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A new mineral, zincolibethenite, $CuZnPO_4OH$, a stoichiometric species of specific site occupancy

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ABSTRACT

Tiny green crystals from Kabwe, Zambia, associated with hopeite and tarbuttite (and probably first recorded in 1908 but never adequately characterized because of their scarcity) have been studied by X-ray diffraction, microchemical and electron probe microanalysis, infrared spectroscopy, and synthesis experiments. They are shown to be orthorhombic, stoichiometric $CuZnPO_4OH$, of species rank, forming the end-member of a solid-solution series to libethenite, Cu_2PO_4OH, and are named zincolibethenite. The libethenite structure is unwilling to accommodate any more Zn substituting for Cu at atmospheric pressure, syntheses using Zn-rich solutions precipitating a mixture of zincolibethenite with hopeite, $Zn_3(PO_4)_2.4H_2O$. Single-crystal X-ray data confirm that the Cu(II) occupies the Jahn-Teller distorted 6-coordinate cation site in the libethenite lattice, and the Zn(II) occupies the 5-coordinate site. The space group of zincolibethenite is *Pnnm*, the same as that of libethenite, with unit-cell parameters a = 8.326, b = 8.260, c = 5.877 Å, V = 404.5 Å^3, Z = 4, calculated density = 3.972 g/cm^3 (libethenite has a = 8.076, b = 8.407, c = 5.898 Å, V = 400.44 Å^3, Z = 4, calculated density = 3.965 g/cm^3). Zincolibethenite is biaxial negative, with $2V_\alpha$(calc.) of 49º, $r<v$, and $\alpha = 1.660$, $\beta = 1.705$, and $\gamma = 1.715$ The mineral is named for its relationship to libethenite.

Keywords: zincolibethenite, libethenite, hopeite, tarbuttite, veszelyite, solid solution, site occupancy and selectivity, new mineral, Kabwe (Broken Hill), Zambia, ‘Northern Rhodesia’.

Introduction

A complete solid-solution exists between olivenite, Cu_2AsO_4OH and adamite, Zn_2AsO_4OH (Guillemin, 1956; Toman, 1978; Braithwaite, 1983), but Zn substitution into the lattice of libethenite, the orthorhombic isostructural phosphate analogue of olivenite, is limited (Guillemin, 1956), the pure Zn end-member Zn_2PO_4OH being unknown in nature, though its triclinic polymorph tarbuttite is well known, but of rare occurrence.

L.J. Spencer (1908) noticed “an undetermined mineral, occurring as small, bright-green (monoclinic?) crystals”, which “appears to be a copper phosphate” on material from Broken Hill mines, Northern Rhodesia (now Kabwe, Zambia). F.P. Mennell (1920) identified similar material in the Natural History Museum, London, as “veszelyite”, containing Zn, Cu, phosphate, little or no arsenate, and 17.62% of H_2O, from the southern margin of the lead orebody adjacent to the enclosing zinc ore at the mine; a note in Mennell’s paper by L.J. Spencer describes the material as sky-blue brilliant crystals <1 mm long, in sub-parallel aggregates, with refractive index of ~1.63 and specific gravity >3.33. Unfortunately, Mennell’s quantitative analysis of this material was not completed, apart from the water determination, as the apparatus blew up, leaving insufficient material for another attempt. Guillemin (1956) examined a sample, said to be identical to the original specimen in the Natural History Museum, London, by powder X-ray

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diffraction (XRD), and concluded that it is a zincan libethenite, but again had insufficient material for quantitative analysis. Guillemin (1956) consequently attempted the synthesis of Zn-substituted libethenites and noted that Zn can substitute for Cu up to ~46% Zn/(Cu+Zn) at pH 5.4, with higher Zn:Cu ratios, or pH <5.4 or >7 resulting in the formation of hopeite.

Notebaart and Korowski (1980) collected similar material in 1971 in a very restricted area on the eastern side of No. 2 pit, which gave a powder XRD pattern identical to that of libethenite, but which microchemical tests showed to contain Zn as well as Cu. These authors concluded that it is a zincan libethenite, formed very late in the paragenetic sequence by the action of Cu-bearing solutions on tarbuttite.

Mr Lewis Clark collected similar material at Kabwe in 1983 and forwarded samples to one of the present authors (R.S.W.B.) for investigation; other samples were collected and donated by Mr Mike Leppington. Studies of this material, using single-crystal and powder XRD, optics, microchemical and electron probe microanalyses, infrared (IR) spectroscopy and synthesis experiments indicate that it is a stoichiometric phase, the Zn end-member of a solid-solution series, in which one of the two cation sites of different geometry in the libethenite structure is occupied by Cu and the other by Zn. Unlike in the analagous series of arsenates (olivenite to adamite) the ^{VI}Cu site is not readily susceptible to substitution by Zn. This phase is named zincolibethenite from its relationship to libethenite, and this name and the species rank have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Parts of the type specimen are preserved in the collections of the Institut für Mineralogie, Universität Salzburg, Austria, and of the Royal Scottish Museum, and the polished section used for the microprobe analysis is lodged in the Natural History Museum, London.

Physical and optical properties

Zincolibethenite forms bright blue-green, transparent, long prismatic crystals, terminated by domes or prisms, with a cleavage perpendicular to the length, <1 mm long, in tightly packed sheaves and radiating clusters (Fig. 1). The clusters are sparsely scattered on spongy 'limonite' gozzan, which is sometimes richly encrusted with hopeite or tarbuttite crystals, and are clearly of very late generation. On most specimens it forms translucent green to blue-green compact radiating spherical clusters ~1 mm in diameter, and aggregates of clusters, in which individual crystals cannot easily be distinguished. The crystals analysed are intimately associated with hopeite, reflecting the results of synthesis experiments in which solutions containing an excess of Zn over Cu produced mixtures of zincolibethenite and hopeite on reaction with phosphate (see below), suggesting a similar method of formation in nature.

The measured density (Guillemin, 1956) of 'zincan libethenite' is given as 3.65 g/cm^3 for the natural material from Kabwe and 3.63 g/cm^3 for his synthetic material. The density caculated from our unit-cell measurements is 3.972 mg/m^3, close to that of libethenite (3.97 [measured], 3.965 [calculated] mg/m^3 (Keller *et al.*, 1979)). Mohs hardness = 3½, slightly less than that of libethenite.

Zincolibethenite is biaxial negative, with $2V_\alpha$(calc.) = 49º, dispersion of the optic axes $r<v$, medium. For white light, with orientation uncertain, $\alpha = 1.660$, $\beta = 1.705$ and $\gamma = 1.715$. Pleochroism is weak or absent, and is difficult to observe because of the small size of the crystal fragments used. For libethenite 2V(meas.) is ~90º, $r>v$, strong, $\alpha = 1.701$, $\beta = 1.743$ and $\gamma = 1.787$, with pleochroism weak.

Chemical composition

A solution of zincolibethenite in dilute hydrochloric acid gave purple crystals when treated with a solution of ammonium tetrathiocyanato-

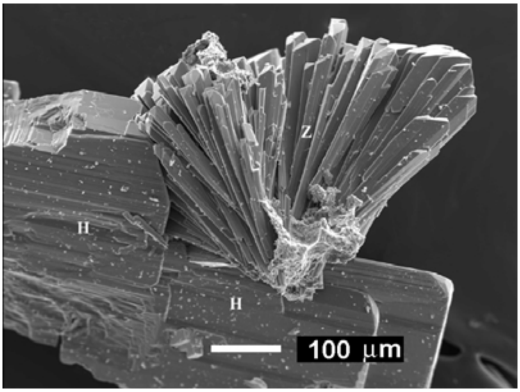

FIG. 1. SEM image of a spray of bright blue-green zincolibethenite crystals on colourless platy hopeite crystals, Kabwe, Zambia. Z = zincolibethenite, H = hopeite.

mercurate(II), indicating the presence of both Zn and Cu.

Crystal aggregates, with attached hopeite, from sample RSWB 83-8, were quantitatively analysed at the Department of Earth Sciences, University of Manchester, using a Cameca Camebax dual wavelength-dispersive spectrometer electron probe microanalyser, fitted with a Link Systems AN 10,000 analysing system. Energy dispersive spectrometry was used, employing an accelerating voltage of 15 kV, a 3 nA beam current and a take-off angle of 40º. The analytical beam spot size was 4 µm in diameter. The primary standards used were synthetic $CuSbS_2$ (for copper), ZnS (for zinc) and natural fluorapatite ($Ca_5(PO_4)_3F$) from Wilberforce, Ontario (for phosphorus); the calibrating standard was cobalt. The data were processed using the Link Systems program 'SPECTA', and analyses are accurate to 0.05 wt.%. Fifteen spot analyses, in areas free from closely underlying hopeite in three grains, gave consistent results indicating a formula of $CuZnPO_4OH$, with a Cu:Zn ratio near unity in all cases (Table 1). A line scan for Zn across a suitable blade of zincolibethenite showed no significant compositional zoning.

X-ray diffraction

A small sample from sample RSWB 83-8 was studied by powder XRD by Mr Merfyn Jones at the Chemistry Department of the University of Manchester Institute of Science and Technology (UMIST), using a Scintag XDS 2000 diffractometer, scanning at 0.1º min^{-1} over 24 h. The results, indexed on an orthorhombic unit cell, are given in Table 2.

TABLE 1. Electron microprobe analyses of zincolibethenite.

Element	1	2	Min.	Max.
Cu	26.4	26.0	25.0	27.2
Zn	27.1	27.7	26.7	29.1
P	12.9	12.8	12.6	13.1
H_2O	3.66	3.63*		
Cu:Zn atomic	1.00	0.97	0.88	1.02

1: Theoretical stoichiometric $CuZnPO_4OH$, wt.%.
2: Average of 15 spot analyses on three grains of zincolibethenite from Kabwe, wt.%.
* By difference.

A 0.025 × 0.015 × 0.015 mm single crystal off the same specimen was examined with a Nonius Kappa CCD diffractometer using 0.71073 Å radiation at 293(2) K, and the results, refined by a full-matrix least-squares method on F^2 to R (all data) = 0.0525, gave an orthorhombic unit cell with a = 8.3263(3), b = 8.2601(3), c = 5.8771(2) Å, V = 404.520(2) Å^3, space group *Pnnm*. For $Z = 4$ and using the analysed formula, the calculated density is 3.972 g/cm^3. These values are similar to those of libethenite, a = 8.076, b = 8.407, c = 5.898 Å, V = 400.44 Å (Keller *et al.*, 1979), with a slightly expanded unit cell and with the magnitudes of a and b reversed; presumably an intermediate phase in the solid solution to libethenite has tetragonal unit-cell dimensions. The results were used to determine the metal site occupancies as follows: given that the ratio of Cu:Zn = 1:1 and the site occupancies of the 6-coordinate site are Cu = P and Zn = 1-P, and of the 5-coordinate site are Cu = 1-P and Zn = P, P was allowed to refine, and converged to a value of 0.974(8). Details of the full structural determination are available on request from the authors.

Infrared spectrometry

Infrared spectra of natural and synthetic libethenites and zincolibethenites, and of a range of synthetic intermediate phases were measured in Nujol mulls, between KBr plates, over the range 4000−400 cm^{-1}, using a Perkin-Elmer PE 397 grating spectrometer, calibrated against polystyrene, and examples are illustrated in Fig. 2. Hopeite gives an easily distinguished spectrum (e.g. Braithwaite, 1988), and is detectable in the spectra of those synthetic samples prepared using excess Zn over Cu (see below). The spectra of the natural and synthetic end-member libethenites are very similar, and in agreement with those reported by previous workers (e.g. Moenke, 1962, 1966 (cited by S.D. Ross in Farmer (1974); Aires-Barros, 1970; Gevork'yan and Povarennykh, 1975; Braithwaite, 1983; Frost *et al.*, 2002; Martens and Frost, 2003).

The spectra of libethenite and zincolibethenite are closely related, apart from small differences in wavenumber and relative intensities (see Fig. 2 and Table 3).

A fairly weak probable CuO−H-bending vibration at 812 cm^{-1} in the spectrum of libethenite and shifted on deuteration (Braithwaite, 1983) persists in that of end-

TABLE 2. Powder XRD data for zincolibethenite compared with that for libethenite.

Zincolibethenite			Libethenite JCPDF 36-404		
d (Å)	*I*	*h k l*	*d* (Å)	*I*	*h k l*
5.8811		*0 0 1*			
5.8676	39	1 1 0	5.8070	80	1 1 0
4.8063		*1 0 1*			
4.7937	100	0 1 1	4.8200	100	0 1 1
			4.7560	70	1 0 1
			4.1360	6	1 1 1
3.7243	11	2 1 0			
3.6993	22	1 2 0	3.7200	50	1 2 0
			3.6330	16	2 1 0
2.9412		*0 0 2*	2.9420	12	0 0 2
2.9351	33	2 2 0	2.9080	75	2 2 0
			2.6441	40	1 3 0
2.6325	47	3 1 0			
2.6287		*1 1 2*	2.6270	60	1 1 2
			2.6060	18	2 2 1
			2.5590	25	3 1 0
			2.5270	13	0 3 1
2.5135	10	3 0 1	2.4440	14	3 0 1
			2.4120	30	1 3 1
2.4049	19	3 1 1			
2.4031		*2 0 2*	2.3760	25	2 0 2
			2.3470	10	3 1 1
2.3073		*2 1 2*			
2.3040	18	3 2 0			
2.3015		*1 2 2*	2.3090	25	1 2 2
			2.2980	5	2 3 0
			2.2870	3	2 1 2
			2.2640	3	3 2 0
			2.1000	1	0 4 0
			2.0690	7	2 2 2
			2.0310	1	1 4 0
			2.0155	2	4 0 0
			1.9674	3	1 3 2
			1.9596	1	4 1 0
			1.9390	2	3 3 0
			1.9324	4	3 1 2
			1.9208	7	1 4 1
1.9119	9	4 1 1			
			1.9110	4	0 1 3
			1.9065	6	1 0 3
1.8994	6				
			1.8596	7	4 1 1 1 1 3
			1.8171	2	4 2 0
			1.8117	2	2 3 2
			1.7950	3	3 2 2
			1.7362	2	4 2 1 1 2 3
			1.7095	14	0 4 2
1.7004	6	4 0 2			
1.6892	11	0 4 2			
			1.6632	9	4 0 2

TABLE 2 (*contd*.).

Zincolibethenite			Libethenite JCPDF 36-404		
d (Å)	*I*	*h k l*	*d* (Å)	*I*	*h k l*
			1.6441	5	1 5 0
1.6298		*2 2 3*			
1.6285	9	3 3 2			
			1.6271	3	2 2 3
			1.6193	12	3 3 2
			1.6069	2	0 3 3
			1.5929	4	3 4 1
			1.5844	11	1 0 3 5 1 0
			1.5745	7	1 3 3 2 4 2
1.5729	9	3 1 3			
1.5723		*4 2 2*			
1.5643	6	2 4 2			
1.5609	5	1 5 1			
			1.5574	3	3 1 3
			1.5461	12	4 2 2
			1.5296	3	5 1 1
			1.5055	3	5 2 0
1.4703	9	0 0 4	1.4719	8	0 0 4
			1.4540	9	4 4 0
			1.4356	2	1 5 2
			1.4301	2	4 3 2
			1.4270	2	1 1 4
			1.4120	1	4 4 1
			1.3948	2	5 1 2
			1.3868	1	4 1 3
			1.3792	1	3 3 3 1 6 0
			1.3722	2	2 5 2
			1.3686	1	1 2 4
			1.3403	2	5 2 2
			1.3224	2	2 6 0
			1.3133	4	2 2 4
			1.3040	2	4 4 2
			1.2907	1	4 5 0
			1.2861	3	1 3 4
1.2840	6	3 1 4			
			1.2820	2	3 5 2
			1.2760	3	0 5 3 3 1 4

Calculated values for lines not observed in italics; in all cases very close to stronger lines, and probably not resolved from them. Observed but un-indexed lines in italics and underlined, probably due to impurity.

member zincolibethenite, weakened and shifted to 828 cm^{-1}, but is then accompanied by a somewhat stronger band at 855 cm^{-1}, which is likely to be its ZnO-H analogue. In synthetic phases of intermediate compositions, the 855 cm^{-1} band is very weak, and only apparent when the composition approaches the Cu:Zn = 1 end-member stoichiometry.

The O−H-stretching absorption shifts with composition (Fig. 2), though not over a wide

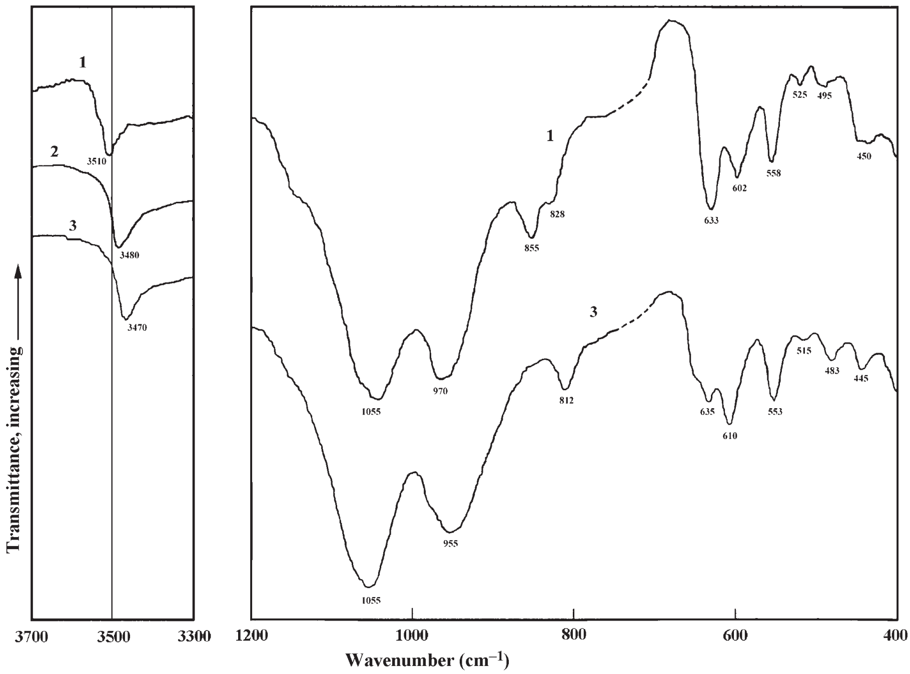

FIG. 2. IR spectra of: (1) zincolibethenite from Kabwe, Zambia (from sample RSWB 83-8); (2) the O–H-stretching region of a synthetic intermediate of composition $(Cu_{0.8}Zn_{0.2})_2PO_4OH$ (microchemically analysed: found Cu 41.9%, the formula requires Cu 42.4%); (3) Zn-free synthetic libethenite (an unanalysed natural specimen from N'Changa, Zambia gave a similar spectrum). No significant absorptions occur between 3300 and 1200 cm^{-1}; the broken lines at ~720 cm^{-1} result from subtraction of a Nujol absorption in this region.

TABLE 3. Absorption maxima (cm^{-1}), and probable assignments in the IR spectra of libethenite, a zincan libethenite and zincolibethenite.

1	2	3	Assignments
3470m	3480m	3510m	O–H stretch
1055vs	1055vs	1055vs	PO_4 v_3 antisymmetric stretch
955s	958s	970s	PO_4 v_3 antisymmetric stretch
		855m	Metal O–H bend
812wm	813wm	828wm	Metal O–H bend
(650)	(648)	(640)?	Metal–O stretch
635m	635ms	633ms	Metal–O stretch
610ms	610ms	602m	Metal–O stretch?
553m	558m	558m	PO_4 v_4 bend
515vw		525w	Metal–O stretch?
483w	490w	495w	Metal–O stretch?
445w	450w	450w	PO_4 v_2 bend

1: libethenite, Zn-free synthetic (a natural specimen from N'Changa, Zambia, gave a similar spectrum).
2: synthetic $(Cu_{0.8}Zn_{0.2})_2PO_4OH$ (requires Cu, 42.4%, found Cu, 41.9%).
3: zincolibethenite, Kabwe, Zambia (from sample RSWB 83-8).
s = strong, m = medium, w = weak, v = very.
Values in brackets are of shoulders.

enough range to be a useful indicator of composition. Chisholm (1985) studied the variation in the O–H-stretching frequencies of similar profile observed by Braithwaite (1983) in the IR spectra of the isostructural olivenite-adamite solid-solution series of analagous arsenates, and was able to assign them to specific metal coordinations.

Synthesis

A wide range of compositions was synthesized from 0.1 M aqueous solutions of Cu and Zn sulphates and trisodium phosphate using Guillemin's (1956) method, in which an initially formed colloid crystallizes after a time, on boiling under reflux. With small or large Cu:Zn ratios this crystallization time was short (30 min or less), but as the Cu:Zn ratios approached unity the crystallization time increased sharply. Crystallization times also increased with pH, being rapid at pH 4, slowing down at higher values, and becoming very slow above pH 7. Starting mixtures with Cu:Zn<1 gave products containing colourless (and hence Cu-free) hopeite crystals, $Zn_3(PO_4)_2.4H_2O$, mixed with zincolibethenite, in agreement with Guillemin's (1956) observations. In no case was the formation of the phosphate analogue of adamite, or its triclinic polymorph tarbuttite observed, hopeite being formed preferentially despite its different chemical nature. This behaviour contrasts with that of the corresponding series of arsenates, in which the complete series from olivenite to adamite may be synthesized by this method (Guillemin, 1956 and subsequent authors, see Braithwaite, 1983).

Magalhães *et al*. (1986) studied the thermodynamics of the formation of Cu and Zn phosphates and showed that the equilibrium constant for the competition between Cu and Zn is such that Zn phosphate species will only form if negligible amounts of Cu are present. However, noting the rare occurrence of zincan libethenite at Kabwe, they suggested that it must have been formed as an alteration product of tarbuttite by a localized, significant input of Cu to the mineralizing solutions. The synthetic experiments show that hopeite is formed under the conditions used, accompanying zincolibethenite, even when the Cu:Zn ratio approaches unity, and even when the pH is >7 (Guillemin, 1956), when, according to Magalhães *et al*. (1986) (see above), tarbuttite is expected to be favoured. At high pressures, in hydrothermal bombs at 150–300ºC, the phosphate analogue of adamite can be formed, but according to Harrison *et al.* (1995), only in the presence of tetraethylammonium hydroxide at pH ~8–8.5, hopeite being produced at higher or lower pH, though Kawahara *et al.* (1994) produced it from hopeite in dilute acetic acid at pH 5. It is clear that at Kabwe a wide range of Cu:Zn ratios of fluids were responsible for the wide range of species found, and that the zincolibethenite was likely to have been formed from a Zn-rich cupriferous fluid; alteration of tarbuttite being only one of the possible sources of such fluids.

Discussion

For Zn_2PO_4OH the tarbuttite (*P*1) structure (Cocco *et al*., 1966) is favoured over that of libethenite (*Pnnm*) as one of the two cation sites in the latter structure is of a distorted octahedral coordination preferred by Cu(II), but unfavourable for Zn(II). The tarbuttite structure contains two distorted trigonal bipyramidal sites only, which are favourable for Zn(II) occupation but unfavourable for Cu(II). The same applies to its isostructural arsenate analogue paradamite, and also explains why tarbuttite and paradamite are not members of solid-solution series to Cu(II) analogues like the adamite–olivenite series.

Hopeite (Hill and Jones, 1976) has two cation sites, both unfavourable for Cu(II) occupation. One is tetrahedral, the other octahedral but unable to accommodate the Jahn-Teller distortion consequent on the introduction of Cu(II). Hopeite is therefore unable to accept Cu(II) into solid solution, hence the hopeite accompanying natural and synthetic zincolibethenite is colourless. In the progressive replacement of Cu(II) by Zn(II) in libethenite, replacement stops at Cu:Zn = 1, Zn(II) being unwilling to enter the Jahn-Teller distorted site, except under forcing conditions. The precipitation of hopeite rather than tarbuttite at lower Cu:Zn ratios in our experiments is a consequence of the experimental conditions, and under conditions favourable for the formation of tarbuttite, Cu-free tarbuttite would be expected to replace the hopeite in the mixtures.

Guillemin (1956) notes that the one specimen available that he studied was No. Ves. 5, in the Sorbonne collection, labelled 'Veszelyite, Broken Hill, Rhodesie', and that he verified its identity by comparison with Mennell's original specimen in the Natural History Museum, London. The late Dr

J. Chisholm checked the Natural History Museum's collections, which contain two relevant specimens: BM 1921,677, presented by F.P. Mennell and registered as veszelyite, was found by powder XRD to carry veszelyite (though zincan libethenite might also be present), and BM 96391, collected by F.N. Ashcroft in 1929 (i.e. after Mennell's paper, but before Guillemin's) and registered as veszelyite from Kopje No. 2, Broken Hill, Northern Rhodesia, with the Mennell reference noted on the index slip. The powder XRD pattern of material from the latter specimen is close to that of libethenite, so it is probably the specimen Guillemin compared with his, and is probably zincolibethenite. Mennell (1920) found 17.62% H_2O in his material, and as zincolibethenite contains only 3.74% (whereas veszelyite with Cu:Zn = 1 contains 16.80% H_2O), it seems that the specimen he studied was indeed veszelyite, and probably from the sample BM 1921,677.

Conclusion

Zincolibethenite is a stoichiometric phase, orthorhombic $CuZnPO_4OH$, the end-member of a solid-solution series to libethenite, with the Cu(II) occupying the Jahn-Teller distorted octahedral cation site, and the Zn(II) occupying the 5-coordinate site in the libethenite (andalusite-type) structure, and is therefore of species rank.

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