MINERALOGICAL MAGAZINE

VOLUME 40 NUMBER 309 MARCH 1975

Wroewolfeite, a new copper sulphate hydroxide hydrate

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SUMMARY. Wroewolfeite is a new mineral from the Loudville lead mine in Loudville, Massachusetts, U.S.A. The mineral occurs as blue, monoclinic crystals, twinned on {001}, very similar in appearance to posnjakite and langite. It is formed as small isolated pinacoidal crystals (up to 1·0 mm) implanted on covelline and chalcosine. There are three cleavages of equal facility of production. The cell dimensions are *a* 6·058 Å, *b* 5·654 Å, *c* 14·360 Å, β 93° 28′, space group *Pc* or *P*2/*c*. The strongest diffraction lines (in Å) are 7·152 (100), 3·581 (70), 2·628 (35), 2·004 (30), 2·431 (20), 2·379 (20), 2·278 (20). Electron-microprobe analysis gives CuO 64·22 %, SO_3 16·48 %, water by difference 19·30 %. Empirical cell contents are $Cu_{7\cdot88}(SO_4)_{2\cdot00}(OH)_{11\cdot76}.(H_2O)_{4\cdot22}$ or $Cu_4(SO_4)(OH)_6.2H_2O$ with $Z = 2$. Wroewolfeite is strongly pleochroic with α light blue, β deep greenish blue, and γ medium greenish blue. Absorption $\beta > \gamma \gg \alpha$. The mineral is biaxial with α 1·637, β 1·682, and γ 1·694, $2V_\alpha = 53°$. The name is for C. Wroe Wolfe, American crystallographer, educator, and philosopher.

IN the course of an investigation of the minerals of the oxidized zone from an abandoned lead mine at Loudville, Massachusetts, one of the authors (PJD) noted some blue platy crystals associated with chalcosine and covelline. The X-ray powder pattern of this mineral does not match that of any known species, so we proceeded on the assumption that the crystals were a new copper sulphate mineral. The X-ray pattern closely resembled those of posnjakite and langite and the mineral was tentatively assigned to this group. Subsequent investigation has verified that the mineral is indeed a new species, and we have named it wroewolfeite in honour of C. Wroe Wolfe, eminent American crystallographer, educator, and philosopher. The mineral and the name were approved by the Commission on New Minerals and New Mineral Names, I.M.A., prior to publication. Type material is deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D.C., catalog #127329.

The Loudville lead mine, also known as the Manhan River lead mine, was described briefly by Silliman (1810) and Emerson (1917). The mine was worked intermittently from 1679 until 1865 but the ore body is presently inaccessible. The new mineral was found on a specimen removed from the old mine dumps near the central adit. The primary minerals in the deposit are galena, chalcopyrite, calcite, fluorite, quartz, and baryte. Oxidation of the primary minerals has produced a suite of secondary lead and copper minerals including wulfenite, pyromorphite, cerussite, anglesite, covelline, chalcosine, malachite, brochantite, and langite.

Wroewolfeite occurs as deep greenish blue crystals intimately associated with brochantite, malachite, and langite in the above mentioned suite of secondary minerals. It forms minute euhedral crystals, apparently monoclinic in morphology, implanted on a thin film of chalcosine, which in turn coats microgranular covelline. The covelline replaced galena and shows relict cleavage traces. Several crystals of wroewolfeite were also found on drusy quartz adjacent to chalcosine and covelline. The maximum observed size of the crystals is 0·5 mm × 1·0 mm, but most are considerably smaller. Wroewolfeite alters to brochantite and malachite. Because wroewolfeite and langite are intimately associated at the Loudville mine, specimens from other langite localities were examined in the hope of obtaining more wroewolfeite but none was found. A recent communication from Dr. M. H. Hey indicates the existence of samples of wroewolfeite from the Ladywell mine, Shelve, Shropshire, England, and the Nantycagal mine, Ceulanywaesmawr, Cardiganshire, Wales. These samples are in the collections of the British Museum (N.H.).

Physical properties. Wroewolfeite crystals are deep greenish blue in colour and exhibit no discernible zoning. There are three cleavages parallel to {010}, {100}, and {001}, which are very easily produced and perfect. The lustre is vitreous and the streak light blue. As the crystals are very deeply coloured, they are only weakly translucent in visible light. The hardness is about 2½. There is no discernible fluorescence in either long- or short-wave ultraviolet radiation. The density was determined by flotation of clear crystals in Clerici solution, which gave a value of 3·27±0·01 g/cm^3. The calculated density is 3·30 g/cm^3, in excellent agreement with the observed value.

In thin section, wroewolfeite is blue and strongly pleochroic with α light blue, β deep greenish blue, and γ medium greenish blue, absorption $\beta > \gamma \gg \alpha$. The mineral is biaxial negative with $2V_\alpha$ 53° Birefringence is moderate (0·057) and the refractive indices for sodium light are α 1·637, β 1·682, and γ 1·694 (all±0·002). By comparison, posnjakite has α 1·625, β 1·680, and γ 1·706 (Komkov and Nefedov, 1967), and langite has α 1·654, β 1·713, and γ 1·722 (Meixner, 1941).

Chemical composition. The formula of wroewolfeite is $Cu_4(SO_4)(OH)_6.2H_2O$. The mineral has been chemically analysed with an ARL electron microprobe, using an operating voltage of 15 kV and a sample current of 0·15 μA. with defocused beam. Under these conditions we found no evidence of mineral decomposition. The intensities were corrected using a modification of the absorption correction program of Fraser *et al.* (1966). Copper and sulphur were determined employing wet-chemically analysed bornite as a standard. Qualitative scans for the presence of other elements abundant in the geochemical environment of wroewolfeite, including F, P, Cl, Ca, Zn, As, Ag, Ba, and Pb, were negative. Unfortunately, the water content could not be determined as there was too little material for analysis. Water was assigned to give the best agreement between the measured and calculated densities. In deriving the formula, hydroxyl was assumed in sufficient quantity to ensure electrostatic charge balance. The assumption that both water and hydroxyl are present is supported by the marked chemical and crystallographic similarities between wroewolfeite, posnjakite, and langite. Posnjakite (Komkcv and Nefedov, 1967) and langite (Pierrot and Sainfeld, 1958) are both $Cu_4(SO_4)(OH)_6 \cdot H_2O$. The formula given by Komkov and Nefedov is based on structural evidence; the material was not chemically analysed. The close crystallographic relationship of langite to wroewolfeite will be discussed later.

TABLE I. *Electron-probe analysis of wroewolfeite*

	1		2	3		4
Cu	51·3±0·8 %	CuO	64·22	65·17	Cu^{2+}	7·88
S	6·6±0·2 %	SO_3	16·48	16·40	SO_4^{2-}	2·00
		H_2O	[19·30]*	18·43	OH^-	11·76
		Sum	100	100·00	H_2O	4·22

* by difference.
1. Electron-probe results and estimated accuracy.
2. Analysis recalculated as oxides. D_{obs} 3·27 g cm^{-3}.
3. Theory for $Cu_4SO_4(OH)_6 \cdot 2H_2O$. D_{calc} 3·30 g cm^{-3}.
4. Empirical unit-cell contents.

Crystallography. As mentioned above, wroewolfeite has a decidedly monoclinic habit. Although suitable crystals were not available for goniometric study, the monoclinic symmetry was verified by single-crystal X-ray methods. Precession photographs indicate that wroewolfeite is monoclinic, *Pc* or *P2/c*, with *a* 6·07, *b* 5·63, and *c* 14·32 Å, and *β* 93·5°. These parameters have been verified by cone-axis and rotating-crystal photographs. Using Gandolfi film data obtained with Cu–*K*α radiation, and quartz as an internal standard, their values were refined to *a* 6·058±0·001, *b* 5·654±0·001, *c* 14·360±0·006 Å, and *β* 93° 28′±2′. The refinement was carried out by the least-squares powder-data refinement program of Appleman, Evans, and Handwerker (1972).

The precession photographs reveal two other features of interest. Although it is not obvious from the morphology, wroewolfeite twins on {001}. Also, the strong reflections of class {*hk*0} define a pseudo-trigonal sub-cell having parameters $a' \approx 2{\cdot}72$ and c' 14·36 Å. Precession photographs of langite from Loudville also display a pseudo-trigonal substructure with the same *a* translation. Since this is approximately the oxygen–oxygen separation in a closest-packed array, the structure of both minerals must be based on oxygen closest-packing. However, 14·36 Å is not an integral multiple of the height of an oxygen layer (≈ 2·3 Å), and thus the structure cannot consist simply of a stacking of oxygen layers along the length of *c*.

Table II contains a list of interplanar spacings for wroewolfeite obtained with a 114·6 mm Gandolfi camera and Cu–*K*α radiation. The pattern was indexed with the help of the single-crystal photographs. Intensities were estimated visually. The powder pattern closely resembles that of langite and even more so that of posnjakite. Powder patterns of langite from Loudville and Mollau, France, the latter from

Pierrot and Sainfeld (1958), are identical to one another except for some lines due to brochantite and malachite in the Loudville material. Brochantite lines also appear in the pattern of Pierrot and Sainfeld, although they did not recognize them as such. No extraneous lines were observed in the wroewolfeite pattern, however.

TABLE II. *X-ray powder pattern of wroewolfeite*

I	d_{meas}	d_{calc}	hkl
100	7·152	7·167	002
10	6·041	6·046	100
5	5·653	5·654	010
1	4·764	4·766	$\bar{1}02$
5	4·434	4·439	012
5	4·135	4·130	$\bar{1}10$
1	3·642	3·644	$\bar{1}12$
70	3·581	3·584	004
10	3·519	3·516	112
1b	3·184	3·190	$\bar{1}13$
		3·168	$\bar{1}04$
5b	3·013	3·023	200
		3·004	104
15	2·773	2·774	021
10	2·646	2·647	$\bar{2}11$
35	2·628	2·630	022
10	2·598	2·596	211
10	2·542	2·543	$\bar{2}12$
15	2·458	2·456	212
20	2·431	2·433	023
		2·431	$\bar{1}22$
20	2·379	2·383	$\bar{2}13$
		2·383	$\bar{2}04$
20	2·278	2·282	$\bar{1}23$
		2·277	213
5	2·219	2·220	024
5	2·192	2·196	$\bar{2}14$
3	2·088	2·086	214
10	2·012	2·016	300
		2·013	025
30	2·004	2·006	$\bar{2}22$
		2·006	$\bar{2}15$
15	1·904	1·902	215
10	1·824		
5	1·795		
5	1·734		
10	1·667		
10	1·660		
15	1·600		
5	1·585		
10	1·572		
5	1·550		
1	1·524		
5	1·513		
3	1·498		
3	1·476		
1	1·463		
5	1·446		

Plus *c.* 70 more lines to 0·775 Å
b = broad line

Related minerals. Strunz (1970) has grouped together posnjakite, langite, ktenasite, mooreite, and perhaps torreyite on the basis of their crystal-chemical similarities. It is clear that wroewolfeite also belongs in this group. Of these, only langite $Cu_4(SO_4)(OH)_6.H_2O$ has undergone a crystal-structure analysis (Wappler, 1971), but even here, there is some uncertainty in the number and position of the anions.

Langite is monoclinic, space group *Pb*, with *a* 6·05, *b* 11·25, *c* 7·14 Å, and α 90·0° (Wappler, 1971; *a* was chosen as the unique twofold axis). The structure contains double layers of approximately closest-packed hydroxyl ions parallel to (001) with copper atoms in the octahedral interstices. Some of the anion sites are vacant, so some copper atoms are really fivefold co-ordinated. Between the double layers are discrete SO_4 tetrahedra, which are thought to be bonded to the Cu–OH layers above and below by hydrogen bonds. Wappler further assumes that the SO_4 groups are linked to one another through the water molecules by means of hydrogen bonds.

Although the position of the mirror plane with respect to the cell translations is different in the two minerals, the cells of wroewolfeite and langite are closely related:

	a	*b*	*c*	space group
Langite	6·05	11·25	7·14 α90·0°	*Pb*
Wroewolfeite	6·06	5·65	14·36 β93° 28′	*Pc* or *P* 2/*c*

Each has the same pseudotrigonal substructure translation of $\approx 2{\cdot}7$ Å, which reflects the oxygen closest-packing. It is therefore reasonable to assume that the wroewolfeite structure also consists of layers of $Cu(OH)_6$ octahedra with SO_4 groups in the interlayer positions. As the number of water molecules in wroewolfeite could not be determined experimentally and the number in langite and posnjakite is not certain either, it is conceivable that these three phases are polymorphous.

Acknowledgements. The authors wish to thank Mr. John S. White, Jr., of the National Museum of Natural History for calling the authors' attention to the work of Wappler and for reading the manuscript. Thanks are also due to Dr. Paul B. Moore of the University of Chicago for helpful discussions on the structural chemistry of these minerals.

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[*Manuscript received 7 March 1974, revised 7 July 1974*]