

# Namuwite, $(\text{Zn,Cu})_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ , a new mineral from Wales

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**ABSTRACT.** Found on a specimen in the mineral collection of the National Museum of Wales, no. NMW 27.111.GR414, from the Aberllyn mine, Llanrwst mining field, North Wales, with hydrozincite on a breccia cemented by sphalerite, quartz, calcite, and ankerite. Atomic absorption and TGA analyses gave ZnO 37.8, CuO 22.0,  $\text{SO}_3$  14.9,  $\text{H}_2\text{O}$  24.5, total 99.2%, corresponding to  $(\text{Zn}_{2.50}\text{Cu}_{1.49})_{\Sigma 3.99}\text{S}_{1.00}\text{O}_7 \cdot 7.32\text{H}_2\text{O}$  on the basis of total O = 7 in the anhydrous part. The ideal formula is  $(\text{Zn,Cu})_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$  where Zn > Cu. It is hexagonal  $a$  8.29,  $c$  10.50 ± 0.01 Å, possible space groups  $P6$ ,  $P\bar{6}$ ,  $P6/m$ ,  $P622$ ,  $P6mm$ ,  $P\bar{6}m2$ ,  $P\bar{6}2m$ , and  $P6/mmm$ . Isomorphous with synthetic  $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$  and  $(\text{Zn,Cu})_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ . Strongest X-ray powder diffractions are: 10.59(100)0001, 5.31(15)0002, 4.15(25)1120, 2.71(42)2130, 2.63(41)2131, 0004, 2.41(22)2132, 1.57(23)3252, 1.55(20)4151. Namuwite is pale sea-green in colour, lustre pearly, streak very pale green,  $H$  (Mohs) 2. Cleavage  $\{0001\}$ , perfect. Density ( $\text{g/cm}^3$ ) 2.77 (meas.), 2.81 (calc. on the normalized empirical formula). It is optically uniaxial, sign not determined owing to the extremely low birefringence. Refractive index  $n = 1.577(5)(\text{NaD})$ . The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA.

DURING a search of the mineral collection of the National Museum of Wales in Cardiff for possible specimens of nickeloan hydrozincite (Alwan and Williams, 1979) and for other specimens of hydrozincite which may be doped with transition and related metal cations, a particular specimen was noticed. This had been purchased by the Museum as part of the G. J. Williams Collection. The item, registered number NMW 27.111.GR414 proved on examination to contain the title compound and to our knowledge is the only specimen in existence.

It was labelled 'Hydrozincite (coloured by malachite) Aberllyn Mine (1917) Bettws-y-coed, Carn 271 111 GR414'. Underneath this label was an older one bearing the legend 'zinc sulphide, Aberllyn Mine, Bettws-y-coed, Carn', together with

a smaller label with the number 'C154'. This latter number is that given to the specimen by G. J. Williams.

The Aberllyn mine is located in the Llanrwst mining district near Bettws-y-coed, Gwynedd, North Wales, national grid reference SH794582,

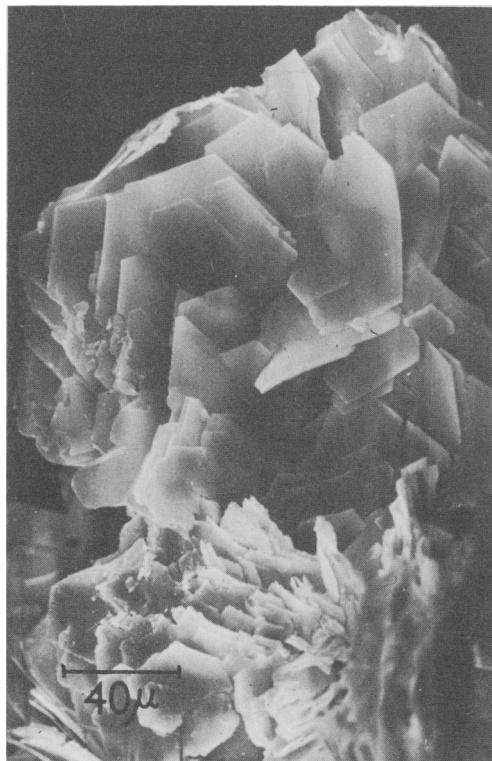


FIG. 1. Scanning electron micrograph of namuwite. Scale marked on photograph.

and was formerly worked for lead (Dewey and Smith, 1922). The matrix of the specimen, which is 5 × 4 cm in size, is composed of a breccia of fragments of black pyritiferous slate from the Crafnant Volcanic Group (Howells *et al.*, 1971) which is cemented by sphalerite, calcite, ankerite, and quartz. On the top of the specimen, altered sphalerite is coated by hydrozincite, which is in turn stained in part by Fe(III) oxyhydroxides. The namuwite occurs as a rounded encrustation on the hydrozincite occupying an area of some 1.5 × 5.0 cm and up to 0.5 cm in thickness. It is somewhat discoloured by dust and superficial iron-staining.

*Physical and optical properties.* Namuwite is amorphous to the naked eye but under the scanning electron microscope is seen to consist (fig. 1) of aggregates of perfect to subperfect hexagonal plates up to 60 μ across. Stacks of platelets are

common. On a fresh surface in the hand specimen namuwite is pale sea-green in colour with a paler green streak. The lustre is pearly and the Mohs hardness is 2. The density was determined to be 2.77 g cm<sup>-3</sup> (by flotation).

Under the microscope, interaxial angles of 120° were recorded on basal sections of crystals immersed in liquid as well as on SEM photographs. Cleavage is perfect on {0001}. Single platelets are colourless, and due to the cleavage most crystals lie flat in the liquid. However aggregates of crystals did show side sections through the platelets and they possess a light-green colouration. Slight pleochroism was seen within the side faces of maximum intensity when the crystal is oriented east-west. With crossed polars basal sections are isotropic, while side sections show straight extinction and interference colours up to upper-first-

TABLE I. X-ray powder data for namuwite. Cu-K<sub>α</sub> radiation, 114 mm camera (1)

1				2		3	
<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>d</i> <sub>meas</sub>	<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub>	<i>hkl</i>
100	10.59	10.50	0001	10.0	100	10.37	0001
2	8.47			8.5	6		
12	7.31	7.18	1000	7.4	10		
10	5.95	5.93	10 $\bar{1}$ 0	5.91	12		
15	5.31	5.25	0002	5.11	10	5.16	0002
25	4.15	4.15	11 $\bar{2}$ 0	4.19	40	4.17	11 $\bar{2}$ 0
14	3.86	3.86	11 $\bar{2}$ 1	3.83	10		
14	3.63	3.59	2000	3.61	4		
1	3.51	3.50	0003				
1	3.40	3.40	20 $\bar{2}$ 1			3.44	20 $\bar{2}$ 1
10	3.25	3.25	11 $\bar{2}$ 2	3.28	12	3.25	11 $\bar{2}$ 2
10	3.14	3.15	10 $\bar{1}$ 3	3.11	10		
2	2.96	2.96	20 $\bar{2}$ 2				
42	2.71	2.71	21 $\bar{3}$ 0	2.75	90	2.73	21 $\bar{3}$ 0
41	2.63	2.63	21 $\bar{3}$ 1, 0004	2.65	35B	2.64	21 $\bar{3}$ 1
8	2.55			2.53	14		
10	2.50	2.51	20 $\bar{2}$ 3	2.45	10	2.48	20 $\bar{2}$ 3
22	2.41	2.41	21 $\bar{3}$ 2	2.41, 2.39	20, 6	2.41	21 $\bar{3}$ 2
4	2.22	2.22	11 $\bar{2}$ 4			2.211124	
14	2.17	2.18	30 $\bar{3}$ 2	2.16	16		
4	2.14	2.15	21 $\bar{3}$ 3			2.14	21 $\bar{3}$ 3
10	2.06	2.07	22 $\bar{4}$ 0	2.09	10		
4	2.03	2.03	22 $\bar{4}$ 1	2.00	6		
1	1.99	1.99	31 $\bar{4}$ 0				
2	1.93	1.93	22 $\bar{4}$ 2	1.90	4		
5	1.88	1.89	21 $\bar{3}$ 4				
7	1.78	1.78	22 $\bar{4}$ 3				
1	1.73	1.73	31 $\bar{4}$ 3				
1	1.66	1.65	32 $\bar{5}$ 0				
23	1.57	1.57	32 $\bar{5}$ 2, 41 $\bar{5}$ 0	1.58	50		
20	1.55	1.55	41 $\bar{5}$ 1	1.56	14		

1. Namuwite, Aberllyn mine,  $a = 8.29$ ,  $c = 10.50 \pm 0.01$  Å.

2. Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·4H<sub>2</sub>O, ASTM Powder file 9-204.

3. Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·4H<sub>2</sub>O, Jacob and Riquier (1969),  $a = 8.35$ ,  $c = 10.33$  Å.

order in the thickest books of crystal plates. A uniaxial interference figure was obtained on the basal section and  $RI_{\omega}$  was determined by the immersion method to be  $1.577 \pm 0.005$  at the NaD line. The crystal form did not allow an accurate determination of the  $RI$  of the extraordinary ray to be carried out.

**Crystallography.** No crystals were found large enough for single-crystal X-ray studies. Powder data were recorded and are presented in Table I. Namuwite is isomorphous with hexagonal synthetic hydrated basic Zn(II) sulphate of stoichiometry  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$  (Jacob and Riquier, 1969; Mann and Deutscher, 1980). X-ray powder data for  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$  from the ASTM powder file and from the report of Jacob and Riquier (1969) are included in Table I for comparison. Indexing of the reflections and calculations of  $d$ -spacings were carried out on the basis of the hexagonal cell with  $a = 8.29$  and  $c = 10.50 \pm 0.01$  Å. From systematic absences, possible space groups are  $P6$ ,  $P\bar{6}$ ,  $P6/m$ ,  $P622$ ,  $P6mm$ ,  $P\bar{6}m2$ ,  $P62m$ , and  $P6/mmm$ .

**Chemistry.** Namuwite is isomorphous with synthetic hexagonal  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$ , but contains Cu(II) substituting for Zn(II). The chemical analysis for namuwite determined by atomic absorption spectrometry and thermogravimetric techniques is given in Table II. The analysis shows that the ideal formula for namuwite is  $(Zn,Cu)_4(SO_4)(OH)_6 \cdot 4H_2O$ , with  $Zn > Cu$ . In the type specimen the ratio  $Zn : Cu$  equals 5 : 3. Not only is the Zn(II) analogue known synthetically, but the Cu(II), Ni(II), and Co(II)-substituted species have also been prepared (Frias Ferreira da Rocha and Glibert, 1972; Glibert, 1977; Lecocq *et al.*, 1971).

Glibert (1977) reported that copper(II) ions can occupy up to one-third of the zinc sites in  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$ . He found that preparations from aqueous solutions containing more than this amount of copper consisted of mixtures of copper-substituted  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$  and zinc-substituted brochantite. Namuwite therefore extends this range and may represent the end-point of Cu(II) substitution in the lattice.

Thermogravimetric (Table II) and differential thermal analysis curves of namuwite agree within experimental error with those given for synthetic material (Glibert, 1977). The calculated unit cell volume of namuwite is  $624.9 \text{ \AA}^3$ , which for  $Z = 2$  gives  $d_{\text{calc.}} = 2.81 \text{ g cm}^{-3}$ . Infrared stretching frequencies for the sulphate group in  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$  have been tabulated by Frias Ferreira da Rocha and Glibert (1972) and are 1112 and 1082 ( $\nu_3$ ) and 985 ( $\nu_1$ )  $\text{cm}^{-1}$ . Vibrations forbidden for a perfectly tetrahedral sulphate ion are IR-active due to lattice distortions. Corresponding values for

TABLE II. Chemical analysis of namuwite

	1	2
ZnO	38.6%	37.8%
CuO	22.5	22.0
SO <sub>3</sub>	15.1	14.9
H <sub>2</sub> O <sup>-</sup>	10.2	11.1
H <sub>2</sub> O <sup>+</sup>	13.6	13.4
	100.0	99.2

1. Theory for  $Zn_{2.5}Cu_{1.5}SO_4(OH)_6 \cdot 4H_2O \cdot H_2O^-$ , theory for  $3H_2O$ ;  $H_2O^+$ , theory for  $4H_2O$ .

2. Namuwite, Aberllyn mine, Llanrwst, Wales. Zn and Cu by AAS on 4.2 mg, H<sub>2</sub>O and SO<sub>3</sub> by TGA on 8.6 mg. H<sub>2</sub>O<sup>-</sup>, loss at 80°C; H<sub>2</sub>O<sup>+</sup>, loss at 340°C; SO<sub>3</sub>, loss at 865°C. Temperatures are given at the mid points of the transitions with a heating rate of 5°min<sup>-1</sup>. Found for Cu<sub>0</sub>ZnO (AAS), SO<sub>3</sub> and H<sub>2</sub>O (TGA) corresponds to  $(Zn_{2.50}Cu_{1.49})_{\Sigma 3.99}S_{1.00}O_{7 \cdot 732}H_2O$  on the basis of total O = 7 in the anhydrous part. Ideal formula is  $(Zn,Cu)_4SO_4(OH)_6 \cdot 4H_2O$ .

namuwite are 1111, 1080, and 973  $\text{cm}^{-1}$ , respectively, measured in KBr disc. Broad bands at 3000–3500 and at 1620  $\text{cm}^{-1}$  are the  $\nu_{OH}$  stretching and H<sub>2</sub>O deformation modes. The 800  $\text{cm}^{-1}$  band found in the synthetic zinc compound is not present in namuwite, nor is it present in synthetic Ni(II)-substituted preparations (Frias Ferreira da Rocha and Glibert, 1972). However, IR absorptions are found for namuwite at 719, 600, and 520  $\text{cm}^{-1}$ . The first and last of these may represent  $\nu_4$  and  $\nu_2$ , respectively, for the unsymmetrical sulphate ion.

Finally we wish to draw attention to a suggestion made by Mann and Deutscher (1980) on the basis of thermodynamic calculations, that  $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$  together with  $Zn(OH)_2$  limits the solubility of zinc in most natural waters (for the phases they considered). Since namuwite or its congeners was unknown at that time, it was suggested that such compounds might only be present as fine-grained well-dispersed phases. The discovery of the new mineral is therefore timely and indicates that Mann and Deutscher's calculations are most applicable to the study of dispersion of metals in aqueous solution from oxidizing sulphide orebodies.

**Comments.** Namuwite is named in honour of the National Museum of Wales, in which collection the type specimen has been redeposited. The authors have visited the Aberllyn mine in an attempt to locate other material but the only accessible working is an adit in an extremely dangerous state of collapse. Entry to the level is strongly discouraged. The site is administered by

the Forestry Commission, to whom all correspondence for permission to visit the mine should be addressed.

## REFERENCES

- Alwan, A. K., and Williams, P. A. (1979) *Mineral. Mag.* **43**, 397-8.
- Dewey, H., and Smith, B. (1922) *Special Rep. Mineral Resources G.B.* 23.
- Frias Ferreira da Rocha, M., and Glibert, J. (1972) *Bull. Soc. Chim. Belges*, **81**, 263-77.
- Glibert, J. (1977) *Bull. Soc. Chim. Belges*, **86**, 1-9.
- Howells, M. F., Leveridge, B. E., and Evans, C. D. R. (1971) *Proc. Geol. Soc. Lond.* **1664**, 284-5.
- Jacob, M., and Riquier, Y. (1969) *A.T.B. Metallurgie*, **10**, 127-39.
- Lecocq, R., Glibert, J., and Breckpot, R. (1971) *Bull. Soc. Chim. Belges*, **80**, 585-94.
- Mann, A. W., and Deutscher, R. L. (1980) *Chem. Geol.* **29**, 293-311.

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