Cupromolybdite, $Cu_3O(MoO_4)_2$, a new fumarolic mineral from the Tolbachik volcano, Kamchatka Peninsula, Russia

Michael E. Zelenski[1,*], Natalia V. Zubkova[2], Igor V. Pekov[2], Yuri S. Polekhovsky[3]
and Dmitry Yu. Pushcharovsky[2]

[1] Institute of Experimental Mineralogy RAS, Osipyan St. 4, 142432 Chernogolovka, Moscow Oblast, Russia
*Corresponding author, e-mail: ppm61@mail.ru
[2] Faculty of Geology, Moscow State University, Vorobyovy Gory, 119991 Moscow, Russia
[3] Faculty of Geology, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia

Abstract: Cupromolybdite is a new fumarolic mineral from the New Tolbachik scoria cones of Tolbachik volcano, Kamchatka Peninsula, Russia. Cupromolybdite forms prismatic crystals up to 150 μm in length or acicular crystals with a thickness and length of 1–5 μm and 100 μm, respectively. The acicular crystals of cupromolybdite are typically combined in radiating aggregates. The mineral is associated with piypite, fedotovite, vergasovaite, hematite, magnetite, aphthitalite, langbeinite, palmierite, As-bearing orthoclase, lammerite, klyuchevskite, alumoklyuchevskite, euchlorine, lyonsite, pseudolyonsite, averievite, rutile and native gold. Cupromolybdite is honey-yellow or brown, and its acicular crystals are bright yellow. The mineral has yellow or light brown streak and an adamantine lustre. Cupromolybdite is brittle, and its fracture ranges from uneven to splintery. The calculated density is 4.512 g/cm^3. The reflectance values (R_1 and R_2, %) in air for the four COM wavelengths are 14.95, 16.3 (470 nm), 13.4, 14.85 (546 nm), 12.73, 14.16 (589 nm), and 12.15, 13.5 (650 nm). The chemical composition (the mean of 7 electron microprobe analyses) of cupromolybdite is: CuO 43.03, FeO 0.08, ZnO 0.53, MoO_3 54.48, SO_3 0.71, V_2O_5 0.28, SiO_2 0.04, total 99.15 wt%, corresponding, on the basis of 9 O atoms, to $(Cu_{2.83}Zn_{0.03}Fe_{0.01})_{\Sigma2.87}(Mo_{1.98}S_{0.05}V_{0.02})_{\Sigma2.05}O_9$. The simplified formula of cupromolybdite is $Cu_3O(MoO_4)_2 = Cu_3Mo_2O_9$. Cupromolybdite is orthorhombic, space group $Pnma$, $a = 7.6638(1)$, $b = 6.8670(1)$, $c = 14.5554(2)$ Å, $V = 766.01(2)$ Å^3 and $Z = 4$. The strongest powder-diffraction lines [d in Å (I) (hkl)] are: 7.312 (67) (002); 3.518 (55) (113); 3.436 (100) (020); 3.301 (99) (210, 104); 3.065 (79) (121); 2.556 (62) (220); 2.506 (66) (301, 024). The crystal structure was solved from single-crystal data and refined to $R = 0.0314$. Cupromolybdite is a natural analogue of the synthetic compound $Cu_3Mo_2O_9$ and the S-free analogue of vergasovaite, $Cu_3O[(Mo,S)O_4][SO_4]$. The crystal structure of cupromolybdite contains strings of corner-shared Cu(1)O$_6$ octahedra elongated in the [010] direction. In cupromolybdite, the Cu(2)O$_5$ square pyramids and the Cu(3)O$_6$ distorted octahedra are linked to the Cu(1)O$_6$ octahedra of the strings by edges and to the MoO$_4$ and (Mo,S)O$_4$ tetrahedra by vertices. A minor admixture of S is concentrated in one of two independent tetrahedral positions. Cupromolybdite is named for its chemical composition.

Key-words: cupromolybdite, $Cu_3Mo_2O_9$, new mineral, copper molybdate, crystal structure, Tolbachik, volcano, fumarole.

1. Introduction

Although molybdenum-containing minerals have been observed in volcanic environment, they do not occur frequently. Under reducing conditions (which usually correspond to undiluted volcanic gas), molybdenite (MoS$_2$) has been detected within the high-temperature zone ($>500\,°C$) of natural incrustations and in silica-glass tubes in fumaroles at Merapi (Indonesia), Momotombo (Nicaragua) and Mount St. Helens (USA), while limited amounts of Mo-bearing scheelite (Ca(W,Mo)O$_4$) have been observed only in natural incrustations at these volcanoes (Bernard *et al.*, 1990). Ilsemannite (Mo$_3$O$_8$·nH$_2$O) has been identified in oxidising zones around fumaroles at the Valley of 10,000 Smokes, Alaska, on the Santiaguito dome, Guatemala, at Cerro Negro, Nicaragua, and at Mount St. Helens, USA (Bernard *et al.*, 1990 and references therein). Along with powellite (CaMoO$_4$) and Mo-bearing scheelite, different Mo oxides such as molybdite (MoO$_3$), tugarinovite (MoO$_2$) and ilsemannite were observed at Kudryavy Volcano (Iturup, Kurile Islands) in sublimates at temperatures less than 400 °C, which formed a zone with elevated fO_2 levels (Bykova *et al.*, 1995).

Except for powellite, the only known MoO$_4$-containing species in volcanic sublimates is vergasovaite, an oxy-molybdate-sulphate Cu$_3$O[(Mo,S)O$_4$][SO$_4$] observed by Bykova *et al.* (1998) at scoria cones of the Tolbachik volcano, Kamchatka, Russia. The Tolbachik scoria cones are well known among volcanologists due to the spectacular and powerful Great Fissure Tolbachik eruption of 1975–1976.

From a mineralogical perspective, Tolbachik scoria cones are a locality where an incredible diversity of new mineral species formed during post-volcanic degassing (Vergasova & Filatov, 1993; Pekov, 2007). As of 2011, 38 new minerals were discovered at these cones. Most of them (including vergasovaite) were found in a single cavity named the Yadovitaya (poisonous) fumarole. The formation of such prolific fumarolic minerals from highly oxidised volcanic gases was briefly described in a paper on pseudolyonsite, another new mineral from the Tolbachik sublimates (Zelenski *et al.*, 2011). Almost all new Tolbachik fumarolic minerals contain oxyanions, and a majority contain copper as the main cation.

Cupromolybdite, $Cu_3O(MoO_4)_2$, is a new molybdate mineral species from the same location. It is in close stoichiometric and paragenetic relationships with vergasovaite; however, cupromolybdite does not contain species-defining sulphur. Cupromolybdite (Cyrillic: купромолибдит) is named after its chemical composition. The name also reflects the stoichiometric relationship of cupromolybdite with cuprotungstite, $Cu_3(OH)_2(WO_4)_2$ (Walenta, 1979). The new mineral and its name have been approved by the IMA (2011–005). The type specimen of cupromolybdite is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, the registration number is 4072/1.

2. Occurrence, paragenesis and general appearance

Cupromolybdite occurs in the Yadovitaya fumarole, Second scoria cone, New Tolbachik scoria cones, Kamchatka Peninsula, Far East Asia, Russia. The scoria cones (55°41′N, 160°14′E, 1200 m asl) formed during the Tolbachik Fissure eruption in 1975 (Fedotov & Markhinin, 1983). Two of the cones are 300 m high and approximately 0.1 km^3 in volume. The Yadovitaya fumarole is a wide-open cavity with a width and depth of 1.5 and 2 m respectively, and is located near the highest point of the Second scoria cone. Rocks inside the cavity are covered by thick crusts of sublimates, which are partially weathered and leached by meteoric water. The temperature inside the Yadovitaya was 338 °C in 2010. Fumarole gas from Yadovitaya contains >99% air, ~ 1% water vapour and less than 0.1% acid species, including 12 ppmv HF and 7 ppmv HCl (data by M. Zelenski). Based on several years of visual observations, most of the sublimates in the fumarole were deposited at an earlier time, possibly several years or months after the eruption. At the same time, the recent deposition of tiny crystals of sublimate minerals cannot be excluded.

Among the sublimates of the Yadovitaya fumarole, cupromolybdite is a rare mineral. Cupromolybdite appears within 2–5-cm thick sublimate crusts, along with other fumarolic minerals including oxides (hematite, magnetite, rutile, tenorite), oxysalts such as piypite (Vergasova *et al.*, 1984), fedotovite (Vergasova *et al.*, 1988), euchlorine, vergasovaite, aphthitalite, langbeinite, palmierite, lammerite, klyuchevskite

(Vergasova *et al.*, 1989), alumoklyuchevskite (Gorskaya *et al.*, 1995), lyonsite, pseudolyonsite (Zelenski *et al.*, 2011), averievite (Vergasova *et al.*, 1998), silicates such as filatovite (Vergasova *et al.*, 2004) and As-bearing orthoclase, and native gold. In this paragenesis, piypite, $K_2Cu_2O(SO_4)_2$, fedotovite, $K_2Cu_3O(SO_4)_3$, and euchlorine, $KNaCu_3O(SO_4)_3$, are the most abundant copper minerals. The exact temperature of mineral formation remains unclear. At the time of sampling, the temperature of the incrustations was 100–110 °C. Bykova *et al.* (1998) argued that the temperature of the gases in the sulphate zone [during mineral deposition] was 150–170 °C. The deposition sequence observed in the collected specimens showed that cupromolybdite formed in a late stage after vergasovaite. In some cases, cupromolybdite overgrew or replaced vergasovaite.

Cupromolybdite is commonly present as well-shaped prismatic crystals, which are mostly 30–50 µm in length; however, some specimens were up to 150 µm long. These crystals overgrow piypite and fedotovite (Fig. 1a) or form clusters within complex intergrowths of associated minerals
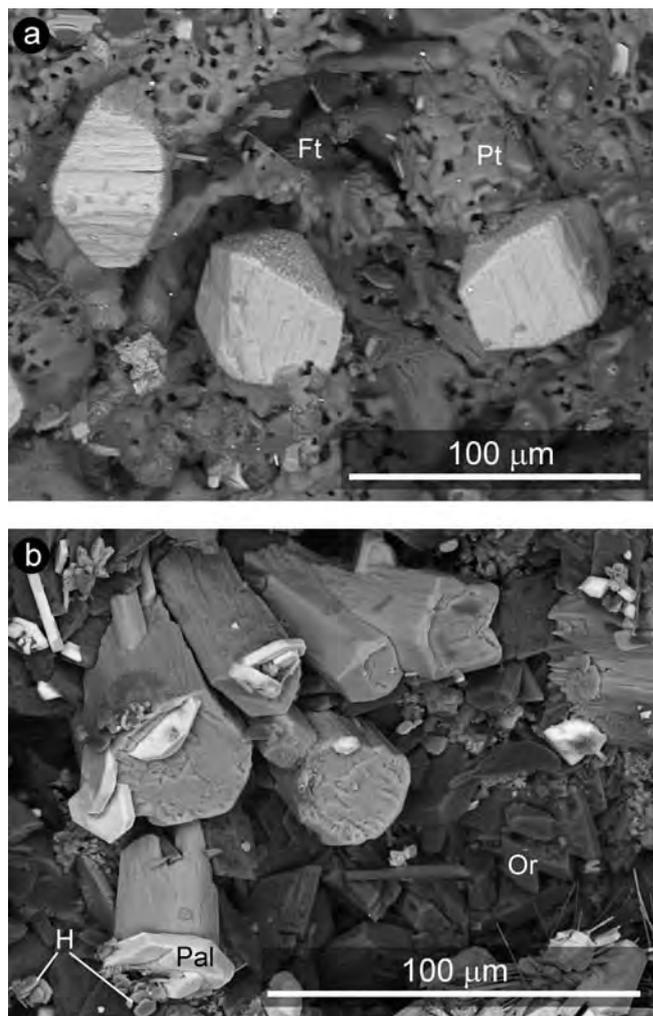
Fig. 1. a, Prismatic crystals of cupromolybdite overgrowing piypite (Pt) and fedotovite (Ft). b, Prismatic crystals of cupromolybdite surrounded by As-bearing orthoclase (Or) and overgrown by palmierite (Pal) and hematite (H). Combined SE + BSE images.
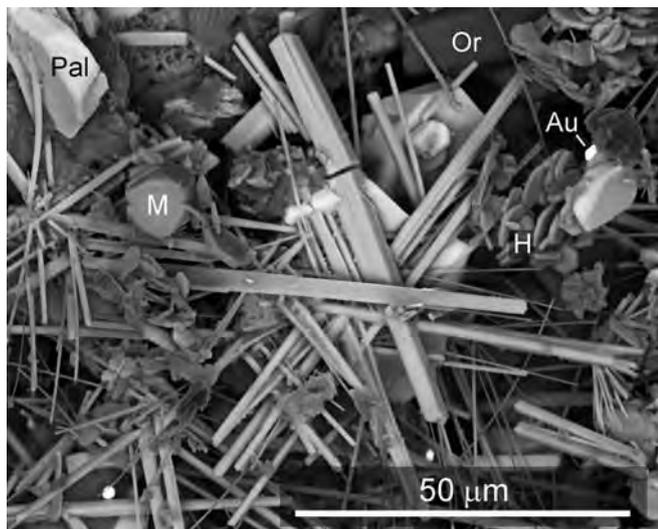
Fig. 2. A cluster of long prismatic to acicular crystals of cupromolybdite. Associated minerals include hematite (H), magnetite (M), palmierite (Pal), As-bearing orthoclase (Or), and native gold. Combined SE + BSE image.

(Fig. 1b). Radiating aggregates of acicular crystals with a thickness and length of 1–5 and 100 μm, respectively, or separate needles are also typical (Fig. 2). Some of the crystals are divergent (Fig. 3a). Moreover, some prismatic crystals of cupromolybdite are overgrown by its acicular variety, which is Zn- and S-enriched (Fig. 3b). Both prismatic and acicular varieties show similar unit-cell dimensions (see below).

The prismatic and acicular crystals of cupromolybdite are well shaped, which suggests that they formed via direct precipitation from the gas phase rather than recrystallisation.

The prismatic variety, which is chemically closer to end-member $Cu_3Mo_2O_9$, is considered to be the holotype material, on which the crystal structure and optical properties were determined.

3. Physical properties and optical data

Prismatic crystals of cupromolybdite have a variety of colours, from honey-yellow to chestnut-brown or dark brown, whereas the acicular variety is bright yellow. The mineral is translucent, has yellow or light brown streak and an adamantine lustre. Cupromolybdite is brittle with distinct cleavage; the fracture is uneven to splintery. The calculated density (from the empirical formula and single-crystal X-ray data) is 4.512 g/cm^3. The micro-indentation hardness was measured with five indentations on two grains, using a load of 50 g. The mean value obtained is 189 kg/mm^2 that corresponds to a Mohs' hardness of *ca.* 3.

Under the microscope in reflected light, cupromolybdite is grey with a weak bluish hue. Pleochroism is not observed, and bireflectance is weak ($\Delta R = 1.4\%$, 589 nm). The mineral has orange-red or orange-brown internal reflections. Anisotropism is distinct. The reflectance was measured with an MSPH-21 microspectrophotometer (LOMO, Russia) equipped with an R928 Hamamatsu
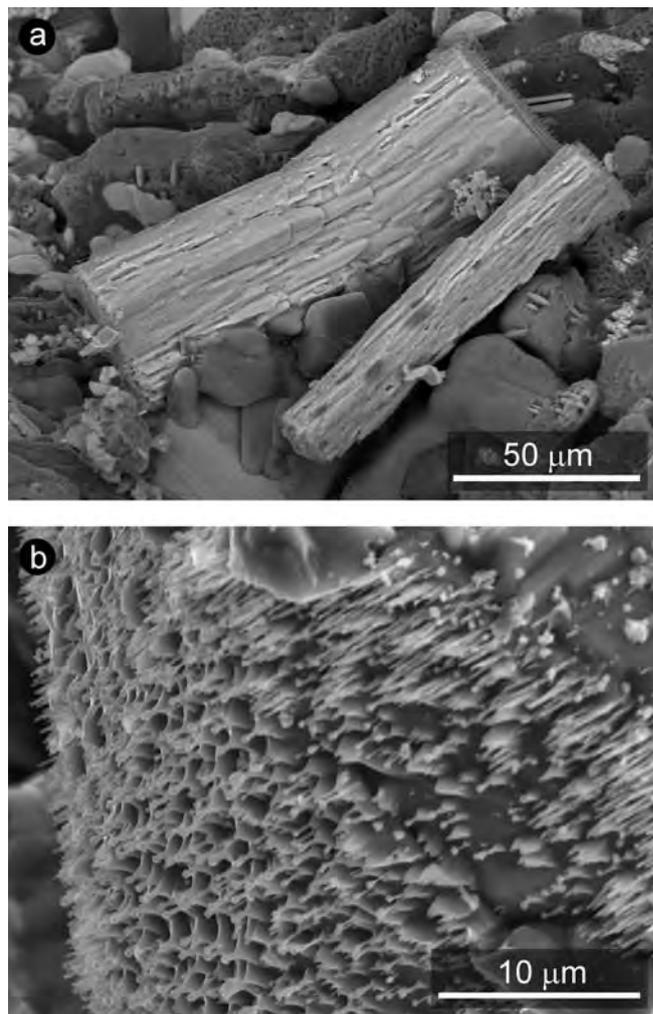
Fig. 3. a, Divergent crystals of cupromolybdite. b, Face of a crystal of cupromolybdite covered by outgrowths with the same composition. Combined SE + BSE images.

photomultiplier tube. Measurements performed on the mineral and the standard (SiC, Zeiss 545) were conducted in air under the same conditions. The diameter of the measured area was equal to 1.5 μm. The bandwidth of the grating monochromator was set to 12 nm, and the intensity data were collected at an interval of 20 nm from 400 to 700 nm. For wavelengths of 470, 546, 589, and 650 nm, reflectance values were calculated by interpolation. The reflectance values (%) for $R1$ and $R2$ are reported in Table 1. For comparison, the reflectance values for vergasovaite, $Cu_3O[(Mo,S)O_4][SO_4]$, are also given. The reflectance and dispersion values of cupromolybdite are different from those of vergasovaite (Fig. 4).

4. Chemical composition

The two varieties of cupromolybdite have different morphologies, colours and chemical compositions. The most prominent distinction is the high content of zinc in acicular crystals that substitutes for copper. The

Table 1. Reflectance values (%) for cupromolybdite and vergasovaite.

λ· nm	Cupromolybdite[a]		Vergasovaite[b]	
	R_1	R_2	R_1	R_2
400	17.0	18.5	10.64	13.03
420	16.3	17.7	10.39	12.62
440	15.7	17.1	10.16	12.17
460	15.2	16.5	9.95	11.86
470 (COM)	(14.95)	(16.3)	9.85	11.69
480	14.7	16.1	9.8	11.61
500	14.3	15.7	9.66	11.4
520	13.9	15.3	9.55	11.22
540	13.5	15.0	9.42	11.06
546 (COM)	(13.4)	(14.85)	9.4	11.01
560	13.1	14.6	9.35	10.93
580	12.9	14.3	9.26	10.78
589 (COM)	(12.73)	(14.16)	9.22	10.76
591	12.6	14.0	9.16	10.68
600	12.4	13.8	9.11	10.63
620	12.2	13.6	9.07	10.52
640	12.15	13.5	9	10.48
644	12.1	13.45	9.03	10.47
650 (COM)	(12.0)	(13.35)	9	10.42
660	11.9	13.2	9.03	10.45
680	17.0	18.5	10.64	13.03
700	16.3	17.7	10.39	12.62

Data in parentheses calculated by interpolation.
[a]This work.
[b]Bykova *et al.* (1998).
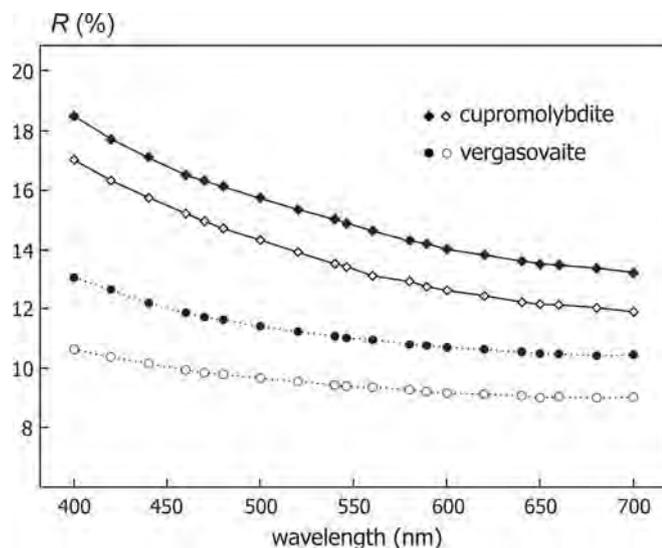
Fig. 4. Air reflectance spectra of cupromolybdite and vergasovaite. Open symbols refer to R_1, and filled symbols refer to R_2.

acicular variety is also slightly enriched in sulphur and vanadium (Tables 2 and 3).

The chemical composition of prismatic cupromolybdite crystals was studied using a Cameca SX-100 microprobe (GEOKHI RAS, Moscow). The following operating conditions were applied: accelerating voltage of 15 kV, beam current of 50 nA, standards (element, counting time for one spot analysis): augite (Fe, 30 s), augite (Si, 30 s), $BaSO_4$ (S, 30 s), $CaMoO_4$ (Mo, 10 s), Cu metal (Cu, 10 s), $Pb_5(VO_4)_3Cl$ (V, 30 s), ZnS (Zn, 30 s), oxygen calculated by stoichiometry. The analytical results in wt% of oxides and average chemical composition are reported in Table 2. The empirical formula of cupromolybdite was calculated on the basis of 9 O *apfu*. The species-defining constituents are (*apfu*) Cu (2.70–2.88) and Mo (1.96–2.04). Cupromolybdite also contains minor amounts of S (0.03–0.08), Zn (0.03–0.04), Fe (up to 0.02), and V (up to 0.02). A minor admixture of silicon was also detected in almost all of the analyses; however, the observed Si content may be due to silica pollution. The content of other elements with atomic numbers greater than that of oxygen was below the detection limits. The absence of Li, Be, B, C and N was confirmed by the structural data. The average empirical formula for cupromolybdite is $(Cu_{2.83}Zn_{0.03}Fe_{0.01})_{\Sigma2.87}(Mo_{1.98}S_{0.05}V_{0.02})_{\Sigma2.05}O_9$. The simplified formula is $Cu_3\,Mo_2O_9$ that can also be expressed as $Cu_3O(MoO_4)_2$, which requires CuO 45.33, MoO_3 54.67, total 100.00 wt%.

The chemical composition of acicular cupromolybdite crystals was studied with a Tescan Vega II XMU scanning electron microscope equipped with Inca Energy and Inca Wave microanalysis systems (IEM RAS, Chernogolovka, Russia). The following operating conditions were used: accelerating voltage of 20 kV, beam current of 0.3 nA, counting time of 100 s, standards: Cu (metal 99.999%), Zn (metal 99.9%), V (metal 99.9%), Mo (metal 99.8%), $BaSO_4$ (S), FeS_2 (Fe), oxygen calculated by stoichiometry. The analytical results for the acicular variety of cupromolybdite are reported in Table 3. X-ray energy dispersive analysis for a substance containing sulphur and molybdenum can be arguable due to partial overlap of the spectral peaks of S ($K\alpha$, 2307 eV) and Mo ($L\beta$, 2456 eV). However, the quality of the analyses listed in Table 3 seems reasonable. The average empirical formula for the acicular variety of cupromolybdite is $(Cu_{2.46}Zn_{0.54}Fe_{0.01})_{\Sigma3.01}(Mo_{1.81}S_{0.14}V_{0.05})_{\Sigma2.00}O_9$, which is close to the stoichiometric formula.

The composition of cupromolybdite and vergasovaite is shown in Fig. 5 and 6. Both minerals demonstrate a good negative correlation between Mo and S and Cu and Zn. On a plot of Mo *vs.* S for cupromolybdite and vergasovaite (Fig. 5), the composition of prismatic crystals of cupromolybdite covers a narrow interval and forms an isolated cluster. Acicular cupromolybdite displays more considerable substitution of Mo^{6+} by S^{6+}. On a plot of Zn *vs.* Cu (Fig. 6), the prismatic crystals of cupromolybdite present a narrow compositional interval with a ZnO content of 0.5 wt%. In contrast, acicular cupromolybdite crystals contain up to 11 wt% ZnO (0.7 *apfu* Zn).

5. X-ray crystallography and crystal structure

X-ray powder-diffraction data for cupromolybdite (Table 4) were obtained with a STOE IPDS II single-crystal diffract-ometer equipped with an image plate detector (Mo$K\alpha$

Table 2. Chemical composition (wt%) of holotype cupromolybdite (prismatic variety).

No.	CuO	FeO	ZnO	MoO$_3$	SO$_3$	V$_2$O$_5$	SiO$_2$	Total
1	43.40	0.04	0.55	54.52	0.58	0.10	0.03	99.22
2	43.74	0.09	0.52	54.36	0.48	0.24	0.06	99.49
3	42.74	0.04	0.44	54.57	0.55	0.29	0.03	98.66
4	42.86	0.01	0.47	54.84	0.65	0.33	0.03	99.19
5	42.55	0.24	0.47	54.02	0.90	0.72	0.07	98.97
6	42.95	0.14	0.64	53.72	1.05	0.17	0.02	98.69
7	42.94	0.03	0.62	55.33	0.78	0.12	0.06	99.88
Average	43.03	0.08	0.53	54.48	0.71	0.28	0.04	99.15
Min	42.55	0.01	0.44	53.72	0.475	0.1	0.02	
Max	43.74	0.24	0.64	55.33	1.05	0.72	0.07	
St. dev.	0.17	0.007	0.006	0.28	0.04	0.04	0.004	

Table 3. Chemical composition (wt%) of the acicular variety of cupromolybdite.

No.	CuO	FeO	ZnO	MoO$_3$	SO$_3$	V$_2$O$_5$	SiO$_2$	Total
1	34.6	0.26	11.4	51.5	2.05	0.82	0	100.63
2	39.2	0.05	8.09	51.7	1.42	1.18	0	101.64
3	38.7	0.0	7.89	49.4	2.82	0.89	0.17	99.87
4	37.1	0.10	8.48	52.4	1.49	0.57	0.19	100.33
5	39.5	0.18	6.76	50.5	1.90	0.73	0	99.57
6	38.3	0.0	7.52	47.6	3.70	1.27	0.086	98.48
7	37.5	0.0	9.20	48.9	1.75	0.93	0.26	98.54
Average	37.8	0.085	8.48	50.3	2.16	0.91	0.10	99.87
Min	34.6	0	6.76	47.6	1.42	0.57	0	
Max	39.5	0.26	11.4	52.4	3.70	1.27	0.26	
St. dev.	2.8	0.01	2.2	3.1	0.67	0.06	0.01	
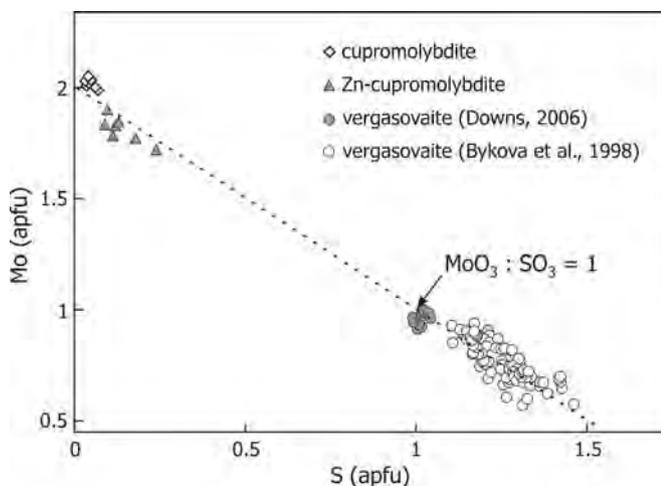
Fig. 5. Plot of Mo *vs*. S for cupromolybdite and vergasovaite. Data for cupromolybdite: present study, vergasovaite – (filled circles) Downs (2006) (RRUFF database), vergasovaite – (open circles) Bykova *et al.* (1998). Dashed lines show the stoichiometric substitution of Mo → S.

Fig. 6. Plot of Zn *vs*. Cu for cupromolybdite and vergasovaite. Data for cupromolybdite: present study, filled circles – Downs (2006) (RRUFF database), open circles – Bykova *et al.* (1998) (only a mean value is available). Dashed lines show the stoichiometric substitution of Cu → Zn.

radiation; the distance between sample and detector was set to 200 mm) using the Gandolfi method. All reflections were well indexed to the orthorhombic unit cell obtained in the single-crystal study (see below). The unit-cell parameters refined from the powder data are: $a = 7.667(7)$, $b = 6.867(6)$, $c = 14.58(1)$ Å and $V = 767(2)$ Å^3.

Single-crystal X-ray studies of both varieties of cupromolybdite were carried out using an Xcalibur S diffractometer equipped with a CCD. The unit-cell dimensions of the holotype, prismatic variety are given in Table 5. The unit-cell dimensions of the acicular variety are:

Table 4. X-ray powder diffraction data for cupromolybdite.

I_{obs}	d_{obs}, Å	I_{calc}	d_{calc}, Å	$h\,k\,l$
67	7.312	52	7.277	002
24	6.855	18	6.781	101
4	5.217	5	5.277	102
20	4.115	21	4.099	103
37	3.842	54	3.832	200
38	3.701	49	3.706	201
30	3.664	33	3.639	004
55	3.518	69	3.520	113
100	3.436	100	3.434	020
99	3.301	50, 100	3.346, 3.286	210, 104
79	3.065	65	3.063	121
27	2.725	30	2.721	105
27	2.644	28	2.639	204
62	2.556	70	2.557	220
66	2.506	15, 56	2.516, 2.497	301, 024
25	2.376	33	2.374	124
10	2.317	4, 9	2.318, 2.312	205, 106
22	2.263	17, 12	2.262, 2.260	223, 303
9	2.150	3	2.169	131
13	2.139	8	2.147	313
14	2.090	15	2.091	304
29	1.995	12, 19	1.998, 1.990	133, 017
7	1.939	4, 5	1.947, 1.926	231, 117
5	1.909	2, 5	1.916, 1.900	400, 401
6	1.888	4	1.888	323
9	1.847	7, 3	1.849, 1.846	315, 410
18	1.833	24	1.831	411
20	1.783	8, 10	1.786, 1.782	324, 403
25	1.771	15, 15	1.770, 1.766	108, 217
5	1.674	12	1.676	325
5	1.638	8	1.644	208
5	1.602	13	1.598	218
16	1.576	4, 15	1.574, 1.573	019, 128
15	1.567	4, 6	1.570, 1.567	317, 240
4	1.541	9	1.539	037
9	1.525	2, 16	1.527, 1.522	236, 144
3	1.494	7, 2	1.491, 1.490	243, 209
2	1.486	1	1.482	308
15	1.460	14, 7	1.462, 1.460	431, 327
10	1.442	3, 8	1.440, 1.439	432, 244
8	1.432	4, 8	1.430, 1.428	513, 237
6	1.366	3, 1, 1, 4	1.367, 1.367, 1.366, 1.362	343, 229, 309, 434
5	1.333	8, 3	1.335, 1.331	238, 515
6	1.325	4, 3	1.327, 1.321	344, 039
2	1.275	1, 2	1.277, 1.274	600, 441
6	1.253	2, 1, 5	1.255, 1.251, 1.251	532, 247, 611
6	1.242	3, 2	1.244, 1.244	338, 3.1.10
11	1.235	2, 4, 1, 7, 3	1.237, 1.236, 1.234, 1.232, 1.232	612, 443, 507, 148, 533
2	1.175	2, 1	1.175, 1.174	3.0.11, 353

$a = 7.618(11)$, $b = 6.85(2)$, $c = 14.45(3)$ Å and $V = 754(1)$ Å³. Some decrease of the parameters of the acicular variety in comparison with the prismatic ones reflects the substitution of part of Mo^{6+} by S^{6+}.

The structure of cupromolybdite was solved by direct methods and was refined anisotropically using SHELX software (Sheldrick, 2008) to $R1 = 0.0314$ for 1223 unique reflections with $I > 2\sigma(I)$. A small amount of S was added to the Mo(2) site, according to the refined number of electrons of the site and chemical composition data.

The occupancy coefficients of the cations were fixed in the final stage of refinement. Crystallographic characteristics of the mineral, details of the X-ray diffraction study and the structure-refinement parameters are given in Table 5, while the atom coordinates and equivalent thermal displacement parameters are shown in Table 6. The selected interatomic distances are presented in Table 7.

Similar to synthetic $Cu_3Mo_2O_9$ (Steiner & Reichelt, 1997; Reichelt *et al.*, 2005), the crystal structure of cupromolybdite (Fig. 7) contains strings of corner-shared

Table 5. Crystal data, data collection information and structure refinement details for cupromolybdite. The data are for the prismatic variety of the mineral.

Formula	$Cu_3O[(Mo_{1.94}S_{0.06})O_4]_2$
Formula weight	522.67
Crystal system, space group, Z	Orthorhombic, $Pnma$, 4
Unit-cell dimensions (Å)	$a = 7.66380(10)$,
	$b = 6.86700(10)$,
	$c = 14.5554(2)$
V (Å^3)	766.012(18)
Density (calculated) (g/cm^3)	4.532
μ (mm^{-1})	11.323
F(000)	966
Crystal dimensions (mm)	$0.05 \times 0.07 \times 0.11$
Diffractometer	Xcalibur S CCD
Temperature (K)	293
Radiation and wavelength (Å)	Mo$K\alpha$; 0.71073
h, k, l ranges	$-11 \leq h \leq 9$,
	$-10 \leq k \leq 10$,
	$-21 \leq l \leq 22$
Total reflections measured	25,879
Unique reflections	1478 ($R_{int} = 0.0959$)
Unique reflections with $I>2\sigma(I)$	1223
Refinement on	F^2
Number of parameters refined	81
R_1[a] for $I>2\sigma(I)$	0.0314
wR_2[b] for all data	0.0566
GooF	1.072
$\Delta\rho_{min}/\Delta\rho_{max}$ (e/Å^3)	$-0.785/1.061$

[a]$R_1 = \dfrac{\sum ||Fo|-|Fc||}{\sum |Fo|}$

[b]$wR_2 = \left[\dfrac{\sum \left[w(F_o^2 - F_c^2)^2 \right]}{\sum \left[w(F_o^2)^2 \right]} \right]^{\frac{1}{2}}$;

$w = \dfrac{1}{\left[\sigma^2(Fo^2) + (0.0248P)^2 + 0.000P \right]}$;

$P = \dfrac{\text{max of } (0 \text{ or } F_o^2) + 2F_c^2}{3}$

Table 6. Atom coordinates and equivalent isotropic thermal displacement parameters (Å^2) for cupromolybdite.

Atom (position)	x	y	z	U_{eq}
Mo(1)	0.26159(5)	0.25	0.16717(3)	0.01409(10)
Mo(2)[a]	0.15141(6)	0.75	0.38593(3)	0.01329(10)
Cu(1)	0.0	0.0	0.0	0.01350(13)
Cu(2)	0.16122(8)	0.75	0.14124(4)	0.01502(14)
Cu(3)	0.20362(9)	0.25	0.43602(4)	0.01650(14)
O(1)	0.0897(5)	0.75	0.0141(2)	0.0138(7)
O(2)	0.1973(7)	0.75	0.2693(3)	0.0378(12)
O(3)	0.4303(5)	0.75	0.0970(3)	0.0377(11)
O(4)	0.2444(4)	0.9600(4)	0.43609(18)	0.0215(6)
O(5)	0.1394(4)	0.0388(4)	0.13535(18)	0.0207(5)
O(6)	0.2962(6)	0.25	0.2831(3)	0.0311(10)
O(7)	0.4651(5)	0.25	0.1112(3)	0.0280(9)

[a]$Mo_{0.94}S_{0.06}$, occupancy derived from electron-microprobe analysis.

Table 7. Selected interatomic distances (Å) in the structure of cupromolybdite.

Mo(1) – O(6) 1.709(4)	Cu(2) – O(2) 1.884(4)
Mo(1) – O(7) 1.759(4)	Cu(2) – O(1) 1.930(3)
Mo(1) – O(5) 1.787(2) $\times$ 2	Cu(2) – O(5) 1.992(2) $\times$ 2
Mean 1.7605	Cu(2) – O(3) 2.160(4)
	Mean 1.992
Mo(2) – O(3) 1.713(4)	
Mo(2) – O(2) 1.734(4)	Cu(3) – O(1) 1.950(3)
Mo(2) – O(4) 1.767(3) $\times$ 2	Cu(3) – O(7) 1.953(4)
Mean 1.745	Cu(3) – O(4) 2.016(3) $\times$ 2
	Cu(3) – O(6) 2.336(4)
Cu(1) – O(1) 1.8606(14) $\times$ 2	Cu(3) – O(3) 2.559(5)
Cu(1) – O(4) 2.186(3) $\times$ 2	Mean 2.138
Cu(1) – O(5) 2.257(3) $\times$ 2	
Mean 2.101	
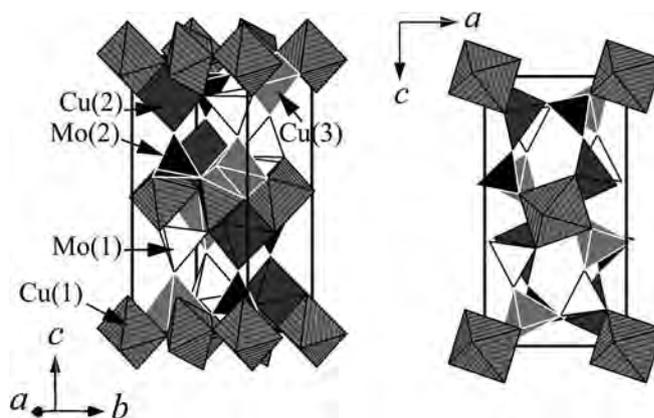
Fig. 7. The crystal structure of cupromolybdite in two projections. The unit cell is outlined.

$Cu(1)O_6$ octahedra elongated in the [010] direction. $Cu(2)O_5$ square pyramids and $Cu(3)O_6$ octahedra are linked to $Cu(1)O_6$ octahedra by edges and to MoO_4 and $(Mo,S)O_4$ tetrahedra by corners. Both Cu(1) and Cu(3) octahedra are distorted due to the Jahn-Teller effect (each octahedron has four short Cu–O distances and two elongated). The minor admixture of S is concentrated in one of two independent tetrahedral positions Mo(2) (Table 4), which is the position occupied by S in vergasovaite (Berlepsch *et al.*, 1999). The Mo(2) tetrahedron in cupromolybdite is smaller than the Mo(1) one (mean Mo–O distances are 1.7605 Å for Mo(1) and 1.745 Å for Mo(2)) whereas in the synthetic $Cu_3Mo_2O_9$ these values are 1.767 and 1.756 Å, respectively.

6. Discussion: relationship to other molybdates and tungstates

Cupromolybdite, a molybdate with the structural formula $Cu_3O[MoO_4][(Mo,S)O_4]$, is isostructural with vergasovaite,

Table 8. Comparative data for cupromolybdite and vergasovaite.

Mineral	Cupromolybdite	Vergasovaite
Formula	$Cu_3O(MoO_4)_2$	$Cu_3O[(Mo,S)O_4][SO_4]$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*
Unit-cell data		
a, Å	7.664	7.42
b, Å	6.867	6.74 – 6.75
c, Å	14.555	13.55 – 13.62
V, Å^3	766	678 – 682
Z	4	4
Strongest	7.312 – 67	3.71 – 30
reflections	3.518 – 55	3.391 – 60
in the X-ray	3.436 – 100	3.342 – 60
powder pattern:	3.301 – 99	3.077 – 100
d, Å – *I*	3.065 – 79	2.990 – 30
	2.556 – 62	2.542 – 60
	2.506 – 66	2.500 – 60
D (calc.), g cm^{-3}	4.51	4.32
Optical data	400: 17.0 – 18.5	400: 10.6 – 13.0
(reflectance	500: 14.3 – 15.7	500: 9.7 – 11.4
values: λ, nm:	600: 12.6 – 14.0	600: 9.2 – 10.7
R_1, % – R_2, %)	700: 11.9 – 13.2	700: 9.0 – 10.5
Visual appearance	Prismatic and acicular crystals up to 150 μm in length, yellow to brown colour	Prismatic crystals up to 300 μm in length, olive-green colour
Deposition sequence	Later than vergasovaite, overgrowths and pseudomorphs after vergasovaite	Earlier than cupromolybdite
Reference	Present study	Bykova *et al.* (1998), Berlepsch *et al.* (1999)

a molybdate-sulphate mineral with the formula $Cu_3O[(Mo,S)O_4][SO_4]$ (Bykova *et al.*, 1998). The structures of both minerals contain two independent tetrahedral sites, which are occupied differently. In vergasovaite, one of the sites is only occupied by S^{6+}, whereas the other site has a composition of $Mo^{6+}_{0.76}S^{6+}_{0.24}$ (Berlepsch *et al.*, 1999). In the vergasovaite samples examined by Downs (2006), the Mo:S ratio was close to 1:1, thus, these constituents are likely strictly ordered in two sites according to their size. In the studied crystal of cupromolybdite, Mo(2) and Mo(1), which correspond to the S and Mo sites of vergasovaite, are occupied by $(Mo^{6+}_{0.94}S^{6+}_{0.06})$ and Mo^{6+}, respectively. Cupromolybdite has higher unit-cell dimensions, interplanar spacings, density and reflectance values than vergasovaite (Table 8). The end-member cupromolybdite is the natural analogue of the well-known synthetic compound $Cu_3Mo_2O_9$ (Steiner & Reichelt, 1997; Reichelt *et al.*, 2005).

In addition to cupromolybdite, two other natural copper molybdates are known. Both minerals are hydroxyl-bearing species: lindgrenite, $Cu_3(OH)_2(MoO_4)_2$, and szenicsite, $Cu_3(OH)_4(MoO_4)$. Monoclinic (space group $P2_1/n$) lindgrenite has the same Cu:Mo ratio as cupromolybdite but quite a different crystal structure (Hawthorne & Eby, 1985). A remote relationship exists for cupromolybdite, lindgrenite and tetragonal (space group $P4_12_12$) cuprotungstite, $Cu_3(OH)_2(WO_4)_2$. The minerals have the same cation ratios and similar values for the *c* parameter: 14.48 Å for cuprotungstite (Walenta, 1979), 14.023 Å for lindgrenite (Hawthorne & Eby, 1985) and 14.555 Å for cupromolybdite. However, the crystal structure of cuprotungstite is unknown, and the X-ray powder diffraction data of the three minerals are different.

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