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WULFFITE, K₃NaCu₄O₂(SO₄)₄, AND PARAWULFFITE, K₅Na₃Cu₈O₄(SO₄)₈, TWO NEW MINERALS FROM FUMAROLE SUBLIMATES OF THE TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

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Abstract

Two chemically and structurally related new minerals were discovered in fumarolic sublimates at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia: wulffite, $K_3NaCu_4O_2(SO_4)_4$, in the Arsenatnaya fumarole with euchlorine, aphthitalite, tenorite, hematite, lammerite, johillerite, fluoborite, etc., and parawulffite, K₅Na₃Cu₈O₄(SO₄)₈, in the Yadovitaya fumarole with euchlorine, fedotovite, hematite, langbeinite, steklite, etc. Later, parawulffite was found in sublimates of fumaroles related to the 2012-2013 Tolbachik Fissure Eruption. Both minerals form prismatic crystals (wulffite: up to 1.2×2 mm; parawulffite: up to 0.3×1 mm) in clusters and crusts. They are transparent with vitreous luster, brittle, with Mohs' hardness ca 2¹/₂. Both minerals are dark green or deep emerald-green. D(meas.) is 3.23(2) and 3.35(2), and D(calc.) is 3.19 and 3.32 g cm⁻³ for wulffite and parawulffite, respectively. Both minerals are optically biaxial (+); wulffite: α 1.582(3), β 1.610(3), γ 1.715(3) and parawulffite: α 1.585(3), y 1.717(4). Chemical data (wt.%, electron-microprobe; first value is for wulffite, second one for parawulffite) are: Na₂O 4.11, 5.61; K₂O 16.46, 13.74; Rb₂O 0.95, 1.42; Cs₂O 0.65, 1.21; CuO 38.88, 38.79; ZnO 0.15, 0.18; SO₃ 39.11, 39.26; total 100.31, 100.21. The empirical formulae are: wulffite (based on 18 O apfu): Na_{1.08}(K_{2.85}Rb_{0.08}Cs_{0.04})_{52.97}(Cu_{3.99}Zn_{0.02})_{54.01} $S_{3.99}O_{18}; parawulffite (based on 36 O$ *apfu* $): Na_{2.95}(K_{4.75}Rb_{0.25}Cs_{0.14})_{\Sigma5.14}(Cu_{7.95}Zn_{0.04})_{\Sigma7.99}S_{7.99}O_{36}. Wulffite is orthorhom$ bic, $Pn2_1a$, a 14.2810(6), b 4.9478(2), c 24.1127(11) Å, V 1703.79(13) Å³, Z = 4. Parawulffite is monoclinic, P2/c, a 13.9043(10), b 4.9765(3), c 23.5855(17) Å, β 90.209(6)°, V 1631.98(19) Å³, Z = 2. The strongest reflections of their X-ray powder patterns [d,Å(I)(hkl)] are: wulffite: 9.27(100)(102), 7.16(22)(200), 3.125(16)(313, 215), 2.882(16)(411), 2.780(33) (117), 2.725(14)(413), 2.472(20)(020); parawulffite: 9.06(100)(-102, 102), 7.00(23)(200), 3.096(31)(313, -215), 2.736(33) (-117, 117), 2.492(24)(020), 2.321(26)(019, 513). The crystal structures of both minerals, solved from single-crystal X-ray diffraction data [R = 0.0721 (wulffite) and 0.0985 (parawulffite)], are closely related with respect to parts of the heteropolyhedral quasi-framework formed by the Cu–O–S chains (built up of Cu^{2+} -centered square pyramids and SO₄ tetrahedra) and the chains of NaO₆ octahedra. The new minerals differ from one another in ratios of alkali cations and their arrangement in

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cavities of the quasi-framework and in the configuration of Cu–O–S chains. Wulffite is named in honor of the Russian crystallographer Georgiy Viktorovich Wulff (1863–1925), who suggested the model of X-ray interference in crystals (1913). The name of parawulffite reflects its similarity to wulffite.

Keywords: wulffite, parawulffite, new mineral, alkali copper sulfate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka.

INTRODUCTION

The Tolbachik volcano at Kamchatka is the world-record holder in diversity of fumarolic minerals: more than 150 mineral species have been reliably identified there, including 57 new minerals (Vergasova & Filatov 2012, our data). One of the brightest mineralogical features of the Tolbachik fumaroles is the abundance and great number of copper compounds: almost 70 minerals with speciesdefining Cu including 38 IMA-approved new species. The active fumarole fields on the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–76 (GTFE) located 18 km SSW of the Ploskiy Tolbachik volcano were even evaluated as a copper occurrence potentially interesting for mining, with tenorite and different Cu sulfates as the main ore minerals (Naboko & Glavatskikh 1983). Perhaps the most widespread copper sulfates found there are fedotovite, K₂Cu₃O(SO₄)₃, and especially euchlorine, KNaCu₃O(SO₄)₃, occurring in the majority of Tolbachik fumaroles with Cu mineralization and sporadically forming incrustations up to several m² in area and up to several cm in thickness (Fedotov & Markhinin 1983, Naboko & Glavatskikh 1983, Vergasova et al. 1988, our data).

In July 2012, during fieldwork on the Second scoria cone, we found in two fumaroles dark green crusts visually similar to the typical deep green euchlorine incrustations but slightly different in color (darker) and in morphology of individual minerals. Further detailed studies of these crusts resulted in the discovery of two closely related K-Na-Cu oxysulfate minerals different from euchlorine and other earlier known natural or synthetic compounds in terms of stoichiometry and crystal structure.

In the present paper we describe these two new species. The orthorhombic mineral with the idealized formula $K_3NaCu_4O_2(SO_4)_4$ was named **wulffite** (Cyrillic: вульфит) in honor of the outstanding Russian crystallographer Georgiy (or Yuriy in another spelling) Viktorovich Wulff (1863–1925), Professor of Mineralogy and Crystallography at Moscow University. Being a specialist in the physical aspects of crystallography, Prof. Wulff was among the pioneers of X-ray diffraction studies. He suggested the model of X-ray interference in crystals (1913) and published some fundamental works showing the relationships between the crystal structure and physical

properties of minerals. The name of monoclinic **parawulffite** (Cyrillic: паравульфит), ideally $K_5Na_3Cu_8O_4(SO_4)_8$, reflects its similarity to wulffite (Greek παρά means *near*). Both minerals and their names have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (wulffite: IMA 2013–035; parawulffite: IMA 2013– 036). The type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; the catalogue numbers are 94130 (wulffite) and 94131 (parawulffite).

OCCURRENCE AND GENERAL APPEARANCE

Specimens considered as the holotypes of both minerals were collected by the authors (IVP, DIB, and ISL) in July 2012 from two active, hot fumaroles located at the apical part of the Second scoria cone of the Northern Breakthrough of the GTFE, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41'N 160°14'E, 1200 m asl). This scoria cone, formed in 1975, is a monogenetic volcano about 300 m high and approximately 0.1 km³ in volume (Fedotov & Markhinin 1983). Its fumarole fields are still active: numerous gas vents with temperatures up to 430 °C were observed by us in 2012-13. Now the fumarolic gases there are compositionally close to atmospheric air, with contents of <1 vol.% water vapor and <0.1 vol.% acid species, mainly CO₂, HF, and HCl (Zelenski et al. 2012), while in 1976-77 the gases were much more enriched in H₂O, SO₂, CO₂, HCl, and HF and some metals, including up to 115 mg m⁻³ Cu (Meniaylov *et al.* 1980).

Wulffite occurs in the Arsenatnaya fumarole discovered by us in July 2012 and described by Pekov *et al.* (2014). Arsenatnaya is a system (about 5 m long and 1–1.5 m wide) of numerous mineralized pockets located between blocks of basalt scoria and volcanic bombs at depths of 0.3 to 1.0 m from the present-day surface. The sublimate minerals are mainly represented by sulfates, arsenates, and oxides. The temperature measured using a chromel-alumel thermocouple in pockets with wulffite immediately after their uncovering in July 2013 was 360–380 °C. Initially, in 2012, wulffite was found in small amounts, but our field studies in 2013 showed that the mineral is common in this fumarole.

Wulffite forms coarse, prismatic, elongated along [010], bar- or plank-shaped crystals up to 2 mm long and up to 1.2 mm thick (Figs. 1a, b and 2), separate or combined in groups up to 1 cm across. Incrustations (up to several dozen cm² in area and up to 2 mm thick) consisting of crude crystals or, more often, irregularly shaped grains of wulffite, sometimes together with euchlorine or fedotovite, on the surface of basalt scoria or on tenorite crystal crusts (Fig. 1c) are the most common. Crystals and granular crusts of aphthitalite with numerous inclusions of separate crystals and crystal clusters of wulffite (Fig. 1a, b) are common. The new mineral is also associated with hematite, langbeinite, calciolangbeinite, arcanite, krasheninnikovite, lammerite, lammerite-β, johillerite, bradaczekite, urusovite, fluoborite, gahnite (Cu-bearing variety), orthoclase (As-bearing variety), and fluorophlogopite. Based on the rectangular crosssection of wulffite crystals (Fig. 2), we assume that the major crystal forms are pinacoids {100}, {001}, and (the terminations) {010}. Coarse crystals with more complex terminations were also observed.

The holotype of parawulffite is a single specimen found in the Yadovitaya ("Poisonous") fumarole that has been well-known since 1976 as one of the richest occurrences of copper sulfates at Tolbachik (Naboko & Glavatskikh 1983) and the type locality for 19 minerals. This fumarole is a cave about 1.5 m wide and 2 m deep. The temperature inside the Yadovitaya fumarole is still high: measurements showed up to 340 °C in 2010 (Pekov *et al.* 2012) and up to 270 °C in 2013. Its walls are covered by thick incrustations of different sublimate minerals, mainly sulfates with prevailing euchlorine or piypite in different parts of the cave.

In Yadovitaya, parawulffite occurs as incrustations (up to 1×1.5 cm in area and up to 0.7 mm thick) formed by very crude crystals or irregularly shaped grains on basalt scoria and on hematite crystal crusts. Closely associated euchlorine crystallized later and overgrows parawulffite (Fig. 3a). Other associated minerals are fedotovite, tenorite, alumoklyuchevskite, langbeinite, calciolangbeinite, chalcocyanite, steklite, orthoclase (As-bearing variety), rutile (Fe- and



FIG. 1. Wulffite: numerous deep green to dark green, coarse, prismatic crystals and their clusters included in colorless aphthitalite (a, b) and a dark green crust of partially covered twinned tenorite crystals (c). FOV: (a) 8.2 mm, (b) 2.8 mm, (c) 2.3 mm. Photo: I.V. Pekov and A.V. Kasatkin.



FIG. 2. Coarse bar-shaped crystal of wulffite (0.2 mm long) with cavernous faces. BSE (SE) image.

Sb-bearing variety), pseudobrookite, lyonsite, and lammerite. Crystals of parawulffite from Yadovitaya are imperfect, prismatic, usually elongated along [010], commonly curved, and have a blocky character. They are up to 0.4 mm long and 0.2 mm thick.

In March 2013 one of the authors (DPS) collected specimens with parawulffite in the exhalations of active fumaroles located on the new lava field under the southern slope of the Ploskiy Tolbachik volcano. This lava field was formed as a result of the 2012–2013 Tolbachik Fissure Eruption that started 27 November 2012 (Gordeev *et al.* 2013) and ended in September 2013. Unlike the Yadovitaya fumarole where parawulffite was found in only one specimen, in fumaroles related to the 2012–2013 Tolbachik Fissure

Eruption this mineral is a common constituent of the polycomponent, mainly sulfate incrustations. These crusts, up to several hundred cm² in area and up to 2-3 mm thick, formed in cracks of basalt lava for a period not longer than one month. The temperature inside the parawulffite-containing fumarole (measured using a TemPro 1200 infrared thermometer) was 620-650 °C at the time of collection. The crusts mainly consist of euchlorine, aphthitalite, parawulffite, and chalcocyanite, with subordinate amounts of ralstonite and unidentified sulfates and chlorides of Cu. K. Na. and Fe that are unstable in moist air. Chalcantite, eriochalcite, erythrosiderite, and some unidentified hydrous phases are the products of rapid alteration of these fumarolic sublimates under atmospheric conditions.

Parawulffite in fumaroles created by the 2012–2013 Tolbachik Fissure Eruption is intimately associated with euchlorine. The two minerals either form simultaneously, or parawulffite crystallizes later and overgrows euchlorine (Fig. 3b). Unlike at Yadovitaya, the new mineral here occurs as well-shaped prismatic crystals elongated along [010], typically skeletal, boxlike (Fig. 4), up to 1 mm long and up to 0.3 mm thick. Their major forms are, presumably, pinacoids {100} and {001}. The crystals are typically divergent and form numerous bush-like clusters (up to 0.5 cm across) on the surface of crusts formed by crude hexagonal tabular crystals or coarse spherulites of euchlorine (Fig. 3b).

We note that parawulffite was independently discovered in the deposits of fumaroles related to the 2012–2013 Tolbachik Fissure Eruption by G.A. Karpov with colleagues in 2013 and was reported as "phase $Na_3K_5Cu_8O_4(SO_4)_8$ ". The electron microprobe analyses, X-ray powder diffraction pattern, unit-cell



FIG. 3. Parawulffite: (a) dark green crust with overgrowing bright green euchlorine: the holotype specimen from the Yadovitaya fumarole; (b) dark green bush-like clusters of prismatic crystals on green euchlorine: typical specimen from a fumarole related to the Tolbachik eruption of 2012–13. FOV: (a) 3.5 mm, (b) 7.0 mm. Photo: I.V. Pekov and A.V. Kasatkin.

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FIG. 4. Box-like skeletal crystals of parawulffite from a fumarole related to the Tolbachik eruption of 2012–13. BSE (SE) images.

dimensions, and crystal structure data published for this phase by Karpov *et al.* (2013) undoubtedly show its identity to be parawulffite.

Wulffite and parawulffite are exhalation minerals. We believe that they were deposited directly from the gaseous phase as sublimates at temperatures not lower than 360–380 °C in fumaroles of the Second scoria cone of the GTFE and not lower than 620–650 °C in fumaroles related to the 2012–2013 Tolbachik Fissure Eruption.

PHYSICAL PROPERTIES AND OPTICAL DATA

Both new minerals are transparent with vitreous luster. Their typical color is dark green, sometimes deep emerald-green or (wulffite) deep green with a bluish hue, like dioptase. The streak of both new minerals is light green. Both are brittle, with Mohs' hardness ca. 21/2. For wulffite, three directions of perfect cleavage are observed under the microscope: two directions are parallel to elongation and the third is coplanar to (010). Parawulffite shows two directions of perfect cleavage: one, the most perfect, is parallel to elongation and the second is coplanar to (010). The fracture is stepped for wulffite and laminated for parawulffite. Density values measured by flotation in heavy liquids are 3.23(2) and 3.35(2) g cm⁻³ for wulffite and parawulffite, respectively. The corresponding values calculated from their empirical formulae are 3.19 and 3.32 g cm⁻³.

Wulffite is optically biaxial (+), $\alpha = 1.582(3)$, $\beta = 1.610(3)$, $\gamma = 1.715(3)$ (589 nm), 2V could be only estimated as medium, 2V(calc.) = 58°. Orientation: Z = b. Extinction is straight. Elongation is positive. Pleochroism is strong, with the following absorption scheme: Z (emerald-green) > Y (green, with medium saturation of color) > X (pale green).

Parawulffite is biaxial (+), $\alpha = 1.585(3)$, $\gamma = 1.717(4)$ (589 nm). Extinction is very close to straight. Elongation is positive. The most perfect cleavage is parallel to the elongation that causes the laminated fracture, and this, together with very strong pleochroism, prevented measurement of β and 2*V* values. Orientation: *Z* = *b*. Pleochroism is very strong: *Z* (deep emerald-green) > *X* (very pale green, almost colorless).

CHEMICAL COMPOSITION

Chemical data for both new minerals 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). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 3 μ m beam diameter. The standards used are as follows: NaCl (Na), orthoclase (K), Rb₂Nb₄O₁₁ (Rb), Cs₂Nb₄O₁₁ (Cs), CuFeS₂ (Cu), and ZnS (Zn, S). Chemical data (wt.%) are given in Table 1.

The empirical formula of wulffite calculated on the basis of 18 O *apfu* (Z = 4) is:

$Na_{1.08}(K_{2.85}Rb_{0.08}Cs_{0.04})_{\Sigma 2.97}(Cu_{3.99}Zn_{0.02})_{\Sigma 4.01}S_{3.99}O_{18}.$

The empirical formulae of parawulffite calculated on the basis of 36 O *apfu* (Z = 2) are: Yadovitaya fumarole (the holotype), Na_{2.95}(K_{4.75}Rb_{0.25}Cs_{0.14})_{25.14} (Cu_{7.95}Zn_{0.04})_{27.99}S_{7.99}O₃₆; and a fumarole related to the Tolbachik eruption of 2012–13, Na_{3.08}K_{4.83} Cu_{8.10}S_{7.98}O₃₆.

Both new minerals slowly dissolve in H_2O at room temperature.

7	0	4

Constituent	1	2	3	4	5
Na ₂ O	4.11 (3.76–4.29)	3.82	5.61 (5.14–6.03)	5.86	5.79
K ₂ O	16.46 (15.82–17.22)	17.43	13.74 (12.91–14.36)	13.86	14.67
Rb ₂ O	0.95 (0.64–1.16)		1.42 (1.20–1.71)	bdl	
Cs ₂ O	0.65 (0.00-1.05)		1.21 (0.96–1.42)	bdl	
CuO	38.88 (37.96-40.02)	39.25	38.79 (37.97-39.76)	39.58	39.64
ZnO	0.15 (0.00-0.39)		0.18 (0.00-0.36)	bdl	
SO ₃	39.11 (38.64-40.15)	39.50	39.26 (38.44-39.81)	39.23	39.90
Total	100.31	100.00	100.21	98.63	100.00

TABLE 1. CHE	MICAL COMPOSI	FION (wt.%) OF	F WULFFITE (1–2	2) AND PARAW	ULFFITE (3-5)
					e = = (e e)

1 – the holotype wulffite; 2 – calculated for the idealized formula $K_3NaCu_4O_2(SO_4)_4$; 3 – the holotype parawulffite from the Yadovitaya fumarole; 4 – parawulffite from a fumarole related to the Tolbachik eruption of 2012–13; 5 – calculated for the idealized formula $K_5Na_3Cu_8O_4(SO_4)_8$.

Average values from six spot analyses are given for the holotype wulffite and from four spot analyses for the holotype parawulffite specimens, ranges are in parentheses. Contents of other elements with atomic numbers higher than carbon are below detection limits (bdl), *i.e.*, < 0.02–0.1 wt.%.

X-RAY POWDER DIFFRACTION DATA

X-ray powder diffraction data for the holotype specimens of wulffite (Table 2) and parawulffite (Table 3) were collected using a STOE IPDS II diffractometer equipped with Image Plate area detector, using the Gandolfi method (MoK α radiation; detector-to-sample distance, 200 mm). Unit cell parameters refined from the powder data using a WinX^{Pow} Software (STOE and CIE GmbH 2002) are: wulffite (orthorhombic), *a* 14.265(5), *b* 4.953(1), *c* 24.111(4) Å, *V* 1704(1) Å³; and parawulffite (monoclinic), *a* 13.908(3), *b* 4.973(1), *c* 23.612(6) Å, β 90.16(2)°, *V* 1633(1) Å³.

X-ray Single-Crystal Diffraction Data and Crystal Structures

Single-crystal X-ray studies for both minerals were carried out using an Xcalibur S diffractometer equipped with a CCD detector. The data were corrected for Lorentz factor, polarization, and absorption effects using CrysAlis software. Crystal data, data collection information, and structure refinement details for the holotype specimens are given in Table 4.

The structure models of both minerals were obtained by direct methods and refined to R = 0.0721 for wulffite and R = 0.0985 for parawulffite with using the SHELX software package (Sheldrick 2008). Parawulffite is characterized by a pseudo-orthorhombic unit cell with β close to 90°. Its crystal structure was initially refined in the monoclinic space group P2/c to R = 0.2694. It was found that the studied crystal is pseudo-merohedrally twinned with twin law 1 0 0 / 0 -1 0 / 0 0 -1 which corresponds to the two-fold rotation about the orthorhombic *a* axis direction. Involving these data decreased *R* to the final

value of 0.0985. The refined twin ratio is 67:33. Wulffite is merohedrally twinned with an inversion center as a twinning operator. PLATON (Spek 2003) did not detect higher metric or crystallographic symmetry for either of the studied minerals. Atom coordinates, their displacement parameters, and bond valence sums are given in Table 5 for wulffite and in Table 6 for parawulffite. Selected interatomic distances in the structures of both minerals are presented in Table 7.

Unfortunately, even the best of all tested single crystals of parawulffite was not of very high quality due to slightly divergent character, causing the somewhat high value of R = 9.85%. However, reasonable values of displacement parameters (Table 6) and interatomic distances (Table 7), as well as good accordance with the measured and calculated X-ray powder-diffraction patterns (Table 3), show that our crystal structure data are correct.

The crystal structures of wulffite (Fig. 5a) and parawulffite (Fig. 5b) contain, as a basic unit, a heteropolyhedral quasi-framework formed by Cu-O-S chains and chains of NaO₆ octahedra [Na(1)O₆ in parawulffite]. In both minerals the heteropolyhedral Cu-O-S chains run along [010] and are built of Cu-centered polyhedra with (4+1) Cu²⁺ coordination (square pyramids) and SO₄ tetrahedra (Fig. 6a, b). For better clarity, all Cu-centered polyhedra in Figures 5 and 6 are shown as approximately planar squares whereas the fifth, apical vertices of pyramids (with elongated Cu-O distances) are not included in the polyhedra. Four crystallographically independent Cu atoms are involved in the construction of the chains. Approximately flat Cu-centered squares form two pairs [Cu(1)-Cu(4) and Cu(2)-Cu(3)] sharing O-O edges. Adjacent pairs share common vertices and are located almost perpendicular to each other. Two of four short Cu-O bonds involve O atoms bound only to Cu, whereas two other O atoms belong

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR WULFFITE

412.06512.0560021009.271009.212102227.76277.141200116.049146.02800415.55515.55410454.6292, 64.670, 4.606301, 20414.41914.42830214.22214.21301324.06624.06721033.87733.86910653.74243.73630473.578103.57040033.4422, 13.453, 3.423015, 40223.36223.357115163.12511, 123.155, 3.109313, 21563.0313, 33.048, 3.014116, 008162.8825, 172.895, 2.875410, 411332.7802, 1, 382.791, 2.777, 2.773307, 208, 117142.725172.72441322.63212.629217202.47219, 92.474, 2.461020, 511132.3662, 8, 82.369, 2.364, 2.356601, 513, 01922.2881, 12.289, 2.025024, 2.0.1042.24162.23721942.1395, 12.136, 2.134611, 60522.07522.07350822.0221, 1 <th>I_{obs}</th> <th>$d_{\rm obs}$</th> <th>I_{calc}*</th> <th>d_{calc}**</th> <th>h k l</th>	I _{obs}	$d_{\rm obs}$	I _{calc} *	d _{calc} **	h k l
100 9.27 100 9.212 102 22 7.16 27 7.141 200 11 6.049 14 6.028 004 1 5.555 1 5.554 104 5 4.629 $2, 6$ $4.670, 4.606$ $301, 204$ 1 4.419 1 4.428 302 1 4.222 1 4.213 013 2 4.066 2 4.067 210 3 3.877 3 3.869 106 5 3.742 4 3.736 304 7 3.578 10 3.570 400 3 3.442 $2, 1$ $3.453, 3.423$ $015, 402$ 2 3.362 2 3.357 115 16 3.125 $11, 12$ $3.155, 3.109$ $313, 215$ 6 3.031 $3, 3$ $3.048, 3.014$ $116, 008$ 16 2.882 $5, 17$ $2.895, 2.875$ $410, 411$ 33 2.780 $2, 1, 38$ $2.791, 2.777, 2.773$ $307, 208, 117$ 14 2.725 17 2.724 413 2 2.632 1 2.629 217 20 2.472 $19, 9$ $2.474, 2.461$ $020, 511$ 13 2.366 $2, 8, 8$ $2.369, 2.364, 2.356$ $601, 513, 019$ 2 2.022 $1, 1$ 2.286 $024, 2.0.10$ 4 2.241 6 2.237 219 4 2.139 $5, 1, 4$	4	12.06	5	12.056	002
227.16277.14120011 6.049 14 6.028 0041 5.555 1 5.554 1045 4.629 2, 6 $4.670, 4.606$ 301, 2041 4.419 1 4.428 3021 4.222 1 4.213 0132 4.066 2 4.067 2103 3.877 3 3.869 1065 3.742 4 3.736 3047 3.578 10 3.570 4003 3.442 2, 1 $3.453, 3.423$ 015, 4022 3.362 2 3.357 11516 3.125 11, 12 $3.155, 3.109$ 313, 2156 3.031 $3, 3$ $3.048, 3.014$ 116, 00816 2.882 $5, 17$ $2.895, 2.875$ 410, 41133 2.780 $2, 1, 38$ $2.791, 2.777, 2.773$ $307, 208, 117$ 14 2.725 17 2.724 4132 2.632 1 2.629 21720 2.472 19, 9 $2.474, 2.461$ 020, 51113 2.366 $2, 8, 8$ $2.369, 2.364, 2.356$ 601, 513, 0192 2.288 1, 1 $2.289, 2.285$ 024, 2.0.104 2.241 6 2.237 2194 2.139 5, 1 $2.136, 2.134$ 611, 6052 2.075 2 2.073 508 2 2.022 1, 1 $2.026, 2.021$ $421, $	100	9.27	100	9.212	102
11 6.049 14 6.028 004 1 5.555 1 5.554 104 5 4.629 2, 6 $4.670, 4.606$ $301, 204$ 1 4.419 1 4.428 302 1 4.222 1 4.213 013 2 4.066 2 4.067 210 3 3.877 3 3.869 106 5 3.742 4 3.736 304 7 3.578 10 3.570 400 3 3.442 2, 1 $3.453, 3.423$ $015, 402$ 2 3.362 2 3.357 115 16 3.125 $11, 12$ $3.155, 3.109$ $313, 215$ 6 3.031 $3, 3$ $3.048, 3.014$ $116, 008$ 16 2.882 $5, 17$ $2.895, 2.875$ $410, 411$ 33 2.780 $2, 1, 38$ $2.791, 2.777, 2.773$ $307, 208, 117$ 14 2.725 17 2.724 413 2 2.632 1 2.629 217 20 2.472 $19, 9$ $2.474, 2.461$ $020, 511$ 13 2.366 $2, 8, 8$ $2.369, 2.364, 2.356$ $601, 513, 019$ 2 2.288 $1, 1$ 2.287 219 4 2.139 $5, 1$ $2.136, 2.134$ $611, 605$ 2 2.075 2 2.073 508 2 2.022 $1, 1$ $2.026, 2.021$ $421, 226$ 3 1.995 $1, 4$ $1.998, 1.985$ $325, 1.1.11$	22	7.16	27	7.141	200
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11	6.049	14	6.028	004
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	5.555	1	5.554	104
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	4.629	2, 6	4.670, 4.606	301, 204
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	4.419	1	4.428	302
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	4.222	1	4.213	013
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	4.066	2	4.067	210
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	3.877	3	3.869	106
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	3.742	4	3.736	304
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	3.578	10	3.570	400
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	3.442	2, 1	3.453, 3.423	015, 402
16 3.125 11, 12 $3.155, 3.109$ $313, 215$ 6 3.031 $3, 3$ $3.048, 3.014$ $116, 008$ 16 2.882 $5, 17$ $2.895, 2.875$ $410, 411$ 33 2.780 $2, 1, 38$ $2.791, 2.777, 2.773$ $307, 208, 117$ 14 2.725 17 2.724 413 2 2.632 1 2.629 217 20 2.472 $19, 9$ $2.474, 2.461$ $020, 511$ 13 2.366 $2, 8, 8$ $2.369, 2.364, 2.356$ $601, 513, 019$ 2 2.288 $1, 1$ $2.289, 2.285$ $024, 2.0.10$ 4 2.241 6 2.237 219 4 2.139 $5, 1$ $2.136, 2.134$ $611, 605$ 2 2.075 2 2.073 508 2 2.022 $1, 1$ $2.026, 2.021$ $421, 226$ 3 1.995 $1, 4$ $1.998, 1.985$ $325, 1.1.11$ 2 1.929 $1, 2$ $1.927, 1.926$ $424, 326$ 1 1.896 1 1.895 128 4 1.850 $2, 1, 2$ 1.695 526 2 1.651 $1, 2$ 1.695 526 2 1.584 1 1.586 $2.1.14$ 2 1.561 2 1.562 $4.1.13$ 2 1.584 1 1.530 333 3 1.499 $2, 1$ $1.499, 1.497$ $1.0.16, 430$ 3 3.1499 $2, 1$ $1.499, 1.497$ $1.0.16, 430$ <tr< td=""><td>2</td><td>3.362</td><td>2</td><td>3.357</td><td>115</td></tr<>	2	3.362	2	3.357	115
	16	3.125	11, 12	3.155. 3.109	313, 215
162.8825, 172.895, 2.875410, 411332.7802, 1, 382.791, 2.777, 2.773307, 208, 117142.725172.72441322.63212.629217202.47219, 92.474, 2.461020, 511132.3662, 8, 82.369, 2.364, 2.356601, 513, 01922.2881, 12.289, 2.285024, 2.0.1042.24162.23721942.1395, 12.136, 2.134611, 60522.07522.07350822.0221, 12.026, 2.021421, 22631.9951, 41.985325, 1.1.1121.9291, 21.927, 1.926424, 32611.89611.89512841.8502, 1, 21.851, 1.847, 1.8463.0.12, 522, 22411.78721.78580031.69321.69552621.6511, 21.654, 1.650717, 62421.58411.5862.1.1421.58411.53033331.4992, 11.499, 1.4971.0.16, 43051.4815, 31.480, 1.478137, 5.2.1021.4291, 1, 11.429, 1.428, 1.4264.2.12, 10.00, 55	6	3.031	3. 3	3.048. 3.014	116, 008
332.7802, 1, 382.791, 2.777, 2.773307, 208, 117142.725172.72441322.63212.629217202.47219, 92.474, 2.461020, 511132.3662, 8, 82.369, 2.364, 2.356601, 513, 01922.2881, 12.289, 2.285024, 2.0.1042.24162.23721942.1395, 12.136, 2.134611, 60522.07522.07350822.0221, 12.026, 2.021421, 22631.9951, 41.998, 1.985325, 1.1.1121.9291, 21.927, 1.926424, 32611.89611.89512841.8502, 1, 21.851, 1.847, 1.8463.0.12, 522, 22411.78721.78580031.69321.69552621.6511, 21.654, 1.650717, 62421.59131.58952821.58411.5862.1.1421.58411.5862.1.1421.53111.53033331.4992, 11.499, 1.4971.0.16, 43051.4815, 31.480, 1.478137, 5.2.1021.4291, 1, 11.429, 1.428, 1.4264.2.12, 10.00, 55	16	2.882	5. 17	2.895. 2.875	410, 411
142.725172.72441322.63212.629217202.47219,92.474, 2.461020, 511132.3662,8,82.369, 2.364, 2.356601, 513, 01922.2881,12.289, 2.285024, 2.0.1042.24162.23721942.1395,12.136, 2.134611, 60522.07522.07350822.0221,12.026, 2.021421, 22631.9951,41.998, 1.985325, 1.1.1121.9291,21.927, 1.926424, 32611.89611.89512841.8502, 1, 21.851, 1.847, 1.8463.0.12, 522, 22411.78721.78580031.69321.69552621.6511, 21.654, 1.650717, 62421.59131.58952821.58411.5862.1.1421.53111.53033331.4992, 11.499, 1.4971.0.16, 43051.4815, 31.480, 1.478137, 5.2.1021.4291, 1, 11.429, 1.4264.2.12, 10.00, 55	33	2.780	2. 1. 38	2.791. 2.777. 2.773	307. 208. 117
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14	2.725	17	2.724	413
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	2.632	1	2.629	217
132.3662, 8, 82.369, 2.364, 2.356601, 513, 01922.2881, 12.289, 2.285024, 2.0.1042.24162.23721942.1395, 12.136, 2.134611, 60522.07522.07350822.0221, 12.026, 2.021421, 22631.9951, 41.998, 1.985325, 1.1.1121.9291, 21.927, 1.926424, 32611.89611.89512841.8502, 1, 21.851, 1.847, 1.8463.0.12, 522, 22411.78721.78580031.69321.69552621.6511, 21.654, 1.650717, 62421.59131.58952821.58411.5862.1.1421.56121.5624.1.1321.53111.53033331.4992, 11.499, 1.4971.0.16, 43051.4815, 31.480, 1.478137, 5.2.1021.4291, 1, 11.429, 1.4264.2.12, 10.0.0, 55	20	2.472	19. 9	2.474. 2.461	020. 511
22.2881, 12.289, 2.285 $024, 2.0.10$ 42.24162.23721942.1395, 12.136, 2.134611, 60522.07522.07350822.0221, 12.026, 2.021421, 22631.9951, 41.998, 1.985325, 1.1.1121.9291, 21.927, 1.926424, 32611.89611.89512841.8502, 1, 21.851, 1.847, 1.8463.0.12, 522, 22411.78721.78580031.69321.69552621.6511, 21.654, 1.650717, 62421.59131.58952821.58411.5862.1.1421.56121.5624.1.1331.4992, 11.499, 1.4971.0.16, 43051.4815, 31.480, 1.478137, 5.2.1021.4291, 1, 11.429, 1.4264.2.12, 10.0.0, 55	13	2.366	2. 8. 8	2.369, 2.364, 2.356	601, 513, 019
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	2.288	1. 1	2.289. 2.285	024, 2.0,10
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	2.241	6	2.237	219
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	2.139	5. 1	2.136. 2.134	611, 605
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	2.075	2	2.073	508
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	2.022	1. 1	2.026. 2.021	421, 226
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.995	1. 4	1.998, 1.985	325, 1.1.11
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	1.929	1, 2	1.927, 1.926	424, 326
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1	1.896	1	1.895	128
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	1.850	2, 1, 2	1.851, 1.847, 1.846	3.0.12, 522, 228
3 1.693 2 1.695 526 2 1.651 1, 2 1.654, 1.650 717, 624 2 1.591 3 1.589 528 2 1.584 1 1.586 2.1.14 2 1.561 2 1.562 4.1.13 2 1.531 1 1.530 333 3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.426 4.2.12, 10.0.0, 55	1	1.787	2	1.785	800
2 1.651 1, 2 1.654, 1.650 717, 624 2 1.591 3 1.589 528 2 1.584 1 1.586 2.1.14 2 1.561 2 1.562 4.1.13 2 1.531 1 1.530 333 3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.426 4.2.12, 10.0.0, 53	3	1.693	2	1.695	526
2 1.591 3 1.589 528 2 1.584 1 1.586 2.1.14 2 1.561 2 1.562 4.1.13 2 1.531 1 1.530 333 3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.426 4.2.12, 10.0.0, 55	2	1.651	1, 2	1.654, 1.650	717, 624
2 1.584 1 1.586 2.1.14 2 1.561 2 1.562 4.1.13 2 1.531 1 1.530 333 3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1 1.429, 1.426 4.2.12, 10.0.0, 53	2	1.591	3	1.589	528
2 1.561 2 1.562 4.1.13 2 1.531 1 1.530 333 3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.426 4.2.12, 10.0.0, 55	2	1.584	1	1.586	2.1.14
2 1.531 1 1.530 333 3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.426, 1.426 4.2.12, 10.0.0, 53	2	1.561	2	1.562	4.1.13
3 1.499 2, 1 1.499, 1.497 1.0.16, 430 5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.428, 1.426 4.2.12, 10.0.0, 55	2	1.531	1	1.530	333
5 1.481 5, 3 1.480, 1.478 137, 5.2.10 2 1.429 1, 1, 1 1.429, 1.428, 1.426 4.2.12, 10.0.0, 53	3	1.499	2. 1	1.499. 1.497	1.0.16, 430
2 1.429 1, 1, 1 1.429, 1.428, 1.426 4.2.12, 10.0.0, 55	5	1.481	5.3	1.480, 1.478	137. 5.2.10
	2	1.429	1, 1, 1	1.429, 1.428, 1.426	4.2.12. 10.0.0. 531
2 1.408 1.2 1.413. 1.406 0.2.14. 533	2	1.408	1. 2	1.413. 1.406	0.2.14. 533
2 1.378 1.1 1.378, 1.378 239, 8,1,10	2	1.378	1, 1	1.378, 1.378	239. 8.1.10
1 1.333 1 1.333 5.0.16	1	1.333	1	1.333	5.0.16
1 1.326 1 1.327 922	1	1.326	1	1.327	922
1 1.274 2 1.274 4.1.17	1	1.274	2	1.274	4.1.17
2 1.239 1.1 1.239 1.237 735.040	2	1.239	1. 1	1,239, 1,237	735.040
1 1.220 2 1.221 10.1.9	1	1.220	2	1.221	10.1.9
1 1.182 1 1.183 6.1.17	1	1.182	1	1.183	6.1.17

* Only reflections with intensities \geq 1 are given. ** Calculated from single-crystal data.

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TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR PARAWULFFITE

I _{obs}	d _{obs}	I _{calc} *	d _{calc} **	hkl
100	9.06	100, 93	9.010, 8.977	-102, 102
23	7.00	49	6.952	200
12	5.903	23	5.896	004
1	5.423	1	5.421	104
6	4.507	5, 8	4.505, 4.489	-204, 204
3	4.309	2	4.308	302
4	4.225	3	4.205	013
2	4.028	2	4.023	113
6	3.805	11	3.786	- 106
3	3.659	5	3.650	-304
3	3.645	4	3.637	304
4	3.605	1	3.601	-213
6	3.439	11, 2, 7	3.476, 3.427, 3.424	400, -206, 015
5	3.343	3, 1	3.358, 3.340	-311, -214
31	3.096	46, 45	3.111, 3.075	313, -215
6	2.889	1, 3	2.886, 2.882	—108, 108
8	2.831	11, 9	2.830, 2.828	—411, 411
33	2.736	38, 25	2.737, 2.734	<i>—</i> 117, 117
11	2.674	10, 23	2.682, 2.677	-413, 413
24	2.492	2, 41	2.497, 2.488	- 118, 020
8	2.413	4, 10	2.416, 2.414	-511, 511
26	2.321	4, 13, 18	2.324, 2.319, 2.317	1.0.10, 019, 513
5	2.204	17	2.202	-219
2	2.155	1, 2	2.156, 2.156	-322, 515
2	2.090	1, 4	2.093, 2.092	—611, 611
3	2.062	1, 1	2.063, 2.056	516, -324
1	2.022	1, 1	2.028, 2.016	613, 421
6	1.959	11	1.960	-702
4	1.921	3, 4	1.922, 1.917	227, 615
2	1.869	1	1.871	518
4	1.831	4, 7, 4	1.833, 1.832, 1.825	228, -522, -608
1	1.789	1	1.789	129
2	1.701	3	1.698	1.2.10
2	1.677	4, 1	1.679, 1.673	-526, -1.0.14
2	1.665	1, 2, 4	1.667, 1.665, 1.661	428, 804, 2.2.10
2	1.641	2, 3	1.642, 1.639	-619, -2.0.14
2	1.634	1, 6	1.636, 1.631	811, -624
1	1.604	1, 5	1.604, 1.604	5.1.11, 3.2.10
2	1.584	1, 1	1.585, 1.583	-3.0.14, -2.2.11
5	1.532	5, 6, 3	1.532, 1.532, 1.531	1.2.12, 3.2.11, 902
3	1.507	2, 2	1.510, 1.505	-334, 2.2.12
2	1.500	1	1.498	6.1.11
4	1.478	5, 4	1.480, 1.479	-137, 137
3	1.416	2	1.418	-337
3	1.410	2	1.408	4.2.12
3	1.376	3	1.374	-239
1	1.337	1, 2, 2	1.337, 1.337, 1.336	-729, 10.1.1, 0.1.17
2	1.305	1, 1	1.304, 1.304	-5.0.16, 922
1	1.296	1, 2	1.296, 1.296	635, -4.2.14
2	1.263	1, 1	1.263, 1.263	-1.2.16, -3.3.11

* Only reflections with intensities ≥ 1 are given. ** Calculated from single-crystal data.

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TABLE 4. CRYSTAL DATA, DATA COLLECTION INFORMATION AND STRUCTURE REFINEMENT DETAILS FOR WULFFITE AND PARAWULFFITE

Mineral	Wulffite	Parawulffite		
Formula	K₃NaCu₄O₂(SO₄)₄	K₅Na₃Cu₂O₄(SO₄)₃		
Formula weight	810.69	1605.27		
Temperature, K	293(2)			
Radiation (wavelength, Å)	MoK _a (0.710)73)		
Crystal system, space group; Z	Orthorhombic, <i>Pn</i> 2₁a*; 4	Monoclinic, P2/c; 2		
Unit cell dimensions, Å	a = 14.2810(6)	a = 13.9043(10)		
	b = 4.9478(2)	$b = 4.9765(3) \beta = 90.209(6)$		
	c = 24.1127(11)	c = 23.5855(17)		
V, Å ³	1703.79(13)	1631.98(19)		
a : b : c	2.886 : 1 : 4.873	2.794 : 1 : 4.739		
Absorption coefficient μ , mm ⁻¹	6.27	6.43		
F000	1568	1552		
Crystal size, mm	0.05 imes 0.09 imes 0.12	0.03 imes 0.05 imes 0.10		
Diffractometer	Xcalibur S C	Xcalibur S CCD		
θ range for data collection, °	2.85-26.37	2.93-24.10		
Index ranges	$-17 \le h \le 17$	<i>−</i> 15 ≤ <i>h</i> ≤ 15		
J. J	$-6 \le k \le 6$	$-5 \leq k \leq 5$		
	$-30 \le l \le 30$	$-27 \le l \le 27$		
Reflections collected	23976	20172		
Independent reflections	3474 (R _{int} = 0.0928)	2583 (R _{int} = 0.1158)		
Independent reflections with $l > 2\sigma(l)$	3364	2406		
Structure solution	direct metho	ods		
Refinement method	full-matrix least-squ	full-matrix least-squares on F^2		
Number of refined parameters	265	181		
Final R indices [/>2σ(/)]	<i>R</i> 1 = 0.0721	<i>R</i> 1 = 0.0985		
	wR2 = 0.1597	wR2 = 0.1898		
R indices (all data)	<i>R</i> 1 = 0.0746	<i>R</i> 1 = 0.1048		
	wR2 = 0.1610	wR2 = 0.1932		
GoF	1.192	1.244		
Largest diff. peak and hole, e/Å ³	1.962 and -1.144	2.036 and -1.207		

* A non-standard setting was chosen for wulffite to emphasize the similarity of the unit cells of these two minerals.

to two SO₄ groups in the same chain. The elongated Cu–O bonds with the oxygen atoms of the third SO₄ group in the same chain complete the (4+1) coordination of Cu cations forming square pyramids. The difference in the configuration of the Cu–O–S chains in wulffite and parawulffite is mainly caused by the arrangement of the Cu(3)-centered square pyramids and S(2)O₄ tetrahedra in wulffite. The pairs of Cu(1) and Cu(4) square pyramids in wulffite and parawulffite are topologically close: the fifth, elongated Cu–O bonds are located in opposite directions to each other. The same situation is observed in the Cu(2)–Cu(3) pair in parawulffite, whereas in wulffite the elongated Cu–O bonds have the same direction.

The structures of wulffite and parawulffite also differ in those parts involving alkali cations.

In wulffite, the Cu–O–S chains are interconnected via distorted NaO₆ octahedra, nine-coordinated K(1) and K(3) polyhedra, and ten-coordinated K(2) polyhedra. Adjacent Na-centered octahedra share vertices to form chains stretching along [010]. Each chain of

Na-centered octahedra is connected with four Cu–O–S chains; three of them are linked *via* common vertices of NaO₆ octahedra and S(2–4)O₄ tetrahedra, and the fourth is connected *via* a common edge of the NaO₆ octahedron and the S(1)O₄ tetrahedron [thus the NaO₆ octahedron has one common vertex with the Cu(2)-centered polyhedron].

In parawulffite, the Cu–O–S chains are interconnected *via* six-coordinated Na(1) and Na(2) polyhedra, ten-coordinated K(1) and K(2) polyhedra, and twelve-coordinated K(3) polyhedra. Na(1) and Na(2) play different roles in the structure of parawulffite. Na(1) cations occupy distorted octahedra. Adjacent Na(1)O₆ octahedra share vertices to form chains along [010], like those in wulffite. Isolated Na(2) polyhedra could be described as very strongly distorted octahedra derived from trigonal prisms by slight rotation of their base pinacoids. These polyhedra connect two Cu–O–S chains by sharing vertices with SO₄ tetrahedra and faces with Cu five-coordinated polyhedra. K(2)- and K(3)-centered polyhedra share common

TABLE 5. ATOM COORDINATES, DISPLACEMENT PARAMETERS (Å²), AND BOND VALENCE SUMS (Σ s) FOR WULFFITE

Atom	xla	y/b	z/c	$U_{ m eq}$	Σs
Cu(1)	0.65321(10)	0.0531(3)	0.64271(7)	0.0143(4)	1.96
Cu(2)	0.76460(10)	0.5567(3)	0.69678(6)	0.0135(4)	2.03
Cu(3)	0.76073(11)	0.6130(3)	0.57822(6)	0.0135(4)	1.98
Cu(4)	0.85352(10)	0.1155(3)	0.62676(6)	0.0111(3)	2.13
S(1)	0.7301(2)	0.0632(8)	0.77288(13)	0.0157(7)	6.08
S(2)	0.7334(2)	0.0998(7)	0.50151(12)	0.0141(6)	6.14
S(3)	0.5170(2)	0.5521(7)	0.62741(13)	0.0145(7)	6.07
S(4)	0.9845(2)	0.6059(7)	0.64249(14)	0.0150(7)	5.93
K(1)*	0.9644(2)	0.0111(8)	0.76325(15)	0.0283(12)	1.30***
K(2)*	0.0705(2)	0.5784(7)	0.04241(13)	0.0309(11)	0.88
K(3)*	0.1210(2)	0.0950(9)	0.57395(15)	0.0331(12)	0.98
Na	0.7403(3)	0.0695(13)	0.3495(2)	0.0190(11)	1.20
O(1)	0.7669(7)	0.840(2)	0.6434(4)	0.013(2)	2.12
O(2)	0.7444(6)	0.337(2)	0.6320(4)	0.007(2)**	2.11
O(3)	0.7300(6)	0.103(2)	0.8328(3)	0.019(2)	2.06
O(4)	0.7576(7)	0.395(2)	0.5098(4)	0.019(2)	2.02
O(5)	0.0850(6)	0.562(3)	0.6346(4)	0.025(2)	1.93
O(6)	0.5350(7)	0.260(2)	0.6403(4)	0.021(2)	2.11
O(7)	0.4217(8)	0.615(3)	0.6447(4)	0.035(3)**	1.93
O(8)	0.9661(7)	0.901(2)	0.6294(5)	0.026(3)	2.06
O(9)	0.9296(7)	0.439(2)	0.6027(4)	0.020(2)	1.95
O(10)	0.6399(6)	0.099(2)	0.7466(4)	0.027(2)	2.03
O(11)	0.7641(8)	0.782(2)	0.7632(4)	0.019(2)	2.23
O(12)	0.7976(7)	0.254(2)	0.7474(5)	0.022(2)	2.12
O(13)	0.5813(7)	0.717(2)	0.6614(5)	0.023(2)	2.04
O(14)	0.6409(7)	0.045(3)	0.5233(6)	0.051(4)	1.85
O(15)	0.9526(8)	0.552(3)	0.6982(5)	0.039(3)	1.95
O(16)	0.7417(8)	0.043(3)	0.4437(4)	0.035(3)	2.15
O(17)	0.8025(8)	0.938(2)	0.5331(4)	0.026(3)	1.99
O(18)	0.5327(11)	0.596(3)	0.5688(4)	0.051(4)	2.03

* e_{ref} values for K(1), K(2) and K(3) are 18.45, 20.65 and 18.64, respectively.

** U_{iso}. *** Could be slightly decreased if Na partially substitutes K.

Parameters for bond valence calculations were taken from Brese & O'Keeffe 1991.

edges and faces to form corrugated layers coplanar to (001); adjacent layers are connected via [010] chains of edge-sharing K(1)-centered polyhedra.

INFRARED SPECTROSCOPY

Infrared (IR) absorption spectra of wulffite and parawulffite were obtained for powdered samples mixed with anhydrous KBr and pelletized. The pellets were analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm⁻¹ and 16 scans. An IR spectrum of an analogous pellet of pure KBr was used as a reference.

Absorption bands in the IR spectra (Fig. 7) and their assignments (cm⁻¹, s – strong band, sh – shoulder) are (wulffite // parawulffite): 1223, 1198, 1153s, 1118s // 1212s, 1202s, 1149s, 1116s [$\nu_3(F_2)$ – asymmetric stretching vibrations of SO₄^{2–} anions], 1026s,

989s // 1036s, 1006s, 981s $[\nu_1(A_1) - \text{symmetric}$ stretching vibrations of SO₄²⁻ anions], 671, 645sh, 635, 612 // 690, 665, 642, 618, 572, 550 $[\nu_4(F_2)$ bending vibrations of SO₄²⁻ anions], 535sh, 511 // 503, 450 [lattice modes involving stretching vibrations of shorter bonds in Cu-centered polyhedra with (4+1) Cu²⁺ coordination and possibly the $\nu_2(E)$ bending mode of SO₄²⁻ anions]. Characteristic bands of BO₃³⁻, CO₃²⁻, NO₃⁻, and hydrogen-bearing groups are absent in the IR spectra of wulffite and parawulffite.

Very strong intensities of non-degenerate $\nu_1(A_1)$ bands in the IR spectra of both new minerals reflect strong distortions of SO₄ tetrahedra (see Table 7). In wulffite, among four non-equivalent SO₄^{2–} groups, three tetrahedra have mean S–O distances from 1.4675 to 1.4697 Å and correspond to the higher frequency and stronger $\nu_1(A_1)$ band at 1026 cm⁻¹; the

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Atom	x/a	y/b	z/c	U _{eq}	Q	Σs
Cu(1)	0.2150(2)	0.2281(5)	0.41922(11)	0.0161(7)	4	1.97
Cu(2)	0.28352(19)	0.2730(5)	0.30366(11)	0.0104(6)	4	1.97
Cu(3)	0.35119(19)	0.7236(5)	0.38614(11)	0.0114(6)	4	1.98
Cu(4)	0.15409(18)	0.7840(5)	0.34538(11)	0.0099(6)	4	2.07
S(1)	0.2528(4)	0.7670(10)	0.2232(2)	0.0114(11)	4	6.14
S(2)	0.2272(4)	0.7429(10)	0.4983(2)	0.0132(11)	4	6.10
S(3)	0.4862(4)	0.2384(10)	0.3760(2)	0.0108(11)**	4	6.24
S(4)	0.0134(4)	0.3017(10)	0.3544(2)	0.0105(11)	4	5.86
K(1)*	0.5	0.7941(15)	0.25	0.025(3)	2	0.88
K(2)*	0.3875(5)	0.2565(13)	0.5463(3)	0.066(4)	4	0.95
K(3)*	0.9256(6)	0.7842(11)	0.4356(4)	0.085(4)	4	0.90
Na(1)	0.7445(6)	0.7423(15)	0.8508(4)	0.016(2)	4	1.20
Na(2)	0.0	0.857(3)	0.25	0.029(3)	2	1.22
O(1)	0.2520(10)	0.737(3)	0.1629(6)	0.014(3)**	4	2.05
O(2)	0.2956(9)	0.036(3)	0.2353(6)	0.011(3)**	4	2.13
O(3)	0.3174(10)	0.565(3)	0.2492(7)	0.017(3)**	4	2.08
O(4)	0.1581(10)	0.739(3)	0.2493(6)	0.014(3)**	4	2.02
O(5)	0.1623(10)	0.901(3)	0.4625(6)	0.013(3)**	4	2.01
O(6)	0.3257(11)	0.804(3)	0.4829(7)	0.023(4)**	4	1.96
O(7)	0.2100(10)	0.813(3)	0.5577(6)	0.014(3)**	4	2.06
O(8)	0.2094(10)	0.449(3)	0.4895(6)	0.014(3)**	4	2.09
O(9)	0.4567(11)	0.292(3)	0.3189(6)	0.019(4)**	4	1.99
O(10)	0.0351(11)	0.271(3)	0.4163(6)	0.018(4)**	4	1.75
O(11)	0.9152(12)	0.232(4)	0.3408(7)	0.030(4)**	4	1.91
O(12)	0.5852(11)	0.282(3)	0.3868(7)	0.020(4)**	4	2.20
O(13)	0.4298(11)	0.401(3)	0.4161(7)	0.020(4)**	4	1.96
O(14)	0.2650(9)	0.000(3)	0.3592(6)	0.009(3)**	4	2.08
O(15)	0.2413(9)	0.503(3)	0.3667(5)	0.002(3)**	4	2.06
O(16)	0.4683(10)	0.943(3)	0.3910(6)	0.014(3)**	4	2.01
O(17)	0.0302(10)	0.584(3)	0.3367(6)	0.010(3)**	4	2.14
O(18)	0.0815(11)	0.121(3)	0.3223(7)	0.019(4)**	4	1.93

TABLE 6. ATOM COORDINATES, DISPLACEMENT PARAMETERS (Å²), SITE MULTIPLICITIES (Q), AND BOND VALENCE SUMS (Σ s) FOR PARAWULFFITE

* e_{ref} values for K(1), K(2), and K(3) are 19.38, 20.33, and 22.04, respectively. ** U_{iso}. Parameters for bond valence calculations were taken from Brese & O'Keeffe (1991).

fourth tetrahedron with a mean S–O distance of 1.479 Å corresponds to the weaker, lower frequency band at 989 cm⁻¹. In parawulffite, three SO₄^{2–} groups have mean S–O distances from 1.465 to 1.467 Å and correspond to the higher-frequency $\nu_1(A_1)$ bands at 1036 cm⁻¹ (with shoulder at 1020 cm⁻¹) and at 1006 cm⁻¹; the fourth tetrahedron with S–O 1.479 Å corresponds to the weaker lower frequency band at 981 cm⁻¹. Note that in the IR spectrum of parawulffite, which has stronger distortion of one SO₄ tetrahedron (with differences between S–O bond lengths reaching 0.103 Å) as compared to wulffite, stronger splitting of the $\nu_1(A_1)$ band is observed than for wulffite with Δ_{S-O} varying from 0.043 to 0.087 Å (Fig. 7).

The IR spectra of both new minerals are unique and can be used as good diagnostic tools. In particular, they are different from IR spectra of other oxysulfates related chemically (euchlorine) or structurally (piypite) (Figs. 7 and 8; Table 8).

DISCUSSION

Wulffite, $K_3NaCu_4O_2(SO_4)_4 = K_6Na_2Cu_8O_4$ (SO₄)₈, and parawulffite, $K_5Na_3Cu_8O_4(SO_4)_8$, have the same general stoichiometry [(K+Na):Cu:S:O ratio] and are characterized by structural Cu–O–S motifs with similar topologies. This gives rise to similarities in the general character of their X-ray powder patterns and physical properties. However, wulffite and parawulffite differ in K:Na ratio and in the ordering of K and Na atoms, which causes some individual features of each mineral and allows them to be easily distinguished. Orthorhombic wulffite with K_6Na_2 differs from monoclinic, pseudo-orthorhombic parawulffite with K_5Na_3 by increased unit cell dimensions and

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TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURES OF WULFFITE AND PARAWULFFITE

wulffite		parawulffite					
$\begin{array}{rrrr} Cu(1) \\ - & O(2) & 1. \\ - & O(1) & 1. \\ - & O(6) & 1. \\ - & O(13) & 2. \\ - & O(10) & 2. \end{array}$	934(9) 936(10) 975(11) 006(11) 522(11)	Cu(3) - O(2) - O(1) - O(4) - O(17) - O(9)	1.896(9) 1.935(9) 1.973(10) 2.030(11) 2.628(10)	Cu(1) - O(15) - O(14) - O(8) - O(5) - O(10)	1.881(13) 1.946(14) 1.991(14) 2.058(14) 2.511(15)	Cu(3) - O(14) - O(15) - O(16) - O(13) - O(6)	1.929(14) 1.936(13) 1.964(14) 2.065(16) 2.347(17)
Cu(2) - O(1) 1. - O(2) 1. - O(11) 1. - O(12) 1. - O(15) 2.	904(11) 925(9) 951(10) 989(10) 686(11)	Cu(4) - O(1) - O(2) - O(8) - O(9) - O(17)	1.883(10) 1.910(9) 1.926(10) 2.019(10) 2.530(10)	Cu(2) - O(14) - O(15) - O(3) - O(2) - O(9)	1.907(14) 1.967(13) 1.995(16) 2.007(14) 2.435(15)	Cu(4) - O(14) - O(15) - O(17) - O(18) - O(4)	1.905(14) 1.918(13) 2.001(14) 2.031(16) 2.279(14)
S(1) - O(10) 1. - O(3) 1. - O(12) 1. - O(11) 1.	447(9) 458(9) 482(11) 491(11)	S(3) - O(18) - O(7) - O(13) - O(6)	1.446(11) 1.456(11) 1.477(10) 1.501(11)	S(1) - O(1) - O(4) - O(3) - O(2)	1.431(16) 1.463(15) 1.480(15) 1.490(14)	S(3) - O(12) - O(9) - O(13) - O(16)	1.415(16) 1.430(16) 1.473(16) 1.531(15)
S(2) - O(16) 1. - O(14) 1. - O(17) 1. - O(4) 1.	426(10) 446(10) 483(11) 512(10)	S(4) - O(15) - O(5) - O(9) - O(8)	1.444(11) 1.465(9) 1.491(10) 1.519(11)	S(2) - O(6) - O(5) - O(7) - O(8)	1.450(17) 1.462(15) 1.464(15) 1.497(15)	S(4) - O(11) - O(17) - O(10) - O(18)	1.444(18) 1.483(15) 1.498(16) 1.511(16)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	555(9) 694(11) 767(15) 818(11) 864(12) 025(13) 076(11) 105(15) 274(13)	$\begin{array}{l} K(3)\\ - & O(3)\\ - & O(8)\\ - & O(5)\\ - & O(4)\\ - & O(16)\\ - & O(5)\\ - & O(17)\\ - & O(9)\\ - & O(16) \end{array}$	2.735(9) 2.756(11) 2.781(12) 2.841(11) 2.989(13) 3.059(13) 3.276(12) 3.292(11) 3.391(14)	$\begin{array}{l} K(1) \\ - & O(3) \\ - & O(9) \\ - & O(9) \\ - & O(2) \\ - & O(16) \\ \end{array}$ $\begin{array}{l} K(2) \\ - & O(16) \\ - & O(12) \\ - & O(2) \end{array}$	$2.784(14) \times 2$ $3.025(17) \times 2$ $3.044(16) \times 2$ $3.104(14) \times 2$ $3.439(14) \times 2$ 2.679(15) 2.813(17) 2.923(10)	$\begin{array}{l} K(3) \\ - & O(7) \\ - & O(8) \\ - & O(10) \\ - & O(10) \\ - & O(10) \\ - & O(5) \\ - & O(11) \\ - & O(5) \\ - & O(7) \end{array}$	2.757(16) 2.832(16) 2.930(15) 3.009(16) 3.121(16) 3.158(19) 3.394(18) 3.399(17)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	738(11) 878(15) 941(11) 975(14) 021(15) 059(11) 091(10) 237(17) 370(13) 371(14)	Na - O(16) - O(7) - O(11) - O(3) - O(5) - O(3)	2.276(11) 2.328(12) 2.334(11) 2.380(13) 2.525(9) 2.705(13)	- 0(6) - 0(8) - 0(12) - 0(13) - 0(13) - 0(6) - 0(7) - 0(1) Na(1) - 0(7) - 0(2)	2.833(18) 2.970(15) 3.132(17) 3.183(17) 3.211(18) 3.223(18) 3.323(17) 3.339(17) 2.275(17) 2.377(16)	- O(7) - O(10) - O(11) Na(2) - O(4) - O(18) - O(17)	3.523(16) 3.543(17) 3.547(19) 2.276(14) × 2 2.429(17) × 2 2.491(16) × 2
				- O(12) - O(11) - O(1) - O(1)	2.378(18) 2.390(19) 2.407(16) 2.612(16)		



FIG. 5. Crystal structures of wulffite (a), parawulffite (b), piypite (c, drawn from data in Effenberger & Zemann 1984) and euchlorine (d, drawn from data in Scordari & Stasi 1990). Unit cells are outlined. Cu-centered polyhedra in wulffite and parawulffite and Cu-centered polyhedra in piypite are shown as almost flat squares for better clarity, *Me* in piypite corresponds to the position occupied by Na and Cu cations.

d spacings on the X-ray powder diagram. The simplest and most reliable diagnostic methods to distinguish wulffite and parawulffite from one another and from all other known minerals are powder XRD (Tables 2, 3, and 8) and IR spectroscopy (Fig. 7). In particular, some reflections in the X-ray powder diagram of parawulffite are impossible for wulffite, *e.g.*, the distinct doublet for -304 and 304 in the 3.7–3.6 Å region of parawulffite instead of the 304 singlet of wulffite.

The individual structural features of wulffite and parawulffite are also caused by the difference in the K:Na ratio. The transition from K_6Na_2 to K_5Na_3 provokes the change in the character of K-Na ordering and, as a consequence (also taking into account the difference between ionic radii of K⁺ and Na⁺), the distortion of the structure lowers the symmetry from orthorhombic (*Pn2*₁*a*) wulffite to monoclinic (*P2/c*) parawulffite.

The parawulffite structure contains two crystallographically independent Na(1) and Na(2) sites selectively occupied by Na cations. The octahedrally coordinated Na(1) site in parawulffite corresponds to only one Na site in wulffite. Alternating Na(2) and K(1) sites in parawulffite can be considered to be the result of the division of the single K(1) site of the wulffite structure (Fig. 5a, b).

These minerals are also different in terms of the positions occupied by K cations. In wulffite, there are nine-coordinated K(1)- and K(3)-centered polyhedra and ten-coordinated K(2)-centered polyhedra with mean K–O distances of 2.909, 3.013, and 3.068 Å, respectively. In parawulffite, K cations occupy ten-coordinated K(1)- and K(2)-centered and twelve-coordinated K(3)-centered polyhedra with mean K–O distances 3.079, 3.070, and 3.176 Å (Table 7), respectively. Thus, all K-centered polyhedra in parawulffite

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FIG. 6. The heteropolyhedral Cu–O–S chains in wulffite (a), parawulffite (b) (each in three projections, from left to right *ab*, *bc*, and *ac*), and piypite (c, drawn from the data in Effenberger & Zemann 1984) (two projections, from left to right *ac* and *ab*) and the heteropolyhedral Cu–O–S layer in euchlorine (d, drawn from the data in Scordari & Stasi 1990). For the legend see Figure 5. The Cu cations are shown as centering almost flat squares in *ab* and *bc* projections for wulffite, parawulffite and in *ac* projection for piypite (for better clarity) and as centering five-coordinated polyhedra in *ac* projection for wulffite and in *ab* projection for piypite.



FIG. 7. IR spectra of parawulffite (1) and wulffite (2).



FIG. 8. IR spectra of piypite (a) and euchlorine (b), both from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. Weak bands at 3335 and 3430 cm⁻¹ and a very weak, broad band near 1650 cm⁻¹ in the piypite spectrum (a) are probably caused by slight hydration of this mineral, which is unstable in air.

7	1	4

TABLE 8. COMPARATIVE DATA FOR WULFFITE, PARAWULFFITE, AND RELATED MINERALS

Mineral	Wulffite	Parawulffite	Piypite*	Euchlorine
Ideal. formula	K ₃ NaCu ₄ O ₂ (SO ₄) ₄	K ₅ Na ₃ Cu ₈ O ₄ (SO ₄) ₈	K ₈ Cu ₉ O ₄ (SO ₄) ₈ Cl ₂	KNaCu ₃ O(SO ₄) ₃
Crystal system	Orthorhombic	Monoclinic	Tetragonal	Monoclinic
Space group	Pn2₁a	P2/c	14	C2/a
Unit cell				
a, Å	14.281	13.904	13.60–13.67	18.41
b, Å	4.948	4.977		9.43
<i>c</i> , Å	24.113	23.586	4.94-4.98	14.21
β, °		90.21		113.7
V, Å ³	1704	1632	921–923	2259
Ζ	4	2	1	8
Formula	K ₁₂ Na ₄ Cu ₁₆	K ₁₀ Na ₆ Cu ₁₆	K ₈ Cu ₈ O ₄ (SO ₄) ₈	K ₈ Na ₈ Cu ₂₄
(Z = 1)	O ₈ (SO ₄) ₁₆	O ₈ (SO ₄) ₁₆	(Cu,Na)Cl _{2-x}	O ₈ (SO ₄) ₂₄
Strongest	9.27-100	9.06-100	9.63–100	8.44-100
reflections of				
the X-ray	7.16–22	7.00-26	6.79–40	3.475-30
powder	3.125–16	5.903-12	4.305–20	3.237-25
pattern:	2.882–16	3.096–12	3.039–70	2.852-37
d, Å–I	2.780-33	2.736–33	3.006–30	2.843-40
	2.725–14	2.674–11	2.666–20	2.816-47
	2.472-20	2.492-24	1.924–20	2.544-45
	2.366–13	2.321–26		
Optical Data				
α	1.582	1.585	ω 1.583–1.598	1.580
β	1.610	not determined		1.605
γ	1.715	1.717	ε 1.695–1.711	1.644
optic. sign, 2V	(+), calc. 57.5°	(+), not determined	(+)	(+), large
D(meas), g m ⁻³	3.23	3.35	3.0–3.10	3.27
Sources	this work	this work	Vergasova <i>et al</i> . 1984, Clark <i>et al</i> .	Scordari &
			1984, Effenberger & Zemann	Stasi 1990,
			1984, Filatov & Vergasova 1989	Anthony <i>et al.</i> 2003

* In some papers published in 1980s the same mineral was described as "caratiite" (Clark *et al.* 1984, Effenberger & Zemann 1984, Effenberger 1985). This is caused by its almost simultaneous, independent discoveries in fumaroles of two volcanoes, Tolbachik (piypite: Vergasova *et al.* 1984) and Vesuvius (caratiite: Clark *et al.* 1984). Later the priority of piypite was accepted by the IMA (Filatov & Vergasova 1989).

are more voluminous in comparison with wulffite. This is probably because the former is richer in Rb and Cs impurities than the latter: the Rb₂O contents in the holotype specimens of wulffite and parawulffite from the Second scoria cone are 0.6-1.2 and 1.2-1.7 wt.%, respectively, and Cs₂O 0.0-1.1 and 1.0-1.4 wt.%, respectively (Table 1). The e_{ref} values (Tables 5 and 6) and K–O distances (Table 7) show that the Rb and Cs cations are mainly concentrated at the K(3) site in parawulffite and at the K(2) site in wulffite.

Note that high contents of Rb and Cs (0.5–1.1 wt.% Rb₂O and 2.7–4.1 wt.% Cs₂O) were earlier determined in averievite, $Cu_5O_2(VO_4)_2 \cdot n(Cs,K,Rb)Cl$, the endemic mineral of fumaroles at the same Second scoria cone (Starova *et al.* 1997, Vergasova *et al.* 1998).

Among minerals only piypite, $K_8Cu_8O_4(SO_4)_8 \cdot (Cu, Na)Cl_{2-x}$ (Vergasova *et al.* 1984, Clark *et al.* 1984, Effenberger & Zemann 1984), shows some common structural features with wulffite and parawulffite, especially with the former; piypite and parawulffite have similar configurations of Cu–O–S chains. The structures of these three minerals are topologically close (Fig. 5a–c), but piypite is strongly distinguished not only in its tetragonal symmetry (sp. gr. *I*4), but also chemically, being a mineral with species-defining Cl and without species-defining Na (Table 8). The octahedral sites, occupied by Na atoms in wulffite and by Na(1) in parawulffite (Fig. 5a, b), are Cu-dominant in piypite (Fig. 5c). Note that synthetic analogues of piypite with the same



FIG. 9. Motifs formed by oxocentred tetrahedra: $[O_2Cu_4]^{\infty}$ chains in wulffite, parawulffite, and piypite (a) and isolated dimers $[O_6Cu_2]$ in euchlorine (b).

octahedral sites occupied by K and Na atoms are known: $K_4Cu_4O_2(SO_4)_2$ ·KCl (Effenberger 1985) and Na₄Cu₄O₂(SO₄)₂·MeCl (Me = Na > Cu, \square) (Kahlenberg *et al.* 2000), respectively. Chemical and structural differences between piypite, wulffite, and parawulffite are reflected in atomic arrangements in their structures (Figs. 5a–c and 6a–c) and give differences in symmetry, unit cell dimensions, X-ray powder diffraction patterns (Table 8), IR spectra (Figs. 7 and 8), and some other characteristics.

Symmetry lowering accompanied by enhancement of the distortion of SO₄ tetrahedra in the series of structurally related minerals [piypite (tetragonal, $\Delta_{S-O} = 0.05 \text{ Å}) \rightarrow$ wulffite (orthorhombic, $\Delta_{S-O} =$ $0.043-0.087 \text{ Å}) \rightarrow$ parawulffite (monoclinic, $\Delta_{S-O} =$ 0.048-0.103 Å)] results in the enhancement of the number of observed bands in the IR spectrum (Figs. 7 and 8). Note that in the case of piypite, K₈Cu₈O₄ (SO₄)₈·MeCl_{2-x}, splitting of $\nu_1(A_1)$ is caused by the mixed population of the Me = (Cu > Na) site coordinating the SO₄²⁻ anion reported by Effenberger & Zemann (1984).

The Cu–O–S chains in parawulffite and piypite are similar and topologically close to that in wulffite, but the latter differs from the two former in its configuration (Fig. 6a–c; see also above). Euchlorine, although chemically related to wulffite and parawulffite, is quite different in its structure, unit cell data, and X-ray powder diffraction pattern (Table 8). The basis of its structure (Scordari & Stasi 1990), unlike wulffite and parawulffite, is a Cu–O–S layer (Figs. 5d and 6d). Some oxygen atoms in wulffite and parawulffite are bound only with Cu and structures of these oxysulfate minerals could be described in terms of anioncentered tetrahedra. In both minerals we can see the $[O_2Cu_4]^{\infty}$ chains, formed by edge-sharing OCu₄ tetrahedra, that run along [010] (Fig. 9a). Analogous chains were reported in piypite (Effenberger & Zemann 1984), its synthetic sodium analogue, Na₂Cu₂O(SO₄)·MeCl (Me = Na, Cu, \Box) (Kahlenberg *et al.* 2000), and coparsite, Cu₄O₂[(As,V)O₄]Cl (Starova *et al.* 1998). Unlike these, euchlorine contains isolated dimers [O₆Cu₂] (Fig. 9b).

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