Zinc-rich zincolibethenite from Broken Hill, New South Wales

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ABSTRACT

Zinc-rich zincolibethenite with the empirical formula $(Zn_{1.06}Cu_{0.94})_{2.00}[(P_{1.02}As_{0.01})_{1.03}O_4]OH$ *(simplified formula* $(Zn,Cu)_2PO_4OH$*), occurs in ferruginous gossan from the No 3 lens, 280 RL level, Block 14 open cut, Broken Hill, New South Wales, Australia, associated with corkite-hinsdalite, tsumebite, pyromorphite, sampleite, torbernite, dufrenite, strengite and beraunite. Zinc-rich libethenite and olivenite are also associated with the zone, together with members of the libethenite–olivenite series. It is possible that solid solution in the phosphate series extends to the orthorhombic polymorph of composition* Zn_2PO_4OH*. The crystal structure of a Broken Hill sample has been refined to* $R1(F) = 0.0227$ *(single-crystal X-ray intensity data;* $a = 8.323(1)$, $b = 8.251(1)$, $c = 5.861(1)$ Å, $V = 402.5(1)$ Å^3*; structural formula* $Zn(Cu_{0.94}Zn_{0.06})[(P_{0.98}As_{0.02})O_4]OH$*). Detailed physical and chemical data are presented, some of which supplement the partially incomplete data for type zincolibethenite from Zambia.*

INTRODUCTION

An extremely diverse suite of secondary arsenates and phosphates occurs towards the base of the oxidised zone of the Broken Hill ore body (Figure 1). Minerals, including this suite, from the Block 14 and Kintore open cuts have been described in detail by Birch and van der Heyden (1997). During a survey of material from the Kintore pit, samples of zincolibethenite (a new supergene mineral recently described by Braithwaite *et al.*, 2005), ideally $CuZnPO_4OH$, with excess Zn were identified. Thus, Broken Hill represents the second occurrence of zincolibethenite.

Species of composition M_2XO_4OH (M = Cu,Zn; X = P,As) are well-known in the mineral kingdom and extensive substitution is recorded for this quaternary system. Structural relationships between end-members are solidly documented (Anthony *et al.*, 2000; Braithwaite *et al.*, 2005). Table 1 lists known species, together with crystal data and space group information. The known basic Zn phosphate tarbuttite, Zn_2PO_4OH, is triclinic, space group $P\bar{1}$ (Fanfani and Zanazzi, 1965; Genkina *et al.*, 1985) whereas libethenite is orthorhombic, space group *Pnnm* (Walitzi, 1963; Cordsen, 1978; Keller *et al.*, 1979; Yakubovich and Mel'nikov, 1993). In the structure of the latter, the two independent Cu sites show a trigonal-bipyramidal and Jahn-Teller distorted 'octahedral' [4+2] coordination, respectively. Recently, Braithwaite *et al.* (2005) described the new mineral zincolibethenite, $CuZnPO_4OH$, an ordered phase, in which the distorted octahedral site is occupied exclusively by Cu and the trigonal-bipyramidal site exclusively by Zn; unfortunately, neither atomic coordinates nor bond lengths or bond angles were reported. Zincolibethenite from the type locality, Kabwe, Zambia, is orthorhombic, space group *Pnnm*, with $a = 8.3263(3)$, $b = 8.2601(3)$, $c = 5.8771(2)$ Å, $V = 402.52(10)$ Å^3 ($Z = 4$). Synthetic studies by Braithwaite *et al.* (2005) showed that, *in boiling aqueous solution*, no excess Zn was accommodated by the lattice, despite the fact that the *Pnnm* polymorph of Zn_2PO_4OH is known as a synthetic, hydrothermally synthesised phase (Harrison *et al.*, 1995; Kawahara *et al.*, 1994). Of course, there is no fundamental reason to suppose that the synthetic material should not exist as a metastable phase formed at temperatures below 100 °C and a solid solution may well exist between the *Pnnm* polymorph of Zn_2PO_4OH and zincolibethenite. This is borne out by the discovery of Zn-rich zincolibethenite, which is described below.

MINERAL CHARACTERISTICS

The specimen bearing Zn-rich zincolibethenite was recovered from ferruginous gossan from the No 3 lens, 280 RL level, Block 14 open cut, Broken Hill, New South Wales (Museum Victoria specimen number M40229). Associated minerals include corkite–hinsdalite, tsumebite, pyromorphite, sampleite, torbernite, dufrenite, strengite and beraunite (Birch and van der Heyden, 1997). Zinc-rich libethenite and olivenite are also associated with the zone, together with members of the libethenite–olivenite series.

Five analyses were carried out using a Cameca SX50 electron microprobe (WDS; 15 kV; 20 nA; beam diameter: 3 µm) using Cu metal, Zn metal, fluorapatite and arsenopyrite as standards. H_2O was not analysed due to the very few crystals available. It is noteworthy that each of five spot analyses gave Zn>Cu (atom %). Analysis

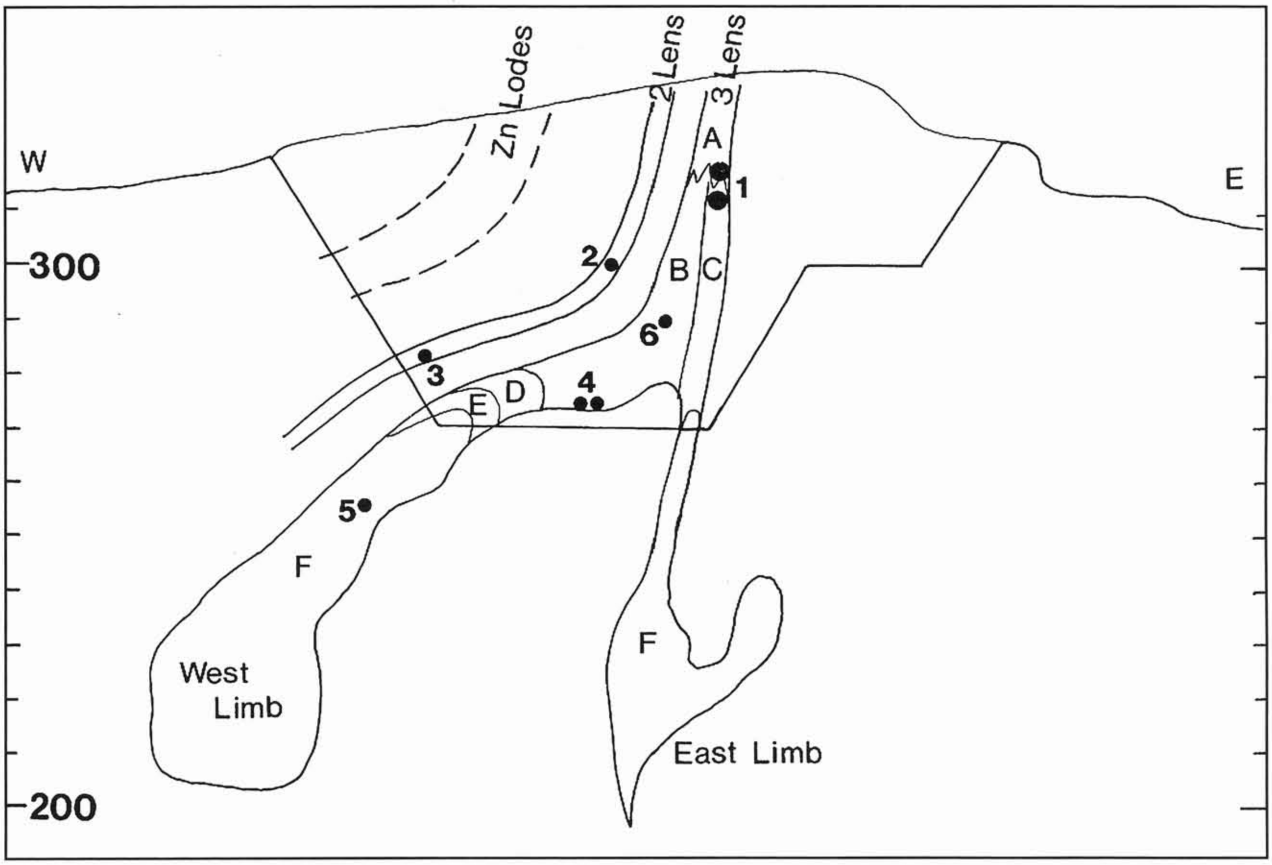

Figure 1: Idealised cross-section of the Block 14 open cut showing the location (position 4) of the phosphate suite carrying zincolibethenite in the oxidised underwall of 3 lens at about the 270-280 m RL (from Birch and van der Heyden, 1997).

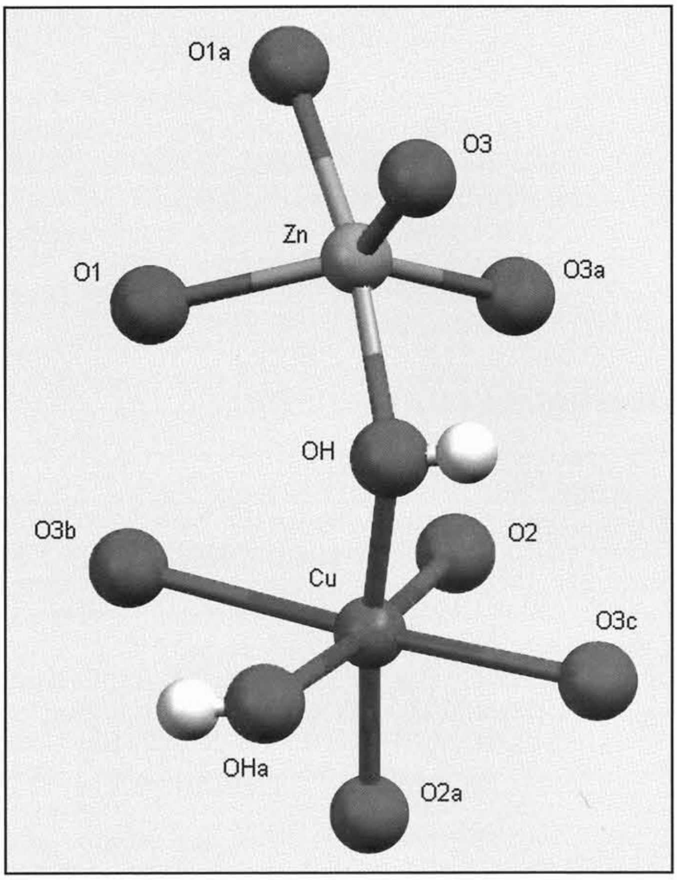

Figure 2: Coordination polyhedra of the metal sites in zincolibethenite.

found (%): Cu, 25.0 (range 23.9-25.8); Zn, 28.8 (range 27.6-30.3); P, 13.2 (range 13.0-13.7); As, 0.3 (range 0.1-0.6); O+H (by difference), 32.7; Total, 100.0. The empirical formula is $(Zn_{1.06}Cu_{0.94})_{2.00}$ $[(P_{1.02}As_{0.01})_{1.03}$ $O_4]OH$ (based on Zn+Cu = 2). A single-crystal structure refinement (see below) with the same atomic displacement parameters and atomic coordinates for Cu and Zn in the Jahn-Teller distorted [4+2]-coordinated site, and for P and As, with refined SOFs (site occupancy factors) converged at a composition of $Zn(Cu_{0.94}Zn_{0.06})[(P_{0.98}As_{0.02})O_4]OH$, in excellent agreement with the results of the chemical analysis. The simplified formula is $(Zn,Cu)_2PO_4OH$ (Zn>Cu); calc. (%) for simplified formula with $(Zn_{1.06}Cu_{0.94})_{2.00}$: Zn = 28.8; Cu = 24.8; P = 12.9.

A single-crystal structure refinement showed that Zn-rich zincolibethenite from Broken Hill is orthorhombic, space group *Pnnm*, with $a = 8.323(1)$, $b = 8.251(1)$, $c = 5.861(1)$ Å, V = 402.5(1) Å^3, Z = 4. The above unit cell is in the same orientation as that of libethenite and zincolibethenite. Other crystal and refinement data for $Zn(Cu_{0.94}Zn_{0.06})[(P_{0.98}As_{0.02})O_4]OH$ are Enraf-Nonius CAD4 diffractometer, M = 241.88, T = 293(2) K, $\lambda = 0.71073$ Å, $D_{calc.} = 3.991$ g cm^{-3}, μ(Mo Kα) = 11.736 mm^{-1}, F(000) = 462, crystal size = 0.15 x 0.15 x 0.10 mm, θ range for data collection = 3.48-33.25°, index ranges -12 h 12, -12 k 12, -8 l 8, reflections collected = 5730, independent reflections = 829 [R(int) = 0.0319]; completeness to $\theta = 33.25°$ = 98.8%, absorption correction by SADABS, refinement method full-matrix least-squares on F^2, data/restraints/parameters = 829/1/51, goodness-of-fit on F^2 = 1.216, final R indices [I>2σ(I)] $R1 = 0.0227$, $wR2$

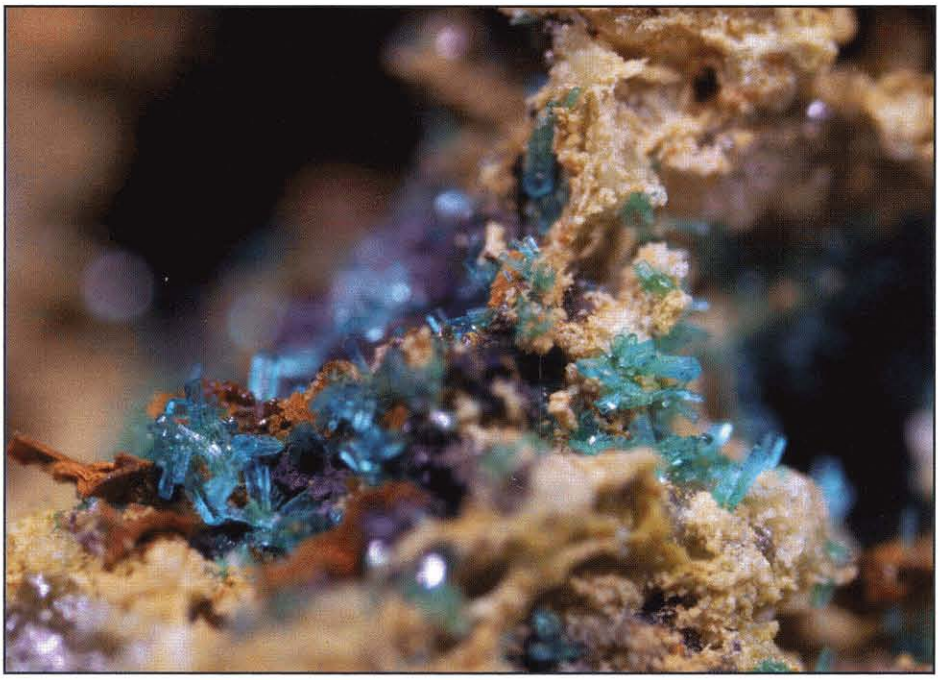

Figure 3: Prismatic crystals (up to 0.2 mm) of zincolibethenite in etched quartz-rich lode rocks from Block 14 open cut. Photo: F. Coffa. Specimen: Museum Victoria collection, M47687.

= 0.0644, R indices (all data) $R1 = 0.0250$, $wR2 = 0.0652$, $w = 1/\sigma(2(F_o)^2 + (0.0347P)^2 + 0.599P)$, where $P = (\max(F_o^2,0) + F_c^2)/3$, as defined by SHELXL-97 (Sheldrick, 1997). Final atomic positions and displacement parameters are given in Table 2, and selected bond lengths in Table 3. Coordination sphere geometries of the Zn and Cu sites in the lattice are shown in Figure 2. The distorted trigonal bipyramidal site is fully occupied by Zn and the tetragonally elongated octahedral site by Cu (94%) and Zn (6%). Copies of full crystallographic data (file CCDC 416047) can also be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax; (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. Lists of observed and calculated structure factors are available from the authors upon request. Additional single-crystal X-ray diffraction data for another crystal from specimen M40229 were measured by one of the authors (U.K.) using a Nonius Kappa CCD diffractometer. Structure refinement gave values essentially identical to those above ($R1(F) = 0.0175$; $a = 8.346(2)$, $b = 8.278(2)$, $c = 5.871(1)$ Å, V = 402.62(15)Å^3; refined formula: $Zn(Cu_{0.96}Zn_{0.04})[(P_{0.98}As_{0.02})O_4]OH$; further details are available on request.

Powder X-ray diffraction data were collected with a 114.6 mm diameter Gandolfi camera using Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å) and intensities estimated visually. The strongest lines (d/Å(I); b = broad line) are 5.88(9), 4.787(10b), 3.712(8b), 2.936(8), 2.627(10b), 2.503(6b), 2.397(7b), 2.307(5b), 1.695(4b) and 1.631(4). The data do not permit an unambiguous differentiation of Zn-rich zincolibethenite from type zincolibethenite, as expected from the very similar Cu:Zn ratios (compare also the nearly identical refined unit-cell parameters in Table 1).

Table 1: Minerals of the M_2XO_4OH (M = Cu, Zn; X = P, As) group, with selected data for the orthorhombic members.

Mineral	Ideal composition	Space group	a (Å)	b (Å)	c (Å)	V (Å^3)	Ref*
Adamite	Zn_2AsO_4OH	$Pnnm$	8.304	8.530	6.047	428.3	1
Libethenite	Cu_2PO_4OH	$Pnnm$	8.076	8.407	5.898	400.44	2
Zincolibethenite	$CuZnPO_4OH$	$Pnnm$	8.326	8.260	5.887	404.5	3a
	$CuZnPO_4OH$	$Pnnm$	8.323	8.251	5.861	402.52	3b
Olivenite	Cu_2AsO_4OH	$P2_1/n$					
Tarbuttite	Zn_2PO_4OH	$P\bar{1}$					
Paradamite	Zn_2AsO_4OH	$P\bar{1}$					

*1: Hawthorne (1976); 2: Keller *et al.* (1979); 3a: Braithwaite *et al.* (2005); 3b: this work. Note the *Pnnm* polymorph of Zn_2PO_4OH is only known as a synthetic hydrothermally synthesised phase (a = 8,3292(9) b = 8.103(2), c = 5.9659(8) Å, V = 402.65 Å^3, Harrison *et al.* (1995); $a = 8.325(1)$, $b = 8.099(1)$, $c = 5.966(1)$ Å, $V = 402.25$ Å^3, Kawahara *et al.* (1994); note that the space group given by Kawahara *et al.* (1994), $P2_12_12$ is incorrect, as clearly shown by a search for higher symmetry using the software PLATON (Spek, 2003).

Table 2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for zincolibethenite from Broken Hill*

Atom	*x/a*	*y/b*	*z/c*	*Ueq*	*Occupancy*
Zn	3606(1)	3709(1)	5000	8(1)	Zn
Cu	0	5000	2509(1)	10(1)	$Cu_{0.94}Zn_{0.06}$
P	2335(1)	2529(1)	0	6(1)	$P_{0.98}As_{0.02}$
O(1)	1098(3)	1131(3)	0	11(1)	
O(2)	1329(2)	4131(3)	0	9(1)	
O(3)	3405(2)	2425(2)	2113(3)	11(1)	
OH	1167(3)	3937(3)	5000	9(1)	
H	920(80)	3070(80)	5000	38(17)	

*The atomic coordinates of synthetic orthorhombic Zn_2PO_4OH (Harrison *et al.*, 1995) were used as starting parameters.

Table 3: Selected bond lengths [Å] and angles [°] for zincolibethenite from Broken Hill[a]

Zn-O(3) x2	2.0006(16)	Cu-OH x2	1.9610(15)
-O(1)	2.014(2)	-O(2) x2	1.9747(14)
-OH	2.038(2)	-O(3) x2	2.4110(16)
-O(1a)	2.078(2)	<Cu-(O,OH)>	2.116
<Zn-(O,OH)>	2.026		
P-O(3) x2	1.5307(16)	Hydrogen bond	
-O(1)	1.546(2)	OH-H	0.74(7)
-O(2)	1.565(2)	OH-H...O(3)	2.47(6)
<P-O>	1.543		
HO-Zn-O(1a)	171.09(9)	HO-Cu-O(2a)	173.91(9)
O(1)-Zn-O(3)	122.40(5)	HOa-Cu-O(2)	173.91(9)
O(1)-Zn-O(3a)	122.40(5)	O(3b)-Cu-O(3c)	169.61(8)
O(3)-Zn-O(3a)	11.515(10)		

[a]For the above, positions of the symmetry-related atoms (a, b, c) are shown in Figure 2.

A photomicrograph of Zn-rich zincolibethenite is shown in Figure 3. It occurs as pale greenish blue, isolated prismatic crystals less than 1 mm long, radiating sprays and flattened rosettes in a ferruginous and quartz-rich gossan matrix. The streak is very pale bluish, lustre vitreous to transparent, Mohs hardness 3.5, cleavage {011} (?) poor with no parting observed, tenacity is brittle and fracture uneven to conchoidal. It does not fluoresce in either short- or long-wavelength UV light. Crystals are short, prismatic along [100] (parallel to the 8.323 Å axis). Forms observed are {011} (prism), {100} (often rounded), {110} (small) and possibly {111} or {101}. No twinning was observed. Optical properties were measured with white light. Zn-rich zincolibethenite is biaxial(-) with $\alpha = 1.664(3)$, $\beta = 1.696(3)$, $\gamma = 1.724(3)$, 2V (meas.) = 80-85°, 2V(calc.) = 85°, dispersion r < v, medium to weak. These values are almost identical to those of type zincolibethenite (α = 1.660, β = 1.705, γ = 1.715; Braithwaite *et al.*, 2005), although for the latter 2V(calc.) = 49° (2V was not measured). The orientation is $Z = a$. Crystals exhibit straight extinction with positive elongation (length-slow). The material is pleochroic with X and Y both nearly colourless with a greenish tint, and Z pale bluish green; absorption $Z > X \sim Y$. The crystal forms, optical orientation and absorption scheme of type zincolibethenite were not given by Braithwaite *et al.* (2005).

DISCUSSION

Harrison *et al.* (1995) showed that the phosphate analogue of adamite could be synthesised at elevated temperatures, but it can also be prepared at ambient temperatures from hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$ (Kawahara *et al.*, 1994). The synthetic procedures of Braithwaite *et al.* (2005) involved boiling aqueous solutions of zinc and copper phosphates at various pH values. Under these conditions, mixtures of Cu-free hopeite and apparently nearly stoichiometric zincolibethenite were exclusively formed. This simply establishes that the Zn-rich *Pnnm* phase is not thermodynamically stable at around 100°C. It does not mean that the phases richer in Zn, such as $Zn(Cu,Zn)PO_4OH$, $Zn(Zn,Cu)PO_4OH$, or chemically pure orthorhombic Zn_2PO_4OH cannot form under ambient conditions as metastable phases. These orthorhombic species are almost certainly manifestations of the Ostwald Step Rule (Ostwald, 1897). In essence, this states

> *If a reaction can result in several products, it is not the stablest state with the least amount of free energy that is initially obtained, but the least stable one, lying nearest to the initial state in free energy.*

The existence of zinc-rich zincolibethenite, $Zn(Cu,Zn)PO_4OH$ (simplified $(Zn,Cu)_2PO_4OH$ with Zn>Cu), from Broken Hill is thus seen as the result of the crystallisation of a metastable intermediate at ambient temperatures. In a formal sense, for only Zn and Cu substitution in the *Pnnm* structure, libethenite is defined by the composition $Cu(Cu,Zn)PO_4OH$, Cu > Zn. The zincolibethenite composition approximates $ZnCuPO_4OH$, with a minor degree of mutual Cu-Zn substitution. Species, should they be found in Nature, with formula $Zn(Zn,Cu)PO_4OH$, Zn > Cu, and *Pnnm* symmetry, would be worthy of new species status.

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