}S_{1.98–2.00}O_8$. Involving other studied samples, we found the following compositional range for dravertite: $Mg_{0.57–0.98}Mn_{0.00–0.02}Cu_{0.94–1.30}Zn_{0.07–0.45}S_{1.97–2.02}O_8$, *i.e.* the mineral occupies a composition field from a variety close to the end-member, $[Mg_{1.0}Cu_{0.9}Zn_{0.1}(SO_4)_2]$, to Mg-depleted varieties enriched in Cu, $[Mg_{0.6}Cu_{1.3}Zn_{0.1}(SO_4)_2]$, or in Zn, $[Mg_{0.56}Cu_{0.94}Zn_{0.45}(SO_4)_2]$. In all studied samples, $0.5 < Mg \leq 1.0$ apfu and $0.9 \leq Cu \leq 1.3$ apfu that formally corresponds to the idealized formula $CuMg(SO_4)_2$.

Table 2. Chemical composition of dravertite.

	1	2	3	4	5	6	7	8
wt.%								
MgO	11.00 (8.59–13.71)	13.71	10.28	8.59	8.39	7.69	9.11	14.39
MnO	0.16 (0.13–0.18)	0.13	0.14	0.18	0.46	0.00	0.00	
CuO	31.18 (27.89–34.80)	28.20	32.34	34.80	29.21	25.38	29.85	28.42
ZnO	2.62 (2.12–3.08)	2.32	3.08	2.77	9.42	12.18	5.86	
SO_3	54.76 (53.43–55.90)	55.40	54.70	53.44	52.83	54.36	54.15	57.19
Total	99.72	99.76	100.54	99.78	100.31	99.61	98.97	100.00
Formula calculated on the basis of 8 O atoms								
Mg	0.79	0.97	0.74	0.63	0.62	0.57	0.67	1
Mn	0.01	–	0.01	0.01	0.02	–	–	
Cu	1.14	1.01	1.18	1.30	1.10	0.95	1.11	1
Zn	0.09	0.08	0.11	0.10	0.35	0.44	0.21	
S	1.99	1.98	1.99	1.98	1.97	2.01	2.00	2

1–6 – Arsenatnaya fumarole: 1–4 – the holotype specimen (1 – averaged data for seven spot analyses, ranges are in parentheses), 5 and 6 – two other specimens, both Zn-enriched; 7 – Yadovitaya fumarole; 8 – ideal composition for $CuMg(SO_4)_2$.

Table 3. Powder X-ray diffraction data for dravertite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
5	5.28	7	5.273	0 1 1
15	4.226	14	4.222	0 2 0
68	4.175	82	4.172	1 1 0
14	4.069	23	4.068	−1 0 1
64	3.666	98	3.665	−1 1 1
63	3.579	68	3.580	0 2 1
59	3.443	83	3.443	1 1 1
6	3.171	6	3.170	1 2 0
20	3.131	4	3.134	0 1 2
4	2.812	5	2.815	1 2 1
41	2.719	58	2.719	−1 1 2
100	2.637	100	2.637	0 2 2
10	2.598	8	2.598	0 3 1
22	2.540	27	2.539	1 1 2
68	2.430	89	2.428	1 3 0
17	2.401	22	2.400	2 0 0
10	2.374	10	2.374	−1 2 2
17	2.308	20	2.308	2 1 0
12	2.252	13	2.252	1 2 2
5	2.176	3	2.175	0 1 3
5	2.136	4	2.134	2 1 1
7	2.102	3	2.103	−1 0 3
6	2.089	9	2.086	2 2 0
12	2.041	12	2.041	−1 1 3
10	2.011	11	2.010	−1 3 2
4	1.977	1, 2	1.978, 1.977	−2 1 2, 1 0 3
13	1.935	14	1.934	1 3 2
4	1.884	3	1.883	−1 2 3
15	1.833	27	1.833	−2 2 2
24	1.791	2, 3, 24	1.791, 1.790, 1.790	1 2 3, −2 3 1, 0 4 2
19	1.723	29	1.722	2 2 2
24	1.689	22	1.688	0 0 4
4	1.655	2	1.655	0 1 4
7	1.607	7	1.604	−1 1 4
13	1.586	1, 6, 18	1.586, 1.585, 1.585	−2 2 3, −3 0 1, 2 4 0
8	1.573	15	1.572	3 1 0
5	1.542	4, 2	1.541, 1.540	1 5 1, 0 4 3
10	1.529	2, 11	1.529, 1.528	3 0 1, 1 1 4
7	1.465	12	1.465	−2 4 2
10	1.456	18	1.456	−1 5 2
7	1.435	7	1.436	−2 0 4
13	1.427	26	1.426	1 5 2
9	1.414	2, 14	1.415, 1.413	−2 1 4, −1 3 4
5	1.391	6	1.391	3 3 0

* For the calculated pattern, only reflections with intensities ≥ 1 are given.
** For the unit-cell, parameters calculated from single-crystal data.

The Gladstone–Dale compatibility index $1-(K_p/K_c)$ (Mandarino, 1981) is −0.030, excellent.

Dravertite dissolves in H_2O at room temperature during several minutes. In humid air, the mineral very slowly alters to a friable aggregate of hydrous Cu and Mg sulfates (chalcantite, epsomite *etc.*), being significantly more stable under room conditions in comparison with chalcocyanite.

6. X-ray crystallography

Powder XRD data of dravertite (Table 3) were collected with a DRON-2 diffractometer (Cu$K\alpha$ radiation). The monoclinic unit-cell parameters refined from the powder data are $a = 4.816(2)$, $b = 8.448(3)$, $c = 6.776(2)$ Å, $\beta = 94.56(3)°$ and $V = 274.8(3)$ Å^3. The powder XRD patterns of dravertite and chalcocyanite have some common features but, in general, they are significantly different, including sets of the strongest reflections (Table 1), and these minerals can be clearly distinguished from one another based on the powder XRD data.

Single-crystal XRD studies of dravertite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using CrysAlisPro Version 1.171.35.21 (Agilent Technologies, 2012). The data were corrected for Lorentz and polarization effects. Empirical absorption correction using spherical harmonics, implemented in SCALE3

Table 4. Crystal data, data-collection information and structure refinement details for dravertite.

Formula weight*	292.13
Temperature, K	293(2)
Radiation and wavelength, Å	Mo$K\alpha$; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1/n$; 2
Unit-cell parameters, Å,°	$a = 4.8141(3)$
	$b = 8.4443(5)$ $\beta = 94.598(5)$
	$c = 6.7731(4)$
V, Å^3	274.45(3)
Absorption coefficient μ, mm^{-1}*	4.920
F_{000}*	286
Crystal size, mm	0.03 × 0.07 × 0.08
Diffractometer	Xcalibur S CCD
θ range for data collection, °	3.86–28.25
Index ranges	$-6 \leq h \leq 6$, $-10 \leq k \leq 10$, $-9 \leq l \leq 8$
Reflections collected	3724
Independent reflections	666 ($R_{\mathrm{int}} = 0.0670$)
Independent reflections with $I > 2\sigma(I)$	566
Data reduction	CrysAlisPro, version 1.171.35.21 (Agilent Technologies, 2012)
Absorption correction	Multi-scan
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	60
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0591$, w$R2 = 0.1126$
R indices (all data)	$R1 = 0.0756$, w$R2 = 0.1182$
GoF	1.181
Largest diff. peak and hole, e/Å^3	1.50 and −0.92

* Calculated on the basis of e_{ref} for Mg position (see Table 3).

ABSPACK scaling algorithm, was applied. The crystal structure was solved by direct methods and refined using the SHELX-97 software package (Sheldrick, 2008) to $R = 0.0591$ for 566 unique reflections with $I > 2\sigma(I)$. The site occupancy factor of the Mg site was allowed to vary freely with Mg scattering curve. Crystal data, data-collection information and structure refinement details are presented in Table 4, atom coordinates and displacement parameters in Table 5 and selected interatomic distances in Table 6.

7. Discussion

The crystal structure of dravertite (Figs. 4 and 5a) contains chains of alternating edge-sharing octahedra centred by Cu^{2+} and Mg (the Mg site contains admixed Cu and Zn; Table 5). These chains run along [0 0 1] and are connected by isolated corner-sharing $\mathrm{SO_4}$ tetrahedra to form a pseudo-framework.[1] The $\mathrm{CuO_6}$ octahedra demonstrate significant Jahn–Teller distortion: four short Cu–O bond lengths lie in the range from 1.910 to 2.016 Å and the lengths of two elongated bonds are equal to 2.594 Å. The $\mathrm{MgO_6}$ octahedra are much more regular, with Mg–O distances varying from 1.988 to 2.135 Å (Table 6).

Table 5. Atom fractional coordinates and equivalent displacement parameters (U_{eq}, in Å^2) in dravertite.

Site	x	y	z	U_{eq}
Cu	0	½	0	0.0112(4)
Mg*	0	½	½	0.0073(7)
S	0.0404(3)	0.18234(18)	0.2299(2)	0.0048(4)
O1	0.0515(9)	0.3610(5)	0.2422(6)	0.0081(9)
O2	−0.2497(9)	0.1294(5)	0.2157(7)	0.0098(10)
O3	0.1787(9)	0.1360(5)	0.0566(6)	0.0096(10)
O4	0.3206(9)	0.6234(5)	0.0836(6)	0.0090(10)

* The e_{ref} value for the Mg site is 18.01. This corresponds to $(\mathrm{Mg_{0.65}Cu_{0.25}Zn_{0.09}Mn_{0.01}})$. The ratio between Mg and sum of "heavier" cations, as well as ratios between Cu, Zn and Mn, are calculated taking into account the average electron-microprobe analysis in part of minor constituents Zn and Mn (#1 in Table 2), with the assumption that both are located only at this site.

Table 6. Selected interatomic distances (Å) in the structure of dravertite.

Cu–O(4)	1.910(4) × 2
Cu–O(1)	2.016(4) × 2
Cu–O(2)	2.594(4) × 2
Mg–O(3)	1.988(4) × 2
Mg–O(2)	2.121(4) × 2
Mg–O(1)	2.135(4) × 2
S–O(3)	1.449(4)
S–O(2)	1.462(5)
S–O(4)	1.468(4)
S–O(1)	1.511(5)

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[1] We use the term pseudo-framework because of the presence of not only corner-sharing connections of oxygen polyhedra that is typical for "true" frameworks but also edge-sharing connections between metal-centred octahedra in the structure of dravertite.

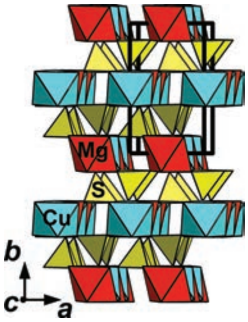

Fig. 4. The crystal structure of dravertite. The unit cell is outlined.

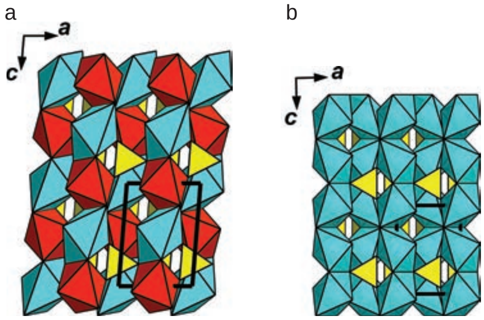

Fig. 5. The crystal structures of dravertite (a) and chalcocyanite (b). The latter is drawn after Wildner & Giester (1988), with the setting changed according to Table 1, projected along the *b* axis. The unit cells are outlined. For legend see Fig. 4.

The structure of dravertite is topologically close to those of chalcocyanite $CuSO_4$ and isostructural orthorhombic (space group *Pnma*) synthetic $M^{2+}SO_4$ compounds with M^{2+} = Mg, Fe, Co, Cu or Zn (Wildner & Giester, 1988, and references therein; Burns & Hawthorne, 1993; Weil, 2007a,b). Note that, $MgSO_4$, $FeSO_4$ and $CoSO_4$ can crystallize, besides the chalcocyanite structure type, in space group *Cmcm* showing a different structure (Rentzeperis & Soldatos, 1958; Samaras & Coing-Boyat, 1970; Wildner, 1990), the same as that known for $MnSO_4$, $NiSO_4$ and $CdSO_4$ (Coing-Boyat, 1961; Will, 1965; Wildner, 1990) for which chalcocyanite-type modifications were not reported.

In terms of structure, dravertite can be considered as a cation-ordered derivative of chalcocyanite, with alternating Cu- and Mg-centred octahedra in cationic chains (Fig. 5). We believe that such cation ordering, leading to significant monoclinic distortion ($\beta \approx 94.6°$ for dravertite), is mainly caused by the strong tendency of Cu^{2+} to form distorted polyhedra, with two relatively elongated bonds, due to the Jahn–Teller effect. This is also a reason to assume that admixed Zn in dravertite is mainly concentrated in the Mg-dominant site but not in the Cu site. This assumption is in agreement with the negative correlation between Mg and Zn in Mg-depleted samples.

Significant ordering of Cu^{2+} and Mg between octahedra with different degree of distortion is typical for many oxysalts, including minerals. Among natural (Cu,Mg)-sulfates, there are three H_2O-bearing species: (1) alpersite with the octahedra (data for two samples, *M*–O in Å are in square brackets) $\{(Cu_{0.60}Mg_{0.40})O_6$ [2.01−2.03 × 4; 2.30 × 2] and $(Mg_{0.96}Cu_{0.04})O_6$ [2.05−2.12 × 6]} and $\{(Cu_{0.74}Mg_{0.26})O_6$ [1.99−2.02 × 4; 2.33 × 2] and $(Mg_{0.85}Cu_{0.15})O_6$ [2.05−2.13 × 6]}; (2) "cuprian pentahydrite" with the octahedra (data for two samples) $\{(Cu_{0.8}Mg_{0.2})O_6$ [2.05−2.07 × 4; 2.46 × 2] and $(Mg_{0.7}Cu_{0.3})O_6$ [2.10−2.18 × 6]} and $\{(Cu_{0.9}Mg_{0.1})O_6$ [2.04−2.09 × 4; 2.51 × 2] and $(Mg_{0.7}Cu_{0.3})O_6$ [2.13−2.17 × 6]} (Peterson *et al.*, 2006) and (3) "Cu-kieserite" with the octahedra $(Cu_{0.88}Mg_{0.12})O_6$ [1.96−1.98 × 4; 2.48 × 2] and $(Mg_{0.86}Cu_{0.14})O_6$ [2.00−2.08 × 6] (Lengauer & Giester, 1995). All these sulfates are Cu–Mg-ordered and the Mg-dominant octahedra are much more regular in comparison to Cu^{2+}-dominant octahedra which demonstrate a significant Jahn–Teller distortion. A similar situation is typical for natural Cu–Mg oxysalts belonging to other chemical classes, namely callaghanite $Cu_2Mg_2(CO_3)(OH)_6{\cdot}2H_2O$, nissonite $Cu_2Mg_2(PO_4)_2(OH)_2{\cdot}5H_2O$, johillerite $NaCuMg_3(AsO_4)_3$, nickenichite $Na(\square,Ca)(\square,Cu)(Mg,Fe^{3+})_3(AsO_4)_3$, guanacoite $Cu_2(Mg,Cu)Mg_2(AsO_4)_2(OH)_4$, raisaite $CuMg[Te^{6+}O_4(OH)_2]{\cdot}6H_2O$, feodosiyite (IMA2015-063) $Cu_{11}Mg_2Cl_{18}(OH)_8{\cdot}16H_2O$ and three modifications of $Cu_3Mg(OH)_6Cl_2$: tondiite, paratacamite-(Mg) and haydeeite (*e.g.* Turchkova *et al.*, 2015, and references therein).

No structural analogue of dravertite among natural or synthetic compounds is known. This seems amazing taking into account that dravertite is chemically simple and contains only constituents very common for minerals. Maybe, this is caused by specific conditions of its formation. Dravertite could be deposited directly from the gas phase as a volcanic sublimate or, more probably, was formed as a result of the interaction between fumarolic gas and basalt scoria at temperatures not lower than 290–300 °C. The basalt scoria seems the most probable source of Mg which has low volatility at temperatures lower than 500 °C (Symonds & Reed, 1993). Chalcocyanite, the sole another anhydrous sulfate with only medium-size bivalent cations known in nature [the natural origin of "zinkosite" $ZnSO_4$ is questionable (Palache *et al.*, 1951)], is also a mineral of fumarole deposits and was not reliably reported from other geological settings.

Polysynthetic twins observed in some grains of dravertite are akin to the deformation twins. This indicates that the mineral could be formed as a result of a phase transition from a hypothetical high-temperature, cation-disordered sulfate (Cu,Mg,Zn)SO_4 during cooling. However, we have no direct evidence concerning this assumption.

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