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Hermannjahnite, $CuZn(SO_4)_2$, a new mineral with chalcocyanite derivative structure from the Naboko scoria cone of the 2012–2013 fissure eruption at Tolbachik volcano, Kamchatka, Russia

Oleg I. Siidra¹ · Evgeny V. Nazarchuk¹ · Atali A. Agakhanov² · Evgeniya A. Lukina¹ · Anatoly N. Zaitsev³ · Rick Turner⁴ · Stanislav K. Filatov¹ · Igor V. Pekov⁵ · Gennady A. Karpov⁶ · Vasiliy O. Yapaskurt⁵

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Abstract A new mineral hermannjahnite, ideally $CuZn(SO_4)_2$, was found in the sublimates of *Saranchinaitovaya fumarole*, Naboko scoria cone, where the recent Fissure Tolbachik Eruption occurred in 2012–2013. The cotype specimen was found in the *Arsenatnaya fumarole*, on the Second scoria cone of the Great Tolbachik Fissure Eruption (GTFE 1975–1976). The mineral is named in honour of Hermann Arthur Jahn. Jahn-Teller effect is pronounced in the structure of hermannjahnite. The empirical formula of the holotype hermannjahnite, calculated on the basis of 8 O *apfu*

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Oleg I. Siidra o.siidra@spbu.ru

- ¹ Department of Crystallography, St. Petersburg State University, University emb. 7/9, 199034 St. Petersburg, Russia
- ² Fersman Mineralogical Museum, Russian Academy of Science, Leninskii Prospect, Bldg. 18, 117071 Moscow, Russia
- ³ Department of Mineralogy, St. Petersburg State University, University emb. 7/9, 199034 St. Petersburg, Russia
- ⁴ The Drey, Allington Track, Allington, Salisbury, Wiltshire SP4 0DD, UK
- ⁵ Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia
- ⁶ Institute of Volcanology and Seismology, Russian Academy of Sciences, Bulvar Piypa 9, Petropavlovsk-Kamchatskiy 683006, Russia

is: $Cu_{1.00}(Zn_{0.43}Cu_{0.31}Mg_{0.25})_{\Sigma 0.99}S_{2.00}O_8$. Hermannjahnite is optically biaxial (+), $\alpha = 1.642(2)$, $\beta = 1.652(2)$, $\gamma = 1.675(2)$ (589 nm) with 2 V (calc.) = 67.6° . Hermannjahnite is monoclinic, $P2_1/n$, a = 4.8076(2), b = 8.4785(3), c = 6.7648(3) Å, $\beta = 93.041(3)$ °, V = 275.35(2)Å³, Z = 2, $R_1 = 0.047$. The eight strongest lines of the X-ray powder diffraction pattern are (I-d-hkl): 31-4.231-(020), 100-4.177-(110), 72-3.630-(11-1), 25-3.486-(111), 29-2.681-(11-2), 69-2.648-(02-2), 29-2.561-(112), 63-2.428-(130). The structure of hermannjahnite is isotypic to that of dravertite, $CuMg(SO_4)_2$, and represents a monoclinically distorted chalcocyanite CuSO₄ structure. Crystallographic and structural data on a natural sample of chalcocyanite are provided. Zinc is very close in ionic radii to copper, but the Jahn-Teller effect on Cu^{2+} causes the segregation of these elements over two symmetrically independent crystallographic sites in hermannjahnite. Bond-length distortion parameters (Δ_{oet}) were evaluated for 44 different MO_6 (M = Cu, Zn) octahedra in Cu, Zn oxysalt minerals containing Cu- or/and Zndominated octahedra. In hermannjahnite CuO₆ octahedra exhibit a value of $\Delta_{oct} \times 10^3 = 14.71$, whereas $\Delta_{oct} \times 10^3 = 0.83$ is calculated for ZnO₆. In chalcocyanite CuO₆ octahedra have a value of $\Delta_{oct} \times 10^3 = 8.25$. Relationships between calculated Δ_{oct} parameters and occupancy of MO_6 (M = Cu, Zn) octahedra by Cu²⁺ and Zn²⁺ cations in various minerals are evaluated and discussed.

Keywords Hermannjahnite · Chalcocyanite · Copper · Zinc · Jahn-Teller effect · Distortion parameters · Sulphates · Fumarolic minerals · Dravertite · Tolbachik fissure eruption 2012–2013 · Naboko scoria cone

Fig. 1 Photomicrographs of hermannjahnite. a Hermannjahnite (nearly colourless with greenish blue tint) associated with hematite, on the holotype specimen from the Saranchinaitovaya fumarole, Naboko scoria cone, FTE. b Hermannjahnite (nearly colourless with pale greenish tint) associated with yellow-brown dolerophanite on reddish basalt scoria, on the cotype specimen from the Arsenatnava fumarole, Second scoria cone, NB GTFE. c Granular crust and d coarse crystals of hermannjahnite (SEM images) on the cotype specimen from the Arsenatnaya fumarole



 Table 1
 Chemical composition of hermannjahnite and chalcocyanite

Constituent	Hermannjahnite*							Chalcocyanite	
	1	2	3	4	5	6	7	8	
Oxide content	s (wt%):								
MgO	3.25 (3.02-3.48 / 0.20)	3.87	4.48	5.22	5.64	5.96	6.19	b.d.l.	
MnO	b.d.l.	0.13	0.12	0.15	0.05	b.d.l.	0.14	b.d.l.	
CuO	33.64 (32.65–34.70 / 0.65)	25.54	25.70	25.50	24.17	23.44	26.24	48.87 (48.51-49.38 / 0.40)	
ZnO	11.26 (10.23–11.62 / 0.38)	19.06	17.57	17.52	16.94	16.12	12.95	1.44 (1.06–1.64 / 0.20)	
Fe ₂ O ₃ **	b.d.l.	0.16	0.12	0.07	0.17	b.d.l.	0.08	b.d.l.	
SO_3	51.71 (50.78-52.48 / 0.69)	50.97	52.20	52.91	52.72	53.50	53.26	50.59 (50.16-51.49 / 0.52)	
Total	99.86	99.73	100.19	101.37	99.69	99.02	98.86	100.90	
Mineral formu	llae (apfu)***:								
Mg	0.25	0.30	0.34	0.39	0.43	0.45	0.47	0.00	
Mn	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.00	
Cu	1.31	1.00	0.99	0.97	0.92	0.89	1.00	0.97	
Zn	0.43	0.73	0.66	0.65	0.63	0.60	0.48	0.03	
Fe	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	
S	2.00	1.98	2.00	1.99	2.00	2.02	2.01	2.00	
0	8	8	8	8	8	8	8	4	

For analyses 1 and 8, means of ten spot analyses each are quoted (with ranges / standard deviations in parentheses)

b.d.l. = below the detection limit

*Analysis 1, holotype material; analyses 2-7, cotype material

** Fe is considered as Fe³⁺, taking into account strongly oxidizing conditions in fumaroles of Tolbachik volcano (see Zelenski et al. 2011).

***calculated on the basis of 8 O apfu for hermannjahnite and 4 O apfu for chalcocyanite

Introduction

A large number of sulphate mineral species were discovered in the fumaroles of the First, and especially, Second scoria cones of the Northern Breakthrough of the Great Tolbachik Fissure eruption (NB GTFE, 1975–1976), located some 18 km south of the Ploskiy Tolbachik volcano, Kamchatka, Far-Eastern Region, Russia (Fedotov and Markhinin 1983; Vergasova and Filatov 2016). Many of these minerals contain Cu²⁺.

The Fissure Tolbachik eruption (FTE) occurred in 2012– 2013 and is characterized in general by the formation of similar mineral assemblages, but these are poorer in diversity and abundance (Karpov et al. 2013). Four new mineral species reported recently are sulphates: saranchinaite $Na_2Cu(SO_4)_2$ (Siidra et al. 2017), itelmenite $Na_4Mg_3Cu_3(SO_4)_8$ (IMA 2015–047, Nazarchuk et al. 2015), ivsite $Na_3H(SO_4)_2$ (Filatov et al. 2016) and bubnovaite $K_2Na_8Ca(SO_4)_6$ (Gorelova et al. 2016).

Anhydrous sulphates $M^{2+}SO_4$ with M = Mg, Mn, Fe, Co, Ni, or Cd are unknown as minerals to date. Binary sulphates $M^{2+}M^{2+}(SO_4)_2$ with only the above listed metals are also unknown as synthetic compounds. Chalcocyanite, CuSO₄, is a very unstable mineral at ambient conditions as it easily alters to hydrous copper sulphates in humid air. It has been reported from exhalative mineral assemblages in active fumaroles at three volcanoes: Vesuvius in Italy, Izalco in El Salvador and Tolbachik (Palache et al. 1951; Anthony et al. 2003). At the latter, it is one of the most abundant copper sulphates in fumaroles related to the Naboko scoria cone. Crystals of chalcocyanite up to 2-3 cm in size and their clusters and crusts are common in the Yadovitava and Arsenatnava fumaroles of the Second scoria cone. Surprisingly, there has been no data on the crystal structure of chalcocyanite published to date. Crystal structure details published in Wildner and Giester 1988 were obtained on synthetic samples.

Herein we describe a new Cu-Zn sulphate with the idealized, end-member formula CuZn(SO₄)₂ found by O.I.S. and E.A.L. in the Saranchinaitovaya fumarole (Siidra et al. 2017) of the Naboko scoria cone, FTE, in July 2014 (holotype) and independently by I.V.P. in the Arsenatnaya fumarole, Second scoria cone, NB GTFE, in July 2013. The mineral was named hermannjahnite (Cyrillic: германнянит) in honour of Hermann Arthur Jahn (31.05.1907-24.10.1979), an English scientist of German origin, who identified together with Edward Teller the Jahn-Teller effect, which strongly influences CuO_6 octahedra geometry (Burns and Hawthorne 1996). This phenomenon is pronounced in the structure of hermannjahnite. Both the new mineral and name have been approved by the IMA CNMNC, as IMA2015-050. The holotype specimen is deposited in the collections of the Mineralogical Museum of St Petersburg State University, St. Petersburg, Russia, catalogue no. 19659. Crystallographic and structural data on a natural sample of chalcocyanite are provided in the present paper also.

Occurrence and general appearance

Hermannjahnite was formed as a product of fumarolic activity, probably being directly deposited from volcanic gases as a sublimate. It was found in two fumaroles related to the Tolbachik volcano.

 Table 2
 X-ray powder diffraction data of hermannjahnite

d_{calc} (Å)	d_{obs} (Å)	Iobs
4.239	4.231	31
4.177	4.177	100
4.015	4.036	2
3.819	3.828	1
3.629	3.630	72
3.591	3.600	14
3.482	3.486	25
3.378	3.391	2
3.138	3.139	1
2.688	2.681	29
2.642	2.648	69
2.570	2.561	29
2.436	2.428	63
2.400	2.389	12
2.356	2.363	2
2.310	2.321	1
2.275	2.279	1
2.082	2.082	3
2.022	2.022	1
2.008	2.010	2
2.001	2.001	3
1.951	1.952	9
1.945	1.939	2
1.909	1.909	1
1.814	1.814	15
1.808	1.808	9
1.795	1.795	7
1.748	1.749	2
1.741	1.741	5
1.689	1.689	4
1.656	1.656	2
1.560	1.560	1
1.592	1.592	1
1.589	1.590	3
1.573	1.573	1
1.569	1.569	1
1.550	1.550	1
1.541	1.541	1
	d_{calc} (Å) 4.239 4.177 4.015 3.819 3.629 3.591 3.482 3.378 3.138 2.688 2.642 2.570 2.436 2.400 2.356 2.310 2.275 2.082 2.022 2.008 2.021 2.008 2.001 1.951 1.945 1.909 1.814 1.808 1.795 1.748 1.741 1.689 1.656 1.560 1.592 1.550 1.550 1.550 1.541	d_{calc} (Å) d_{obs} (Å)4.2394.2314.1774.1774.0154.0363.8193.8283.6293.6303.5913.6003.4823.4863.3783.3913.1383.1392.6882.6812.6422.6482.5702.5612.4362.4282.4002.3892.3562.3632.3102.3212.2752.2792.0822.0822.0222.0222.0082.0102.0012.0011.9511.9521.9451.9391.9091.9091.8141.8141.8081.8081.7951.7951.7481.7491.7411.7411.6891.6561.5601.5601.5601.5601.5501.5501.5501.5501.5411.541

The eight strongest lines (relative intensity >10%) are shown bold

The holotype material was collected in the *Saranchinaitovaya* fumarole located at the Naboko scoria cone (55°46′ N, 160°19′E, 1650 m ASL) of the Fissure Tolbachik eruption, which occurred in 2012–2013 on the southern slope of the Ploskiy Tolbachik volcano. The temperature of gas at the sampling location was about 600 – 620 °C. Hermannjahnite (Fig. 1a) is closely associated with anhydrite and itelmenite $Na_4Mg_3Cu_3(SO_4)_8$ (IMA 2015–047, Nazarchuk et al. 2015) and forms intimate intergrowths with them. Other associated minerals are saranchinaite $Na_2Cu(SO_4)_2$ (Siidra et al. 2017), chalcocyanite, euchlorine, thénardite, aphthitalite, and hematite. The majority of data provided in this paper, including the crystal structure, powder XRD pattern and optical characteristics were obtained for this holotype specimen.

The cotype material (Fig. 1b) was found in the *Arsenatnaya* fumarole, Second scoria cone of NB GTFE, 1975–1976 (55°41'N, 160°14'E, 1200 m ASL). The temperature in the fumarole was 360–380 °C. Hermannjahnite is intimately associated with dolerophanite, tenorite, euchlorine, fedotovite, chalcocyanite, langbeinite, aphthitalite, anhydrite, hematite and, in some cases, with dravertite, CuMg(SO₄)₂ (Pekov et al. 2017).

At both localities hermannjahnite typically occurs as isometric anhedral grains (Fig. 1) up to 0.05 mm across with massive aggregates or crusts up to 2×2 mm on basaltic scoria. The colour of hermannjahnite is somewhat variable: white or colourless, sometimes with light greyish, yellowish, greenish or bluish tints. The streak is white. The luster is vitreous. The mineral is transparent in individual grains and translucent in

Table 3 Crystallographic dataand refinement parameters forhermannjahnite andchalcocyanite

	Hermannjahnite	Chalcocyanite
Crystal data:		
Crystal system	monoclinic	orthorhombic
Space group	$P2_{1}/n$	Pnma
Unit cell dimensions		
<i>a</i> (Å)	4.8076(2)	8.4123(10)
<i>b</i> (Å)	8.4785(3)	6.7040(8)
<i>c</i> (Å)	6.7648(3)	4.8303(6)
β (°)	93.041(3)	
Unit-cell volume (Å ³)	275.35(2)	272.41(6)
Ζ	2	4
Calculated density (g·cm ⁻³)	3.740	3.892
Absorption coefficient (mm ⁻¹)	8.091	8.578
Crystal size (mm)	$0.04 \times 0.04 \times 0.04$	$0.10\times0.12\times0.05$
Data collection:		
Temperature (K)	296(2)	296(2)
Radiation, wavelength (Å)	ΜοΚα, 0.71073	ΜοΚα, 0.71073
F(000)	302	308
θ range (°)	3.86–28.00	4.847-35.706
h, k, l ranges	$-6 \rightarrow 6$	$-12 \rightarrow 13$
	$-11 \rightarrow 11$	$-10 \rightarrow 11$
	$-8 \rightarrow 8$	$-7 \rightarrow 7$
Total reflections collected	3911	3255
Unique reflections (R_{int})	666 (0.0277)	654 (0.0249)
Unique reflections $F > 4\sigma(F)$	582	591
Structure refinement:		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Weighting coefficients a, b^*	0.089000, 0.00	0.016900, 0.242300
Data/restraints/parameters	666/0/59	654/0/35
$R_1 [F > 4\sigma(F)], wR_2 [F > 4\sigma(F)]$	0.0468, 0.1199	0.0175, 0.0446
R_2 all, wR_2 all	0.0515, 0.1294	0.0209, 0.0457
Gof on F^2	1.129	1.137

Atom	x/a	y/b	z/c	$U_{\rm eq}$	U_{11}	U ₂₂	U ₃₃	<i>U</i> ₂₃	U_{13}	U_{12}
Cu	0	0	0	0.0151(4)	0.0174(6)	0.0111(5)	0.0160(5)	0.0039(2)	-0.0050(4)	-0.0070(2)
Zn*	0	0	1/2	0.0129(4)	0.0120(6)	0.0113(6)	0.0154(6)	-0.0004(2)	0.0022(4)	-0.0032(2)
S	0.04144(19)	0.68241(11)	0.23478(13)	0.0092(4)	0.0071(5)	0.0065(5)	0.0139(6)	-0.0001(3)	0.0004(4)	0.0005(3)
O(1)	0.0536(6)	0.8608(4)	0.2421(4)	0.0125(6)	0.0143(14)	0.0067(13)	0.0164(15)	0.0004(8)	0.0004(11)	-0.0013(10)
O(2)	-0.2489(6)	0.6297(3)	0.2256(4)	0.0152(7)	0.0092(15)	0.0132(12)	0.0235(16)	0.0011(10)	0.0031(11)	-0.0028(10)
O(3)	0.1797(6)	0.6333(3)	0.0578(4)	0.0142(6)	0.0137(15)	0.0151(14)	0.0140(14)	-0.0025(10)	0.0022(11)	0.0023(11)
O(4)	0.1824(6)	0.6266(3)	0.4195(4)	0.0149(7)	0.0149(14)	0.0146(13)	0.0150(15)	0.0012(10)	-0.0009(11)	0.0038(11)

 Table 4
 Atomic coordinates and displacement parameters (Å²) in hermannjahnite

*Zn_{0.43}Cu_{0.31}Mg_{0.25}

aggregates. Hermannjahnite is brittle. Cleavage or parting has not been observed. The fracture is uneven. Hardness and density could not be measured because of the very small size of individual grains and the porosity of the aggregates. The density calculated based on the empirical formula of the holotype is 3.74 g cm⁻³. Hermannjahnite is optically biaxial (+), $\alpha = 1.642(2), \beta = 1.652(2), \gamma = 1.675(2)$ (589 nm) with 2 V (calc.) = 67.6°. Hermannjahnite is light grey and nonpleochroic under the microscope. The Gladstone-Dale compatibility index, $1 - (K_p/K_c) = -0.014$, is superior.

Chemical composition

Chemical composition of our samples (Table 1) was determined using an electron microprobe. Analyses were performed in three laboratories. The holotype of hermannjahnite (a crystal $(40 \times 40 \ \mu m)$ was studied in the Fersman Mineralogical Museum using a JEOL Superprobe 733 scanning electron microscope equipped with INCA energy-dispersive spectrometer, acceleration voltage of 20 kV, a beam current of 2 nA, and a 10 µm beam diameter (1), the cotype in the Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelengthdispersive spectrometer, 20 kV, 20 nA, 3 µm beam diameter (2) and chalcocyanite in Geomodel Resource Centre, St. Petersburg State University using a Hitachi S-3400 N scanning electron microscope equipped with an Oxford Instruments X-Max 20 Energy Dispersive Spectrometer, 20 kV, 2.5 nA, 5 µm beam diameter (3). The standards used in laboratories 1, 2, and 3 are as follows: Mg –olivine (1), diopside (2); Mn –MnTiO₃ (2); Fe –CuFeS₂ (2); Cu –Cu (1), CuFeS₂ (2), Cu (3); Zn –Zn (1), ZnS (2), Zn (3); S –SrSO₄ (1), ZnS (2), CaSO₄ (3). No elements with atomic number ≥ 9 other than those reported in Table 1 were detected.

The holotype hermannjahnite and chalcocyanite from Naboko scoria cone do not exhibit significant chemical heterogeneity and average data are represented (## 1 and 8 in Table 1). The cotype hermannjahnite from the *Arsenatnaya* fumarole of the Second scoria cone reveals distinct chemical (cationic) variations in different crystals and separate spot analyses are presented (## 2–7 in Table 1).

The empirical formula of the holotype hermannjahnite, calculated on the basis of 8 O *apfu* taking into account the structural data (see below), is: $Cu_{1.00}(Zn_{0.43}Cu_{0.31}Mg_{0.25})_{\Sigma_{0.99}}S_{2.00}O_8$. The simplified end-member formula is $CuZn(SO_4)_2$ which requires CuO 24.38, ZnO 25.35, SO₃ 49.87, total 100.00 wt.%.

The studied chalcocyanite contains minor Zn admixture (1.1–1.6 wt.% ZnO) and its formula, calculated on the basis of 4 O *apfu*, is $(Cu_{0.97}Zn_{0.03})_{\sum 1.00}(SO_4)$. Hermannjahnite is soluble in H₂O at room temperature and slowly transforms into hydrate in humid air. All the recovered samples were hermetically packed immediately after collecting and isolated to avoid any contact with atmosphere for this reason.

X-ray crystallography and crystal structure

Powder X-ray diffraction data for the holotype hermannjahnite were obtained using a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye-Scherrer geometry (with d = 127.4 mm), after crushing of fragments of the crystal used for the single crystal analysis. Data (in Å for CoK α) are given in Table 2. The unit-cell parameters were refined in the monoclinic unit cell, space group $P2_1/n$, a = 4.813(6) Å, b = 8.46(1)Å, c = 6.777(8) Å, $\beta = 93.1(1)^\circ$, V = 275.5(5) Å³.

A small equant crystal of hermannjahnite and larger crystal of chalcocyanite (Table 3) were each mounted on a Bruker

 Table 5
 Selected interatomic distances in the crystal structure of hermannjahnite

Cu-O(4)	1.921(3) × 2	S-O(3)	1.461(3)
Cu-O(1)	2.024(3) × 2	S-O(2)	1.464(3)
Cu-O(2)	2.520(3) × 2	S-O(4)	1.468(3)
		S-O(1)	1.514(3)
Zn-O(3)	1.966(3) × 2		
Zn-O(1)	2.133(3) × 2		
Zn-O(2)	2.191(3) × 2		

	O(1)	O(2)	O(3)	O(4)	$\sum_{v} c$
Cu	0.39 ^{2×}	0.10 ^{2×}		$0.52^{2\times}$	2.02
Zn*	$0.31^{2\times}$	$0.27^{2\times}$	$0.49^{2\times}$		2.14
S	1.35	1.54	1.55	1.52	5.96
$\sum v a$	2.05	1.91	2.04	2.04	

 Table 6
 Bond-valence analysis for the crystal structure of hermannjahnite

All values expressed in valence units (vu)

*Calculated using bond-valence parameters for Zn-O bonds

APEX II DUO X-ray diffractometer operated at 50 kV and 40 mA and equipped with a micro-focus X-ray tube with the Mo anode. The data were integrated and corrected for absorption using a multi-scan type model with the Bruker programs APEX and SADABS. More than a hemisphere of X-ray diffraction data was collected with the frame widths of 0.3° in ω , and with 50 s (hermanniahnite) / 10 s (chalcocyanite) spent counting for each frame. The structure of hermannjahnite was solved in the space group $P2_1/n$ by direct methods. The crystal structure was refined to $R_1 = 0.047$ by means of the SHELX software package (Sheldrick 2015) on the basis of 582 independent reflections with $I > 4\sigma(I)$. Atom coordinates and displacement parameters are given in Table 4 and selected interatomic distances in Table 5. Bond-valence calculations (Table 6) were performed using bond-valence parameters taken from Brown and Altermatt (1985) for the Cu²⁺-O, Zn-O and S⁶⁺-O bonds. Calculated values of bond-valence sums are in good agreement with the expected ones for all atoms in the structure of hermannjahnite. Initial atomic coordinates for the refinement of the crystal structure of chalcocyanite were taken from Wildner and Giester (1988). Structure of chalcocyanite from the Naboko scoria cone was refined to $R_1 = 0.018$ on the basis of 591 independent reflections with $I > 4\sigma(I)$. Atom coordinates, displacement parameters, selected interatomic distances and bond-valence sums for studied chalcocyanite are provided in supporting information (Table 1S-4S).

The crystal structure of hermannjahnite (Fig. 3) contains two symmetrically inequivalent cationic sites (Table 3) coordinated by six O^{2-} anions each (Fig. 2). The question of the distribution of Zn^{2+} and Cu^{2+} cations among two different octahedra in

hermanniahnite can be qualitatively answered on the basis of the different octahedral distortions of the Cu and Zn sites and applied earlier in the structure descriptions of ktenasite Zn₂(Cu_{4.8}Zn_{3.2})(SO₄)₄(OH)₁₂(H₂O)₁₂ (Mellini and Merlino 1978) and veszelyite $Zn(Cu_{1.76}Zn_{0.24})(PO_4)(OH)_3(H_2O)_2$ (Ghose et al. 1974; Danisi et al. 2013). There are four short Cu-O bonds in the range of 1.921(3)-2.024(3) Å and two very long Cu-O bonds of 2.520(3) Å each in the structure of hermannjahnite. The coordination of the Cu site is typical for Cu^{2+} cation and displays a [4 + 2] distortion of octahedral coordination geometry owing to the Jahn-Teller effect (Jahn and Teller 1937; Burns and Hawthorne 1995, 1996). The Zn site in the structure of hermannjahnite is significantly more symmetrical with Zn-O bond lengths in the range of 1.966(3)-2.191(3) Å. Since the X-ray scattering power of Cu and Zn atoms cannot be distinguished Cu and Zn were regarded as one group with one scattering factor in the process of refining the occupancy of the Zn site. The refined Zn site occupancy $(Zn + Cu)_{0.786(5)}Mg_{0.214(5)}$ is in good agreement with the chemical data. Mixed occupancy of this site was adjusted on the final stage to Zn_{0.43}Cu_{0.31}Mg_{0.25} in accordance with electron microprobe data. The S site is tetrahedrally coordinated in a somewhat distorted manner with three S-O bond lengths in the range of 1.461(3)-1.468(3) Å and one longer S-O bond of 1.514(3) Å.

The CuO₆ = CuO₄O₂ polyhedra share common edges with ZnO₆ octahedra (Fig. 3c) thus forming chains along the *c* axis. SO₄ tetrahedra provide interconnection of these chains into 3*D* framework (Fig. 3a). The structure of hermannjahnite can be considered as consisting of pseudolayers formed by SO₄ tetrahedra and octahedral chains. SO₄ tetrahedra alternate in *up* and *down* orientations within the sulphate layer (Fig. 3b).

The orthorhombic structure of chalcocyanite represents a heteropolyhedral framework similar to that in hermannjahnite (Fig. 4a). Sulphate layers are identical in both structures. There is only one symmetrically independent Cu site in the structure of chalcocyanite (Fig. 4c). A very minor amount of Zn^{2+} (Table 1) is substituting for Cu²⁺ in chalcocyanite. Coordination environments of this site are typical for Cu²⁺ and similar to those for the Cu site in hermannjahnite. However, in hermannjahnite coordination of this site is even more distorted from the regular octahedron. Two CuO₄O₂ octahedra share edges to form chains elongated along the *b*





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Fig. 3 Heteropolyhedral framework crystal structure of hermannjahnite. **a** General projection along the *a* axis. **b** Sulphate tetrahedral layers (SO₄ tetrahedra alternate in "up" and "down" orientations designated as *u* and *d*, respectively. **c** Octahedral chains formed by ZnO₆ and CuO₆ edge-sharing octahedra and elongated along the *c* axis. Cu–O–Zn interpolyhedral angles and Cu–Cu distances are highlighted



axis (Fig. 4b) in chalcocyanite. It is of interest that geometry of the octahedral chains is very similar in hermannjahnite and chalcocyanite despite the compositional differences. Cu-Cu distances as well as Cu-O-Cu angles (Fig. 3c, Fig. 4b) in the octahedral chains are nearly identical in both structures.

Discussion

The structure of hermannjahnite represents a monoclinically deformed chalcocyanite structure. Hermannjahnite is isotypic with the recently described mineral dravertite, $CuMg(SO_4)_2$

(Pekov et al. 2017). Zinc is very close in ionic radii to copper, but the Jahn-Teller effect on Cu^{2+} causes the segregation of these elements over two symmetrically independent crystallographic sites. The pronounced influence of the Jahn-Teller effect is also responsible for the lowering of symmetry (*Pnma*) from orthorhombic in the chalcocyanite structure with Jahn-Teller distorted octahedra only, to the monoclinic (*P*2₁/*n*) one in hermannjahnite with both regular and distorted *M*O₆ ($M = Cu^{2+}$, Zn²⁺) octahedra.

Since the octahedral coordination of Cu and Zn sites in hermannjahnite demonstrate different distortion degrees, it is of interest to evaluate this parameter quantitatively and



Fig. 4 Crystal structure of chalcocyanite. **a** General projection along the *c* axis. Note that the heteropolyhedral framework of chalcocyanite is based on sulphate tetrahedral layers identical to those in hermannjahnite (Fig. 3). **b** Octahedral chains formed by CuO_4O_2 edge-sharing octahedra

and elongated along the *b* axis (shown in b). Cu–Cu distance and Cu–O–Cu angles are very similar to those in hermannjahnite. **c** The CuO₄O₂ octahedron in chalcocyanite is distorted (Jahn-Teller effect); it is similar to the CuO₄O₂ octahedra in hermannjahnite (Fig. 2)

Table 7 Extents of distortion in MO_6 ($M = Cu, Zn$) octahedra of	of various Cu, Zn oxysalt minerals			
Mineral, formula	Occupancies*		$\Delta_{oct} \times 10^{3 **}$	Reference
	Cu site	Zn site	CuO ₆ ZnO ₆	
Sabelliite, (Cu,Zn) ₂ Zn(AsO ₄ ,SbO ₄)(OH) ₃	1.00 (Cu1)	0.64 (Zn1)*** 0.37 totrahodron (Zn2)	7.57 0	Olmi et al. 1995
Rosasite, CuZn(OH) ₂ (CO ₃)	1.00 (Cu1)	0.80 / 0.20 (Zn2 / Cu2)	12.06 2.03	Perchiazzi 2006
Kipushite, Cu ₅ Zn(OH) ₆ (H ₂ O)(PO ₄) ₂	1.00 (Cu1) 1.00 (Cu2)	1.00 tetrahedron (Zn1)	25.38 14.67	Piret et al. 1985
	0.62 / 0.38 (Cu3 / Zn3) 0.62 / 0.38 (Cu4 / Zn4) 0.62 / 0.38 (Cu4 / Zn4)		9.14 8.47 7.65	
Quetzalcoatlite, $Zn_6Cu_3(TeO_3)_2O_6(OH)_6(Ag_xPb_y)Cl_{x+2y}, x + \dots - 2$	(CIIZ / CUU) 8C.0 / 20.0 1.00 (Cu1)	1.00 tetrahedron (Zn1)	7.00 35.15	Burns et al. 2000
$y \ge z$ Hermannjahnite, CuZn(SO ₄) ₂	1.00 (Cu1)	0.43 / 0.31 / 0.25 (Zn1 / Cu1 / Mg1)	14.71 0.83	this work
Philipsburgite, (Cu,Zn) ₆ (AsO ₄ ,PO ₄) ₂ (OH) ₆ H ₂ O	1.00 (Cu1)	1.00 tetrahedron (Zn1)	25.62	Peacor et al. 1985
	1.00 (Cu2) 0.77 / 0.23 (Cu3 / Zn4) 0.77 / 0.23 (Cu4 / Zn5) 0.77 / 0.23 (Cu5 / Zn6)		14.68 9.56 8.36 7.68	
Keyite, (Cu ₃ ,Pb _{1-x})Cu ₂ Zn ₄ Cd ₂ (AsO ₄) ₆ '(H ₂ O) _{2x}	1.00 square (Cu1) 0.77 (Cu2)** 0.16 (Cu3)**	(1.00 (ZnZ) 00.1	21.73 0.81 9.59 0.64	Malcherek and Schlueter 2013
Zincolibethenite, CuZnPO ₄ OH	0.94 / 0.06 (Cu1 / Zn1)	1.00 tetragonal pyramid (Zn1)	9.78	Braithwaite et al. 2005, Williams et al. 2006
Pseudolyonsite, $Cu_3(VO_4)_2$	0.88 / 0.12 (Cu1 / Zn1) 0.88 / 0.12 (Cu2 / Zn2)		18.28 13.31	Zelenski et al. 2011
Veszelyite, (Cu,Zn)Zn(PO ₄)(OH) ₃ (H ₂ O) ₂	0.88/0.12 tetragonal pyramid (Cu1) 0.88/0.12 tetragonal myramid (Cu2)	1.00 tetrahedron (Zn1)		Danisi et al. 2013
Zincolivenite, Zn(Cu,Zn)(AsO ₄)(OH)	0.84 / 0.16 (Cu1 / Zn2)	1.00 tetragonal pyramid (Zn1)	6.55	Toman 1978, Chukanov et al. 2007.
Thometzekite (sulfatian), Pb(Cu,Zn) ₂ (AsO ₄ ,SO ₄) ₂ 2(H ₂ O,OH)	0.75 / 0.25 (Cu1 / Zn1)		3.5	Krause et al. 1998
Ktenasite, $Zn(Cu,Zn)_4(SO_4)_2(OH)_6$ 6H ₂ O	0.75 / 0.25 (Cu2 / Zn2)	1.0 (Zn1) 0 55 / 0 45 (Zn3 / Cn3)	9.06 0.14 3.33	Mellini and Merlino 1978
Christelite, $Zn_3Cu_2(SO_4)_2(OH)_6(H_2O)_4$	0.78 / 0.22 (Cu1 / Zn1)	0.93/0.07(Zn3 / Cu3) 0.93/0.17 /7-4 / CA	9.99 0.09	Adiwidjaja et al. 1996
Serpierite, $Ca(Cu,Zn)_4(OH)_6(SO_4)_2(H_2O)_3$	0.66 / 0.34 (Cu2 / Zn1) 0.66 / 0.34 (Cu2 / Zn2)	(+1) (11) (11)	1.78 1.48	Sabelli and Zanazzi 1968
	0.66 / 0.34 (Cu3 / Zn3) 0.66 / 0.34 (Cu4 / Zn4) 0.66 / 0.34 (Cu5 / Zn5)		15.17 0.01 12.87	
Aurichalcite, Zn ₃ Cu ₂ (OH) ₆ (CO ₃) ₂	0.5 / 0.5 (Cul / Znl) 0.5 / 0.5 (Cu2 / Zn2) 0.5 / 0.5 tetragonal pyramid (Cu3 / Zn3)	1.00 tetrahedron (Zn1)	2.66 6.68	Harding et al. 1994

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Mineral, formula	Occupancies*		$\Delta_{oct} imes 10^{3**}$ Refere	nce
	Cu site	Zn site	CuO ₆ ZnO ₆	
Bechererite, Zn ₇ Cu(OH) ₁₃ [SiO(OH) ₃ SO ₄]		0.875 / 0.125 (Zn1 / Cu1)	5.21 Hoffini	ann et al. 1997
		0.875 / 0.125 (Zn2 / Cu2)	0.76	
		0.875 / 0.125 (Zn3 / Cu3)	0.01	
		0.875 / 0.125 (Zn4 / Cu4)	0.06	
* Occupancies of Cu-dominant or Zn-dominant sites in AC	O_6 (A = Cu, Zn) octahedra or other* typ	es of coordination environments (mark	ced in italic)	
** Bond-length distortion parameters were not calculated :	for other than octahedral types of M^{2+} ((M = Cu, Zn) coordination environmen	its	
***These sites are underoccupied but can be taken to be 1	1.00 for plotting of relationship in Fig. 5			

compare it with the other Cu. Zn oxysalt minerals containing Cu- and/or Zn-dominant octahedra (Table 7). Octahedral coordination environments are the most typical for Zn^{2+} and are similar to Cu^{2+} . In some structures, both of these metals are distributed equally over different octahedral crystallographic sites, despite very different polyhedral distortions [e.g. serpierite (Sabelli and Zanazzi 1968) and bechererite (Hoffmann et al. 1997)]. Tetragonal pyramidal coordination is possible for both of these transition metal cations. A square planar coordination is unique for Cu²⁺, whereas tetrahedral coordination is exclusive for Zn^{2+} . In some of the minerals listed in Table 7, Cu²⁺ and Zn²⁺ are separated over these unique polyhedra and simplify the task of metal distribution over different crystallographic sites. The following Δ_{oct} bond-length distortion parameter, suggested in Wildner 1992, was used for octahedrally coordinated Cu, Zn sites: $\Delta_{oct} = \frac{1}{6} \sum_{i=1}^{6} \left[\frac{(d_i - d_m)}{d_m} \right]^2$ where $d_i = (M-O)$ bond-length, $d_m = \langle M - O \rangle$ bond-length (M = Cu, Zn). All of the *M*-O bonds \leq 3 Å were taken into consideration. Minerals with mixed oxo-chloride coordination of Cu and Zn atoms were excluded. Note, the presence of either H₂O or OH in Cu²⁺ or Zn^{2+} coordination environments also influences the geometry of MO_6 (M = Cu, Zn) octahedra, but even then, some obvious trends can be evaluated. Relationships between calculated octahedral bond-length distortion ($\Delta_{oct} \times \, 10^3)$ parameters for 44 different MO_6 (M = Cu, Zn) octahedra in Cu, Zn oxysalt minerals are given in Fig. 5. Cu-dominant and Zn-dominant octahedra significantly differ in $\Delta_{oct} \times 10^3$ values. The largest value of 35.5 is observed for Cu(1) site in the crystal structure of quetzalcoatlite (Burns et al. 2000), where two very long but weak Cu-O bonds of 2.83 Å each are formed. The smallest distortion parameter value of 0.0 is observed for 'pure' zinc and the very symmetrical ZnO₆ octahedra in sabelliite (Olmi et al. 1995). Two examples with pronounced Jahn-Teller effects, reflected in large distortion parameters for Cu(1)- and Cu(2)-centered octahedra are observed in the structures of kipushite (Piret et al. 1985) and phillipsburgite (Peacor et al. 1985). Whereas Cu(3)-Cu(5) sites partially occupied by zinc demonstrate significantly lower $\Delta_{oct} \times 10^3$ values. Further inspection of bond-length distortion parameters indicates that in some minerals, the assigned copper and zinc distributions require some elaboration. Two Cu sites are reported to have identical mixed occupancy by Cu²⁺ and Zn²⁺ with a Cu: Zn ratio of 0.88: 0.12 in pseudolyonsite (Zelenski et al. 2011). Calculated $\Delta_{oct} \times 10^3$ values (Table 7) and an observed significant rebound of $\Delta_{oct} \times 10^3$ value for the Cu(1)O₆ octahedron (Fig. 5) shows the Cu(1) site to have more Cu^{2+} than in Cu(2). There is no quantitative assignment of Cu²⁺ and Zn²⁺ distribution over five symmetrically independent Cu sites in serpierite (Sabelli and Zanazzi 1968) and these are assumed to be equal in the ratio of 0.66: 0.34 (Table 7), despite the authors noting that "likely the

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Fig. 5 Plot of the octahedral bond-length distortion against the Cu^{2+} content in MO_6 (M = Cu, Zn) octahedrons. Data pairs for herrmanjahnite $\{\Delta_{\text{oct}} \times 10^3 [\text{Cu}(1)\text{O}_6] = 14.71 \text{ and}$ $\Delta_{\text{oct}} \times 10^3 [\text{Zn}(1)\text{O}_6] = 0.83$ are visualised by green stars, and data pairs for CuO₆ octahedra in pseudolyonsite and sulphatian thometzekite are labelled ply and tom, respectively. Calculated $\Delta_{\rm oct} \times 10^3$ values for MO_6 (M = Cu, Zn) octahedra in Cu, Zn oxysalt minerals are provided in Table 7. Refined site occupancies from Table 8 are plotted for serpierite and bechererite



substitution of copper ions by zinc ions takes place preferentially in the octahedral positions". The 0.01 value for Cu(4)centered octahedron shows this site to be occupied by Zn atoms only. Cu(1) site ($\Delta_{oct} \times 10^3 = 1.78$) is occupied predominantly by Zn²⁺ with a minor amount of Cu²⁺. In contrast, $\Delta_{oct} \times 10^3$ values of 11.48, 15.17 and 12.87 for Cu(2)O₆ Cu(3)O₆ and Cu(5)O₆, respectively, are typical for 'pure' Cu²⁺ sites or with very minor substitution by Zn²⁺. The new Cu site assignments in serpierite taking into account chemical data reported in Faraone et al. (1967) are represented in Table 8. Calculation

Table 8Suggested refined occupancies of Cu and Zn sites in serpieriteand bechererite in accordance with calculated Δ_{oct} parameters (seeTable 7)

Atom Wyckoff position		Occupancy	
Serpierite			
Cu(1)	8 <i>f</i>	Zn _{0.86} Cu _{0.14}	
Cu(2)	8 <i>f</i>	Cu	
Cu(3)	8 <i>f</i>	Cu	
Cu(4)	4 <i>e</i>	Zn	
Cu(5)	4 <i>e</i>	Cu	
Bechererite			
Zn(1)	3 <i>d</i>	Zn _{0.66} Cu _{0.33}	
Zn(2)	3 <i>d</i>	Zn	
Zn(3)	1 <i>a</i>	Zn	
Zn(4)	1 <i>a</i>	Zn	

of Δ_{oct} parameters for ZnO₆ octahedra in bechererite (Hoffmann et al. 1997) allows us to unambiguously define occupation of the Zn(3) and Zn(4) sites exclusively by Zn atoms (Table 8), whereas most of the Cu^{2+} is segregated in Zn(1). It is also very likely for that the Zn(2) site has a very minor amount of Cu²⁺. Similar $\Delta_{oct} \times 10^3 = 0.78$ is observed for Zn(4) site in christelite (Adiwidjaja et al. 1996) with a Zn: Cu ratio of 0.83: 0.17. Similar Δ_{oct} values are indicated for 'pure' Zn sites in keyite (Malcherek and Schlueter 2013). During the analysis of correlation between obtained $\Delta_{oct} \times 10^3 = 3.5$ and Cu:Zn ratio in Cu(1) site in the structure of thometzekite (sulphatian) (Krause et al. 1998) (Fig. 5, Table 7) significant discrepancy was found. $\Delta_{oct} \times 10^3$ value reveals this site to have more Zn²⁺ and may suggest additional evaluation of reported chemical analyses. Note, there is only one symmetrically independent M site (M = Cu, Zn) in the sulphatian thometzekite structure and assigned Cu_{0.75}Zn_{0.25} occupancy is not due to incorrect redistribution of copper and zinc.

Bond-length distortion parameters for Cu(1) and Zn(1) sites in hermannjahnite are in excellent agreement with the trend discussed above. In hermannjahnite Cu(1)O₆ octahedra demonstrate $\Delta_{oct} \times 10^3 = 14.71$, whereas $\Delta_{oct} \times 10^3 = 0.83$ is observed for Zn(1)O₆ (Fig. 5). $\Delta_{oct} \times 10^3 = 8.25$ for Cu(1)O₆ octahedra in chalcocyanite. Fig. 5 shows 'pure' unsubstituted by zinc Cu sites to have very different but invariably rather large $\Delta_{oct} \times 10^3$. MO_6 (M = Cu, Zn) octahedral distortions are also induced from neighbouring polyhedra and should be taken into account. The simultaneous combination of both of

these phenomena make it impossible to establish direct correlation.

Hermannjahnite is represented by three chemical varieties, different one from each other in cationic composition (Table 1). The cotype material demonstrates the Cu:(Zn +Mg) ratio close to 1.0 and significant variations of the Zn:Mg ratio. #2 in Table 1 shows the Zn-richest variety of hermannjahnite (Cu_{1.00}Zn_{0.73}Mg_{0.30}Mn_{0.01}Fe_{0.01}S_{1.98}O₈) observed in the course of this study. #7 in Table 1 corresponds to variety very close to compositional border with dravertite: Cu_{1.00}Zn_{0.48}Mg_{0.47}Mn_{0.01}S_{2.01}O₈. The holotype specimen (#1 in Table 1) of hermannjahnite $(Cu_{1,31}Zn_{0,43}Mg_{0,25}S_{2,00}O_8)$ is depleted by both Zn and Mg and enriched by Cu in comparison with the cotype. A similar situation was reported for dravertite compositional variation of Cu_{0.94-1.30}Mg_{0.57-0.98}Mn_{0.00-} _{0.02}Zn_{0.07-0.45}S_{1.97-2.02}O₈ (Pekov et al. 2017). Thus, hermannjahnite and dravertite form a solid-solution series covering the following compositional field (simplified to major cations): Cu_{0.9-1.3}Mg_{0.2-1.0}Zn_{0.1-0.7}S_{2.0}O₈. Hermannjahnite and dravertite may contain up to 30% of Cu2+ in the Zn- or Mg-dominant site, respectively. Substitution in the Cudominant site by the admixture of Mg and Zn is much less preferable due to the Jahn-Teller effect. This is indirectly confirmed by the higher Cu deficiency in some analyses of hermannjahnite (## 5 and 6 in Table 1) compared to dravertite, and distinct admixture of Zn (up to 1.6 wt.% ZnO) but not Mg in chalcocyanite (#8 in Table 1). Hermannjahnite can be also described as an intermediate phase in the chalcocyanitedravertite-'zinkosite' ternary field.

The intimate association of chemically and structurally similar minerals as hermannjahnite and chalcocyanite may arise from their common exhalative origin from volcanic gases at both localities (FTE and GTFE). The occurrence of hermannjahnite in both localities as well as observation of similar Cu-rich sulphate mineral associations indicates the similarity of exhalative post-eruption processes at Tolbachik Fissure Eruption and GTFE. Zinc is the dominant constituent in a number of mineral species in fumaroles of famous in mineral diversity at the GTFE Second scoria cone. Condensates of GTFE eruption in 1975–1976 were highly enriched in Zn compared to the recent eruption (2012–2013), where concentrations of zinc are rather low (Chaplygin et al. 2016).

Anhydrous sulphates such as chalcocyanite and hermannjahnite are unstable in air due to moisture content. But these sulphate minerals may be more widespread and stable under extra-terrestrial conditions.

Binary $MM(SO_4)_2$ ($M^{2+} = Mg$, Mn, Fe, Co, Ni, Zn, Cd) anhydrous sulphates are unknown as synthetic materials. Observation of these phases in exhalative mineral assemblages may suggest a route for synthesis by chemical vapour transport (CVT) reactions, thus emulating exhalative processes. Such methods were recently successfully applied (Kovrugin et al. 2015, 2017). Acknowledgements We are grateful to Christian L. Lengauer, an anonymous reviewer, editor-in-chief Lutz Nasdala and handling editor Nikita Chukanov for their valuable comments. Technical support by the St. Petersburg State University X-ray Diffraction and Geomodel Resource Centres is gratefully acknowledged. This work was financially supported by the Russian Science Foundation through grant 16-17-10085.

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